

EFFECTS OF HYDROPHOBIC TREATMENTS OF STONE ON PORE WATER STUDIED BY CONTINUOUS DISTRIBUTION ANALYSIS OF NMR RELAXATION TIMES



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Abstract

The effects of protective hydrophobic products applied to porous media such as stone or mortar vary greatly with the product, the porous medium, and the mode of application. Nuclear Magnetic Resonance (NMR) measurements on fluids in the pore spaces of both treated and untreated samples can give information on the contact of the fluid with the internal surfaces, which is affected by all the above factors. Continuous distributions of relaxation times T_1 and T_2 of water in the pores of both synthetic and natural porous media were obtained before and after hydrophobic treatment. The synthetic porous media are ceramic filter materials characterized by narrow distributions of pore dimensions and show that the treatment does not produce large changes in the relaxation times of the water. For three travertine samples most of a long relaxation time component, presumably from the largest pores, remains after treatment, while the amplitude of an intermediate component is greatly reduced. For three pudding-stone samples, treatment leads to a substantial loss from the long component and an even greater loss from the intermediate component.

1. Introduction

The distribution of applied hydrophobic materials within a porous structure, such as stone or mortar, is of particular interest in the field of techniques used to safeguard the cultural heritage. Nuclear Magnetic Resonance (NMR) relaxation analysis of pore fluids can supply information concerning the distribution of the filming agents on the surfaces of a porous medium by comparing the distributions of the relaxation times of the fluid confined there before and after treatment. This study gives the preliminary results of a research aimed at defining more suitable protocols for the protection and consolidation of the stone materials of Aosta's Roman Theater. Some samples of materials, both synthetic and natural, were analyzed by traditional methods and also by continuous distribution analysis of relaxation times T_1 and T_2 of ^1H of water, both before and after a hydrophobic treatment with a silicone resin. The treatment and also the saturation of the samples with water for the NMR measurements before and after treatment were carried out on evacuated samples. This does not reproduce normal treatment conditions, but it offers the advantage of a simpler interpretation of the variations in behavior of the relaxation in the water before and after treatment, reducing the number of parameters to be controlled to a minimum, with only a single fluid phase in the pore system.

2. Materials and Methods

The natural samples, 3 travertine (TR) and 3 pudding-stone (PU), are cylinders 1.9 cm in diameter and 2 cm in height. The two artificial samples are ceramic filter material with homogeneous pore spaces (1.5 and 3.0 μm diameter) and are cylinders 2 cm in diameter and 1 cm in height.



Aosta's Roman Theater

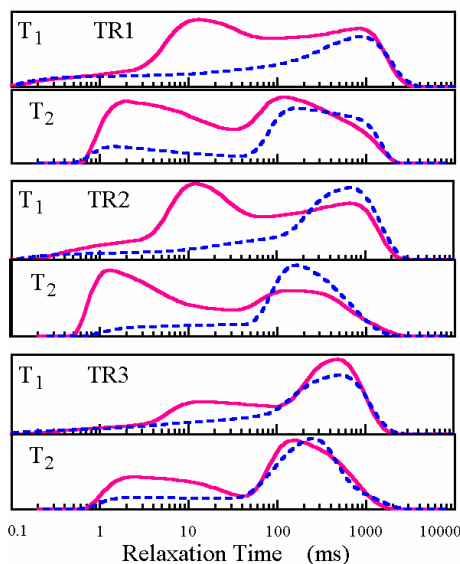
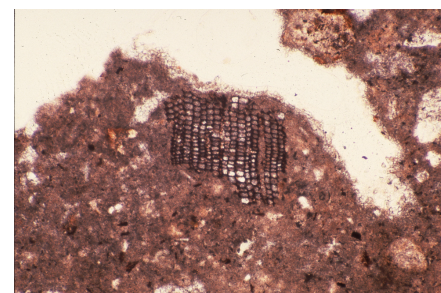


Fig. 1. T_1 and T_2 curves for three travertine (TR) samples. Dashed lines are for the treated samples.

3. Results and Discussion

The ceramic samples show single fairly narrow peaks on distributions of relaxation times, with T_2 greatly shortened by diffusion through inhomogeneous fields from susceptibility differences, which masks effects of surface relaxation for T_2 . For the 1.5 μm sample T_1 was increased 23% by the treatment, and for the other T_1 was substantially unchanged. The 1.5 μm sample was 86% saturated with water, so it appears clear that the treatment does not have any very large effect on the surface relaxivity. The rock samples have structures more inhomogeneous and have larger pores, but they, too, suggest that the treatment does not change the surface relaxivity by large factors. The longest relaxation times in the distributions are not much different for the treated and untreated samples.

In Fig 1 (travertine, TR) and Fig. 2 (pudding-stone, PU) the distributions of relaxation times are plotted in such a way that the total area of each distribution for a treated sample (dashed lines) is that for the untreated sample, multiplied by the fraction given above for the relative water content. It is immediately evident that there is much variation among the three samples of either type of rock but also that there are some general differences between the two types. All PU samples show substantial T_1 amplitudes up to 3 s, indicating part of the water with nearly bulk relaxation times, whereas none of the TR samples has times this long. More of the long component is lost by the treatment for PU than for TR. This is compatible with the fact that PU is a conglomerate with most pores larger than those of TR, with the possibility that some large voids in the PU can be filled only through some of the matrix material in which low porosity rock inclusions are imbedded.



Travertine

Sample preparation and control measurements are divided into three phases. Phase One is the standard measurement of water absorption and color change, following NORMAL [1] procedures in use by the cultural heritage sector. First, the sample is brought to its dry weight in an oven in air at 60 °C, and then the color is measured by means of a portable colorimeter with diffuse illumination (Minolta CR-200). Then water absorption is measured as a function of time over several hours. Phase Two is treatment of the samples with one of the hydrophobic products generally used for restoration, namely, Wacker Polysiloxane 290. The solvent for dilution was White Spirit. Before treatment the samples were held at 20 °C and 50% Relative Humidity (RH) for 48 hours. The only variation from the standard procedure is that the samples were then pumped to remove air before saturation in order to reduce the variability in the penetration and distribution of the product. The product is then admitted to the evacuated sample from the bottom until it reaches a height 2/3 that of the sample. After ten minutes the level is then raised to cover the sample by about a cm and allowed to stand for an hour. After this, the samples are maintained at 20 °C and 80% RH for fifteen days to allow evaporation of the solvent and polymerization of the product, which is aided by the humidity. Phase Three consists of repetition of all parts of Phase One. Color changes for the ceramic and the pudding-stone samples were not significant, while, for the travertine samples, they were perceptible even to the naked eye. The natural samples absorbed about a tenth percent by weight of the treating material, while the artificial materials absorbed two to three percent. These amounts are low enough that it seems unlikely that the connected porosity of the samples was reduced by the treatment. Treatment of the ceramic samples provides a reduction in amount of water absorbed of the order of 98%. The behavior of the natural samples is less regular, because they are more complex structurally and also have some larger pores. The absorption by the PU samples is reduced by about 80%. The water absorption for TR is reduced by only about 70%.

For the NMR measurements, samples were pumped for at least 24 hours to remove air and then saturated by water. There is no reason to believe that the untreated samples were not fully saturated, but the treated samples had only fractions of the weights of water before treatment. The porosities and these fractions for the three travertine and three pudding-stone samples are (as percents): 8, 54; 8, 61; 11, 75; 8, 55; 9, 58; 8, 60. For the 1.5 and 3.0 m artificial samples: 44, 86; 34, 62.

NMR measurements were performed at 10 MHz and 24 °C by means of a spectrometer based on a Varian variable-field electromagnet, equipped with an NMR data station (Stelar, Pavia, Italy). Longitudinal relaxation curves were obtained by Inversion Recovery pulse sequences, with 126 inversion times equally spaced in log-time from 0.05 ms up to 7.5 s for the rock samples and from 0.3 ms up to 1.4 s for the ceramic samples. Transverse relaxation curves were acquired by CPMG sequences with 2500 echoes at intervals $TE = 0.8$ ms. Distributions of relaxation times were computed using the program UPEN [2].

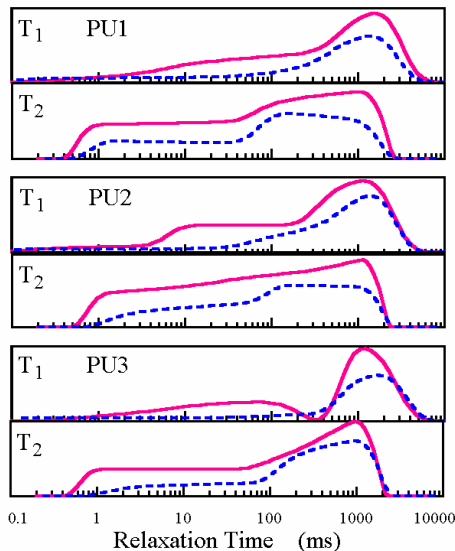
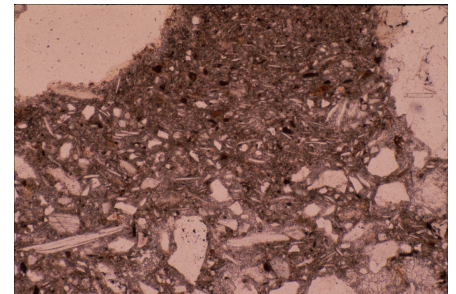


Fig. 2. As in Fig. 1, for Pudding-Stone (PU) samples.



Pudding-Stone

It is interesting to note that sample TR2 has higher amplitudes for the treated sample at long times for both T_1 and T_2 . A probable mechanism is that, for the treated sample, water molecules in the large pores can no longer mix with molecules in smaller neighboring pores, with higher surface areas and shorter relaxation times, which may not be occupied in the treated sample.

All have wide ranges of relaxation times. All the T_1 distributions extend from below 1 ms to over 1 s. For both treated and untreated samples, TR1 has significant T_1 amplitudes from below 0.2 ms to over 2 s, a range of a factor of 10^4 . For all samples, the small T_1 components at times below 1 ms are not lost by the treatment, although the intermediate components are greatly reduced, presumably meaning that many intermediate sized pores did not get filled.

Although the T_1 data extend down to 0.05 ms, the T_2 data go only to 0.8 ms, limited by the number of echoes available and the need to cover times up to 2 s. It may be seen that all the T_2 distributions are limited at short times by the data coverage. For untreated TR samples the T_2 distributions are slightly bimodal and have substantial amplitudes below 10 ms. These amplitudes for the treated samples are greatly reduced.

The T_1 distribution for PU3 actually shows two peaks separated by a minimum almost to baseline, whereas all the other samples show more of a continuum of relaxation times. The amplitude for the treated sample is very small for times below that of the minimum for the untreated sample.

It is thus evident that the distributions of relaxation times vary greatly and that relaxation features correlate with known physical features of the samples and give information on classes of pores from which water is excluded by the hydrophobic treatment.

Acknowledgments

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