



The roles of hydration and evaporation during the drying of a cement paste by localized NMR



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ABSTRACT

The moisture distribution during the setting of a thin mortar layer can be particularly complex to manage under dry (20% RH) and hot weather (above 25 °C) conditions. To better understand the fundamental phenomena at stake, we used static gradient relaxation NMR tools such as Profile MOUSE and STRAFI. This allowed disentangling the mutual effect of evaporation and self-desiccation by hydration. The interest of combining the two techniques is that the capillary water is observed with the MOUSE while STRAFI reveals quantitatively the build-up of the hydrate gel nanostructure. Spatially resolved and 2D relaxation exchange experiments on a model white cement paste revealed that although evaporation induced a capillary water gradient, the kinetics of the building of the pore structure and its homogeneity remained unaffected.

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1. Introduction

The knowledge of the moisture distribution in building materials and more generally the transport properties of the adsorbed water phase are a key-point for the understanding of their durability. Drying can induce cracking and is a matter of permanent concern for the mortar and concrete industry. At a smaller scale, the mechanical resistance of cementitious materials is linked to the density of the C–S–H phase which is largely determined by the relative volume of the water saturated C–S–H gel nanopores. The physics of drying has been described with great success both at the theoretical [1] and experimental [2] levels for model porous systems. However a cement paste represents a more complex challenge as the pore volume cannot be considered constant and water is a chemically reactive phase.

When a Portland cement powder is mixed with water, a chemical hydration reaction occurs [3]. The soluble components present in the cement powder, when in contact with water, dissolve quickly, creating a saturated solution from which the hydrates precipitate. The hydrates grow on the surface of the cement grain, connecting the grains to each other and hardening the then solid material. Cement-paste hardening is thus intrinsically accompanied by a liquid water consumption called self-desiccation. Self-desiccation corresponds to the

transformation of part of the liquid water into solid hydrates. It must be distinguished from true drying which corresponds to the removal of liquid water by transfer to the gas phase, that is evaporation at the paste/air interface. The matter is further complicated by the possible interplay between self-desiccation and evaporation: the tortuous hydrate network affects the water transport toward the interface for evaporation, while one can expect, in turn, that evaporation, by decreasing the local water/cement ratio, affects the formation of the hydrate network. In the following, we will refer to the simultaneous effects of evaporation and self-desiccation as “drying”.

The ultimate aim of our study is to assess during drying the mutual roles of evaporation and self-desiccation on the final porous structure. In that respect, the state and the distribution of water molecules within the cement paste is fundamental for the understanding of its evolving pore structure, and Nuclear Magnetic Resonance (NMR) is one of the few non invasive methods that can deliver this information. Indeed, it is now well established that proton NMR relaxation-rate measurements (both spin–spin relaxation referred to as T_2 relaxation and spin–lattice relaxation referred to as T_1 relaxation) give access not only to the water content but also to the saturated pore-size distribution of a hydrating cement paste.

For all kinds of cement, it is now accepted that the paramagnetic impurities at the surface of the pores control the NMR relaxation rate of all the water protons in the pore, even for white cement (with low concentration of Fe). The relaxation process is the following: the

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water molecules undergo a 3D diffusion in the pore, and, at some point, a water molecule reaches the surface of the pore where its diffusion is restricted, before returning to the bulk of the pore [4]. During its stay on the surface, the water molecule can enter the vicinity of a paramagnetic impurity embedded within the pore wall. The magnetic interaction with the paramagnetic centers is then the dominant contribution to the relaxation, even for cement with low Fe content.

Since the surface residence time is very short compared to the NMR measurement time (fast exchange limit), the effective relaxation rate $(T_2^{\text{eff}})^{-1}$ of water is an average of the bulk liquid relaxation rate $(T_2^{\text{bulk}})^{-1}$ and the enhanced surface relaxation rate, weighted according to the surface-to-volume ratio S/V of the pore [5]:

$$\frac{1}{T_2^{\text{eff}}} = \frac{1}{T_2^{\text{bulk}}} + \rho \frac{S}{V} \quad (1)$$

where ρ is the surface relaxivity. Thus, the relaxation rate reflects the pore size and morphology.

For the complete pore network, the total experimental magnetic decay $S(t)$ is the superposition of the exponential decays T_2^{eff} characteristic of each pore size weighted by their relative population A_i :

$$S(t) = \sum_n A_i \exp\left(-\frac{t}{T_2^{\text{eff}}}\right). \quad (2)$$

Therefore, in principle, NMR relaxation analysis can provide the relative abundance of each water population in the cement paste (in the hydrate structure, in the C–S–H gel pores, and in the capillary pores) and can even provide the corresponding pore size distribution [6]. The problem is thus to recover the pore size distribution from the time relaxation of the NMR signal. The corresponding mathematical procedure is formally a Laplace inversion. This operation, a key-point of the analysis, was recently facilitated by the availability of stable multi-dimensional algorithms executable on desktop computers [7].

In a typical white cement paste hydrated during a few days with a water/solid ratio of 0.4, the extraction of each T_2^{eff} component of the relaxation leads to a discrete distribution which ranges from 10 μs up to 1 s [8]. Numerous NMR experiments carried out at different frequencies (from kHz up to MHz) have led to the following conclusions: all the water molecules in a hydrated cement paste can be categorized as belonging to different relaxation components. The first component is fast relaxing with T_2^{eff} s of 15 μs [9]. It corresponds to the hydroxyl group in the Portlandite. The second component with T_2^{eff} between 100 μs and 400 μs corresponds to the water associated to the hydrate nanostructure. In this category, the structural water of the C–S–H interlayer and the water contained in the nanopores of the C–S–H gel were included. Indeed, the C–S–H is inherently nanoporous, and although the water contained in those very small pores (2 nm) is not chemically speaking structural, its removal would imply the development of extreme capillary pressures that would destroy the gel nanostructure as well. Another T_2^{eff} component of the cement paste proton NMR signal ranges from about 1 ms to 200 ms. It arises from water in pores scaling from a few nanometers up to less than a micrometer and is called the capillary water. The specificity of this type of water is that it can be reversibly removed without any destruction of the nanostructure of the cement paste. Finally, a last component of slowly relaxing protons (circa 1 s) corresponds to free liquid-like water. It must be noted upfront that in presence of a gradient, this population cannot be distinguished as its T_2^{eff} is compressed by diffusive effects toward the range of T_2 's capillary water. In this study, we placed a cut-off at T_2^{eff} equal to 150 μs which means that all the water moistures with a T_2^{eff} below 150 μs are included in the same component (hydroxyl groups and gel water). Table 1 summarizes the T_2^{eff} values that were actually accessible in our study.

Table 1
 T_2^{eff} values actually accessible versus pore size and proton populations.

T_2^{eff} range	Pore size according to [8]	Proton population
Above 150 μs	2 nm	“Gel” water
1 ms to 200 ms	(1 ms) 16 nm (50 ms) 170 nm (200 ms) 270 nm	Capillary water
1 s		Free water

The same conclusions can be essentially drawn from T_1 relaxation rates analysis. By T_2 analysis even without a predictive relaxation model, some authors [10] were able to draw precise conclusions about the evolution of each kind of water during the hydration cement paste.

To follow the drying, the simplest study can be performed on the bulk material. However, to actually discriminate drying and desiccation mechanisms, the monitoring of the total water in the sample versus time is not sufficient. Due to the anisotropy of the evaporation process, it is necessary to follow the distribution and evolution of water within the pore system not only in time but also in space. This justifies the combination of NMR relaxation with MRI (Magnetic Resonance Imaging) techniques. As all of the evaporation occurs at the paste/air interface, one-dimensional profiling methods are the most adequate tool. When dealing with a cement paste, the MRI technique must rely on stable and large gradient to overcome the rapid relaxation rates (see Table 1). This reduces the techniques of choice to the ones involving strong static gradients, such as STRAY Field Imaging (STRAFI). Indeed, there is already a significant body of literature concerning the study cement paste using the high stray fields of superconducting magnets [11–15], but never as a function of the temperature and humidity, which however influences deeply the drying. As a result, most studies have focused on self-desiccation and pore network built-up. Alternatively, some authors have chosen to use single sided permanent magnets with lower fields and static gradients such as the GarField [16] or the Profile NMR MOUSE [17].

The present study is thus by far not the first one to apply STRAFI or single-sided magnet methods to the setting of a cement paste but here we focus on the simultaneous effects of self-desiccation and evaporation by varying the temperature and humidity conditions. Furthermore, we combined the two complementary NMR profiling methods: NMR imaging in the Stray Field of the superconducting magnet (referred to as STRAFI experiment in the following) [14,18] and imaging by NMR-Mobile Universal Surface Explorer (referred to as Profile MOUSE experiment in the following) [17]. The versatile Profile MOUSE experiment is a powerful tool to profile the water distribution in a cement paste at different temperature as it is portable and can easily fit into climate chambers. In a first part, the Profile MOUSE results are presented. They show the effect of drying on the upper face of the paste (the face in contact with air) and the effect of temperature on the water distribution as a function of the depth in the sample. The complete interpretation of the drying process needs the observation of all kinds of water in the cement (free water or water in the pore structure, gel water, as well as structural water in the hydrates). The STRAFI experiments carried out with a home-made NMR probe combine imaging (open geometry of the probe so that the sample can be moved through the coil) and solid state NMR advantages (short pulse, short dead time, short echo time). In a second part of the paper, the evolution of the porous network in a slice of the paste is presented. It is shown how bulk proton NMR relaxation experiments usually performed in a cement paste ($T_1 - T_2$ correlation maps, T_1 and T_2 distribution) can be adapted to be spatially resolved. In a third part of the paper, the effect of relative humidity is studied independently of temperature. In the last part, the combined effect of temperature and relative humidity is addressed.

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