NMR: What is it? How could it help cultural heritage?

Nuclear Magnetic Resonance (NMR) is a powerful analytical tool that allows quantitative mapping of certain chemical elements in materials. NMR has been used in medicine since the 1960s. More recently, it proved to be also suitable to study transport processes in porous building materials like stone, mortars and ceramics. In this case, however, the measurement of NMR signal is not straightforward because in general building materials contain magnetic impurities such as ferromagnetic ions. Specific experimental procedures are therefore needed, and specially adapted NMR machines have to be used.

NMR revealed excellent possibilities to non-destructive monitoring of the evolution of the moisture content inside porous building materials during drying, both in the case of specimens saturated with pure water or with salt solutions. The sodium content can also be measured, giving a direct indication of its concentration in the material. This type of application is of large interest for the conservation of the architectural heritage. Here, most decay processes are related to the presence of water, in particular one of the most damaging, the crystallization of soluble salts. NMR can help understand the mechanisms behind salt decay processes, as well as assessing the efficacy and durability of materials and treatment methods for salt decayed buildings.

Our objectives

This presentation takes place within the research project DRYMASS which focuses on the drying of porous building materials possibly contaminated with soluble salts. Indeed, one of the strategic objectives of this project is to contribute to the implementation of the use of NMR in the study of civil engineering materials in Portugal. In this framework, we describe two types of drying experiments which were monitored by one-dimensional (1D) and two-dimensional (2D) NMR techniques, respectively.

Basic concepts

In NMR techniques, the specimen is placed in a strong magnetic field $B_0$, which causes the individual magnetic moments of the nuclei in the molecules to align. Radio frequency (RF) pulses at the resonance frequency of the nuclei are then used to apply a secondary oscillating magnetic field $B_1$ perpendicular to $B_0$. $B_1$ will cause the magnetic moments to rotate away from their equilibrium position. At the termination of the RF pulse, the nuclei return to equilibrium, in a process called relaxation, by emitting electromagnetic radiation and by re-transfering the energy to the surrounding molecules. This emission of energy is what is observed as NMR signal.

To allow spatial discrimination, a magnetic gradient is applied. Hence, the protons will have a Larmor frequency that depends on their position. RF pulses at the appropriate frequency are then used to measure the density of the nuclei at a given position.

The 1D technique

The 1D NMR setup uses an iron-cored electromagnet that produces a magnetic field of 0.78 T. Anderson gradient coils generate a constant gradient of 0.3 T/m over this main field in the vertical direction. This set-up incorporates an iron-cored electromagnet operating at a field of 0.8 T. It uses two sets of Anderson gradient coils, in the x and y directions, which allows the rotation of the magnetic gradient $G$. A constant $G$ of 0.15 T m$^{-1}$ was used, giving a 1D resolution of around 2 mm. For each image, radial profiles were measured in 2D directions over 180º (Fig. 3).

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Cylindrical specimens of 20 mm diameter were used (Fig. 1). After being contaminated with pure water or salt solution, they were wrapped in Teflon tape in order to prevent bottom or lateral evaporation. Immediately afterwards they were inserted in the sample-holder, in the middle of the NMR coil, and allowed to dry under an airflow at 0% RH and 18°C. A step motor moves the specimen in the vertical direction, at steps of at least 1 mm, and the NMR measurements are carried out at each position. The smaller the steps the higher the spatial resolution but the longer the time needed to obtain one complete profile.

The results of a drying experiment are given as profiles expressing the concentration, in arbitrary units (a.u.), of $H^+$ over the length of the specimen (Fig. 2). Each profile corresponds to a different moment of the drying. The several profiles obtained within one drying experiment give the evolution of the moisture content across the specimen.

The 2D technique

This set-up incorporates an iron-cored electromagnet operating at a field of 0.8 T. It uses two sets of Anderson gradient coils, in the x and y directions, which allows the rotation of the magnetic gradient $G$. A constant $G$ of 0.15 T/m$^{-1}$ was used, giving a 1D resolution of around 2 mm. For each image, radial profiles were measured in 2D directions over 180º (Fig. 3). These profiles correspond to projections of the nuclei density in the direction of $G$. They are measured by changing the frequency of the RF pulse. Afterwards, by using a backward projection method out of these radial profiles, the 2D distribution images can be calculated.

Prismatic specimens (Fig. 4) were contaminated with pure water or salt solution and then wrapped in Teflon tape. Drying took place trough the top surface under an airflow at 0% RH and 18°C. A multiple slice spin-echo sequence was used to reduce the time needed to measure one profile. But the NMR signal had to be averaged to improve the signal/noise ratio (SN). Hence, each measurement was repeated three times, which resulted in a total image acquisition time of 30 min.

The results are given as a sequence of 2D images where the concentration of the $H^+$ ion is expressed by a colour scale (Fig. 5). The several images can afterwards be used to produce time-lapse animations which provide a very clear understanding of the drying process.

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NMR Nobel Prizes

Physics 1944

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NMR study of moisture transport during drying

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