MOISTURE TRANSPORT AND DEHYDRATION IN HEATED GYPSUM, AN NMR STUDY

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Abstract

Nuclear magnetic resonance (NMR) is used to non-destructively measure the moisture profiles in gypsum during one sided intense heating. Simultaneously with the moisture measurement the temperature profiles were recorded. Moreover, in gypsum it was possible to measure the degree of hydration, i.e., the hydration profiles.

The moisture content has a significant influence on the moisture transport processes taking place inside the gypsum. The dehydration reactions of gypsum are directly influenced by the partial vapour pressure under which the reaction takes place. With NMR we are able to separate the liquid and chemically bound moisture and to monitor the progression of the dehydration front in time.

To our knowledge we present the first quantitative time evolution of moisture, hydration, and temperature profiles. Furthermore, the existence of a moisture peak resulting from the vapour released by dehydration is presented. We will present a simple heat and mass transfer model including dehydration aiming to describe the NMR results. The NMR experiments presented in this paper can be used to evaluate and validate thermo-hygral models in the field of fire research on building materials.

1. INTRODUCTION

The question how a porous building material responds to a fire is one of the main questions in fire safety. During a fire, a building material can suddenly be heated up to temperatures of approximately 1000 oC. At temperatures above 100 oC water inside the pores will start to boil. Simultaneously, in materials such as concrete and gypsum, chemically bound water will be released by dehydration of the porous matrix. The released water vapour has to be transported through the porous material. If the material has a low permeability, the vapour pressure inside the material will increase. Furthermore, close to the heated surface a large temperature gradient can generate stresses in the surface. In addition the dehydration reactions will decrease the strength of the material. These three processes can result in a sudden (explosive) failure of the material [10]. The question how a material reacts to a fire has been raised for numerous building materials such as concrete [1,10], fired-clay brick [12,13], and gypsum [2,3].

The research on fire behaviour of building materials is generally focussed on large scale fire testing. These tests are expensive, require large equipment, and do not give any physical insight in processes such as evaporation, boiling, and dehydration. In most of these large scale tests only the temperature is recorded, and the overall outcome after the test is evaluated. In this way, one of the most important factors: the moisture content is left out of the equation. The presence of moisture during heating can have a large effect on different material properties such as: the heat capacity, the heat conductivity, and the dehydration kinetics. As a consequence of the dehydration the porous structure and hence permeability is changed. A better understanding of the underlying physical processes will help to improve materials to become better fire resistant. At the same time, minimizing the need for expensive large scale fire testing.

To this purpose, we have recently developed a Nuclear Magnetic Resonance (NMR) setup to measure the moisture transport in heated building materials. With this NMR setup, it is possible to non-destructively measure the evolution of the moisture content inside a porous building material while it is heated [12,13]. In literature, to our knowledge, no detailed moisture profiles during heating of building materials can be found.

In this paper we present moisture, temperature, and dehydration profiles of gypsum. Gypsum was chosen as a benchmark material for different reasons. First, all of the above mentioned mechanisms such as boiling, and dehydration take place in gypsum. The dehydration reaction(s) take place at well defined and relatively low temperatures. Secondly, it is widely used as a building material in different applications such as plasterboard or building blocks. The large latent heat stored in free and chemically bound water, combined with a low thermal conductivity make it an excellent insulating and fire retarding material. Therefore, gypsum plasterboard is used as a protective barrier for the load bearing wood or steel frame it is attached to. Thirdly, it is a very clean material from an NMR point of view, because it does not contain any paramagnetic impurities.

In Section 2 the behaviour of gypsum at higher temperatures is characterised using NMR. The measured moisture and temperature profiles from the heating experiments will be presented in section 3. The results of the vapour transport model are discussed in Section 4. Conclusions and outlook will be given in section 5.

2. CHARACTERISATION OF GYPSUM

2.1 Pore space

In the one sided heating experiments the moisture content is determined from the magnitude of the NMR signal. However, additional information on the porous structure can be obtained from the time dependence of the NMR signal. This type of characterisation is called NMR relaxometry. The spin-spin relaxation time (T_2) distribution of water in gypsum can give information on the interaction of water molecules with the pore walls. The pore space of gypsum is built up by entangled needle- or plate-shaped crystals.

The NMR signal decay of saturated gypsum is shown in Fig. 1. An inverse Laplace transform of the exponential decay curve (inset graph) clearly shows a bi-exponential behaviour, which is typical for gypsum. The relaxation times can be related to a pore size via the surface relaxivity ($\rho_2 \sim 5$ μm s^{-1} [7]. The top axis of the T_2 distribution graph displays the estimated pore size from the NMR experiment. Although the pore sizes obtained by NMR are a factor of 4 smaller, one must keep in mind that the results were obtained by two completely different measurement techniques.

The bi-exponential behaviour represents two different water populations present in the porous structure. Both populations have a strong interaction with the pore surface. The bi-exponential decay indicates that the exchange between the two water populations is small [4]. In fact, for a water-to-plaster ratio lower than 0.6 there is no exchange possible due to the geometry of the pore space [7]. Note that the gypsum in our experiments has a water-to-plaster ratio of 0.5.

We can now combine the previous data on the pore space geometry obtained by MIP and the sorption isotherm with the results obtained by NMR relaxometry. Let us take a closer look at how the pore space can be represented. In Fig. 1b a schematic view of the pore sizes in gypsum is shown (picture recreated after [5]). The water between the entangled gypsum needles and plates accounts for the long relaxation times and the dominant pore size as measured by MIP and sorption isotherm. The water population with the faster decay (30 ms) can be related to regions where the gypsum crystals are more densely packed or to pores inside the gypsum crystals (see Fig. 1b) [5,6,8]. The total volume of the small pores is much smaller compared to the volume of the larger pores.

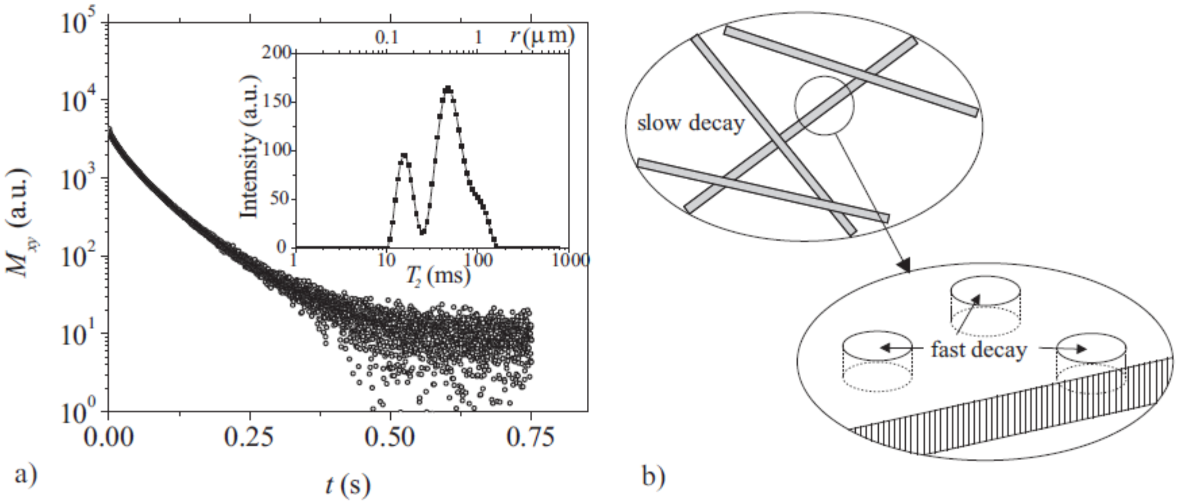

Figure 1: a) Transverse nuclear magnetisation as a function of time as measured in saturated gypsum. In the inset: inverse Laplace transform of the exponential decay curve, revealing two dominant relaxation regimes. b) Schematic representation of the porous structure of gypsum, adapted from [5]. The pore structure is built up from entangled needle and plate shaped crystals.

2.2 Thermal characterisation

All water molecules are probed in an hydrogen NMR experiment, e.g., chemically bound, absorbed to a surface, or surrounded by other water molecules. In the previous NMR section we focussed on the free moisture content inside the gypsum pore space. In this section we will try to measure the chemically bound water with NMR.

The mobility of a water molecule will determine the transverse relaxation time of the corresponding NMR signal. The water molecules which are adsorbed or chemically bond to the porous matrix have a much shorter relaxation time ($T_2 < 100$ μs) than bulk water ($T_2 = 3$ s) or water inside a pore (100 μs $< T_2 <$ 3 s) [6]. If the NMR signal of the chemically bound water can be measured, than the degree of hydration can be obtained.

To test whether our setup is capable of measuring the degree of hydration, a gypsum sample was dried at 20 °C. The sample was then slowly dehydrated during 5 days. The NMR signal and the mass of the sample were monitored simultaneously. The results are shown in Fig. 2. The measured NMR signal is plotted against the relative mass of the gypsum sample, which represents the degree of hydration (α). Where α=1 corresponds to fully hydrated and α=0 to completely dehydrated. A linear fit of the data clearly shows that the NMR signal can be directly related to the degree of (de)hydration. The total NMR signal obtained from a gypsum sample at a given relative humidity is thus a combination of both free hygroscopic water (long relaxation time), and chemically bound water (short relaxation time).

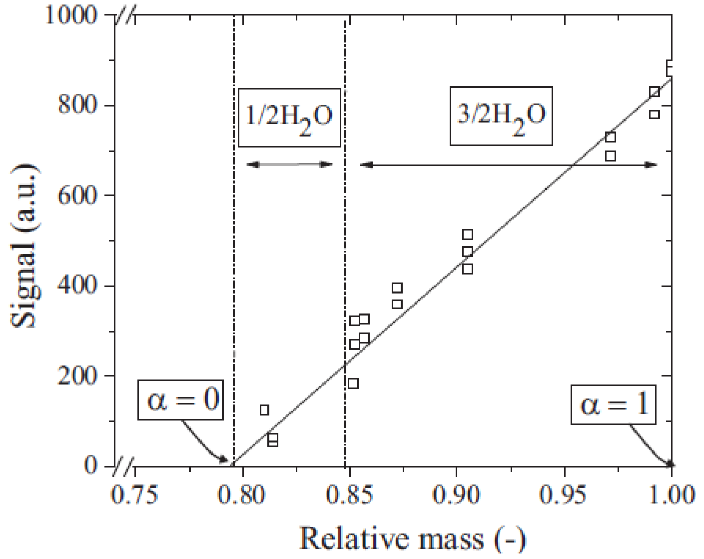

Figure 2: Measured NMR signal of dry gypsum during slow dehydration. The signal is shown as a function of the relative mass of the sample. A relative mass of 1 corresponds to complete hydration (α = 1).

3. MATERIALS AND METHODS

NMR is used to measure the one-dimensional moisture content distribution in a gypsum sample. In this section a short overview of NMR is given. For a more detailed overview of NMR and the NMR setup, the reader is referred to [13].

The cylindrical gypsum samples used in the experiments were cut from larger gypsum blocks, and have a diameter of 80 mm and a length of 100 mm. The samples were pressed in a PTFE holder leaving only the front end of the cylindrical sample open for moisture to escape. Furthermore, the samples were insulated using 3 cm of mineral wool, minimizing the temperature gradient in the radial direction to less than 10 % of the longitudinal gradient. In this way, both moisture and heat transport are limited to 1 dimension. For the sample holder

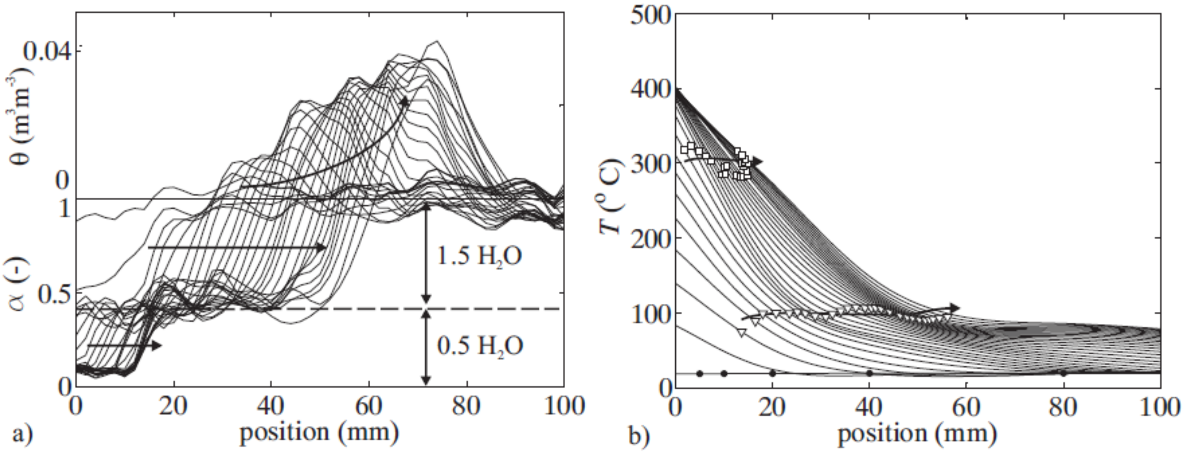

Figure 3: Hydrogen (a) and temperature (b) profiles during heating of dried gypsum. The profiles are shown every 4.1 minutes. Initially the sample is fully hydrated (α=1). Two separate dehydration fronts can be observed (horizontal arrows). The temperatures on these fronts are marked in the temperature profiles (∇,□). A large amount of water is released in the first dehydration reaction, which results in an increase in free moisture content θ (see curved upward arrow).

PTFE was used, because it does not contain any hydrogen, which could cause an unwanted background signal. Thermocouples (type K) were fitted in pre-drilled holes with a diameter of 1 mm. The holes were closed using PTFE tape. The gypsum samples were pre-conditioned at three different moisture contents: capillary saturated, and a moisture content corresponding to 0 % RH and 50% RH, respectively.

Before the heating is started one moisture and temperature profile is measured to record the initial state of the sample. Each subsequent moisture profile is divided by the reference moisture profile to correct for the inhomogeneous RF coil profile. The time between two successive profiles is about 3-4 minutes in each experiment. To prevent hot vapour, which is coming out of the sample, from condensing on 'cold' surfaces inside the coil, air of 1--2 % RH was blown over the sample surface.

4. RESULTS

In this section the results of the NMR heating experiment on gypsum will be presented. The applied heat flux was approximately 12 kWm-2. The heated surface is also the drying surface. The gypsum sample was first dried before heating, in order to verify whether a small amount of moisture present in the previous experiment has any influence on the dehydration kinetics and the observed moisture peak built up. The sample was dried under a controlled environment (1--2 \% RH and a temperature of 40 \dc) until a constant mass was obtained. The hydrogen and temperature profiles are shown every 4.1 minutes in Fig. 3. The gypsum sample is initially fully hydrated ($\alpha = 1$). Any increase of the signal above the maximum hydration degree of one must therefore originate from free moisture.

Three observations can be made from the hydrogen profiles. First, a front is moving through the sample (horizontal arrow). The temperature at the front is about 100 oC. The signal is decreasing below the initial hydration degree of one, indicating dehydration of the sample. At the dehydration front the sample is not completely dehydrated. The hydration degree decreases to about 0.45. Based on the temperatures and the decrease in signal, this front can be attributed to the first dehydration reaction. The first dehydration reaction releases 75 % of the chemically bound water. This water is released as water vapour, thereby increasing the local partial vapour pressure.

Secondly, behind the dehydration front, a significant increase in hydrogen content above α=1 is observed. The increase in signal cannot be originating from chemically bound water, and must be coming from free moisture. The maximum signal intensity at the peak of the hydrogen profile can be approximated by comparing the signal with the signal from the saturated heating experiment. The moisture content is in the order of 10-3 m3 m-3.

Thirdly, a second front can be observed moving through the sample behind the first front (indicated by the bottom arrow, hydrogen content between 0.45 and 0). The temperatures of the dehydration front are marked in the temperature profiles (□). The temperatures are in the order of 300 oC, which is significantly higher than the first front. The temperatures measured on this front are comparable to the temperatures related to the second dehydration of gypsum. This second front can therefore be identified as the second dehydration reaction.

The build up of a moisture peak can be explained on the basis of the vapour pressure in the material. Close to the drying surface, the water vapour can escape from the gypsum sample without difficulty. However, it can be seen that as the dehydration front reaches a position of approximately 30 mm from the surface the peak in hydrogen content starts to built up. As the dehydration front moves further into the sample the vapour released at the dehydration front is not only moving towards the heated surface, but also towards the back of the sample. The vapour moves into a region of lower temperatures, and as a result it will condensate. The condensing water is accumulating behind the dehydration front. This effect has also previously been described in gypsum in numerical heat and mass transfer models [2,3].

In a closed environment, TGA and DSC experiments have shown that, under influence of the partial vapour pressure, the dehydration of gypsum is a two step process. The two fronts observed in the hydration profiles are a clear indication that inside the gypsum sample dehydration is taking place in two steps. The temperatures on the two fronts are constant, indicating that the partial vapour pressures are not changing significantly. Furthermore, it can be seen that immediately at the start of the experiment, close to the surface, the dehydration already takes place in two steps. This indicates that the partial vapour pressure is high enough to inhibit the second part of the dehydration process to take place.

4.4 NMR Relaxometry

We have used NMR relaxometry as a method for characterising the sizes of water filled pores. Furthermore, based on the relaxation time a distinction could be made between free and chemically bound water. In this section we will use NMR relaxometry to verify whether the peak in hydrogen content is in fact caused by an increase in free moisture. The NMR signal decay curves were measured during the 50 % RH experiment, at a position of 50 mm from the heated surface. The two fronts moving through the sample will pass this position. In this way the evolution of both the moisture peak and dehydration fronts can be monitored in time. Analysis of the different relaxation components present in the signal decay curves can be used to identify origin of the peak.

The results from the NMR relaxometry measurements are shown in Fig. 4a. The signal decay curves are shown at three different times during the experiment. The bottom curve represents the initial state of the sample before the experiment is started. We can identify two components in the exponential decay of the signal. A fast decay (T2 ~ 100μs) which can be attributed to the chemically bound water in gypsum, and a slower decay (T2 = 3 ms) from the 'free' water. The ratio between the amplitudes of the slow and the fast component is about 0.01, which is consistent with the low moisture content of 6.10-4 m3m-3.

In Fig. 4b the amplitudes of the two main components (short □, long ○), and the total signal (Δ) are plotted as a function of temperature. As the sample is heated, the temperature reaches 60 oC. At this temperature the long component starts to increases, while the amplitude of the short component remains constant. At the same time the total signal increases, indicating that the long component is responsible for the signal increase.

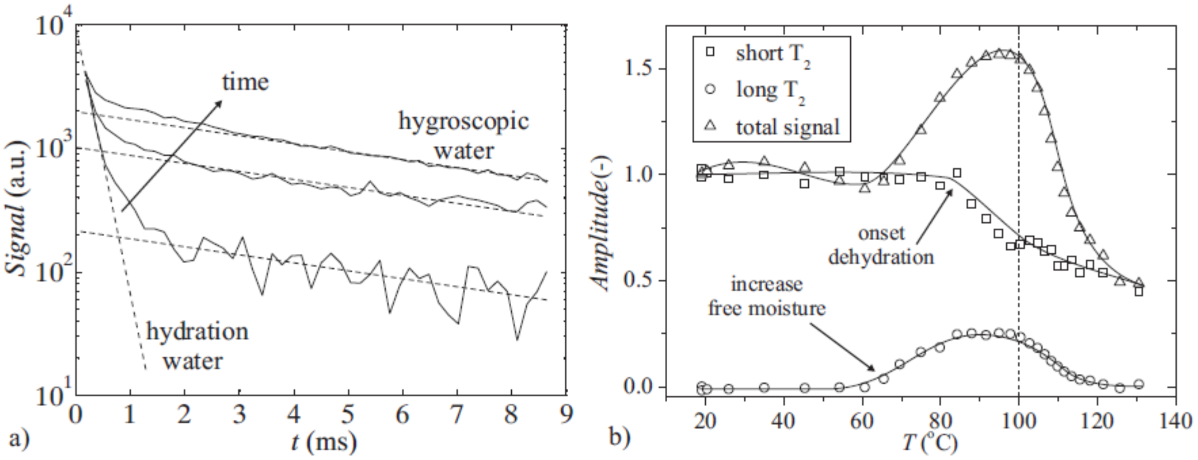

Figure 4: a) Three signal decay curves as measured at 50 mm from the heated surface. Two components can be identified: a fast decay and a slower decay. The fast and slow decay can be associated to the chemically bound, and free water respectively. b) The normalised amplitudes of the two decay components (short □, long ○), and the total signal (Δ) are shown in the right graph. The vertical dashed line indicates a temperature of 100 oC.

The amplitude of the short component starts to decrease at a temperature of 80-90 oC. The amplitude decreases to about half of the initial magnitude at a temperature of 130 oC. The second dehydration should further decrease the magnitude to zero. At 100 oC the long component starts to decrease along with the total signal. This decrease can be explained by boiling of water. The fact that the free moisture content increases before dehydration is taking place indicates that the free moisture originates from a position closer to the surface. The only sources of vapour is the dehydration reaction. As a result of the steep temperature gradient, a steep gradient in relative humidity is present. The water vapour will condense in the region just behind the dehydration front. The vapour released by the dehydration reaction itself will influence the dehydration kinetics. The increased vapour pressure splits the dehydration process in two steps.

We have observed that the T2 of the slow component (free moisture) increases from 1 to 3 ms as the amplitude of the peak increases. The surface relaxivity of gypsum can be used to estimate the size of the condensation layer, which is about 5-15 nm.

5. CONCLUSIONS

With our dedicated NMR heating setup it is possible to measure in a non destructive way the moisture and temperature distribution in gypsum during intense heating. In this way, we were able to measure not only the free moisture profiles, but also the (de)hydration profiles. The combination of the relaxometry results, the moisture profiles, and temperature profiles provide a full explanation of the processes taking place inside gypsum. Boiling and dehydration can be separately observed through the evolution of the free and chemically bound moisture contents. The maximum in vapour pressure at the dehydration front, causes the vapour to be transported in two directions. The vapour which is diffusing towards the back of the sample will flow into a cooler region. At lower temperatures the relative humidity will increase, causing the vapour to condensate, resulting in the built up of the observed moisture peak.

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