NMR and MRI observation of water absorption/uptake in hemp shives used for hemp concrete

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Abstract: Hemp concrete used as a construction material is known to provide excellent thermal insulation and hydric regulation, and prevents condensation. Initial water content in the hemp and water exchanges between hemp and binder play a major role in these processes. Here we study how hemp absorbs liquid water. In that aim we rely on ^{1}H NMR (Nuclear Magnetic Resonance) measurements which make it possible to distinguish water situated inside from water situated outside the hemp. Then, following the evolution of the distribution of NMR relaxation times we are able to quantify the effective amount of water entering the hemp as a function of time. We show that such a measure is better controlled than usual techniques such as weighing an immersed sample or the TC (Technical Committee) RILEM *(*Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages*)* method which cannot easily distinguish water inside hemp from water situated outside or wetting the external hemp surface. The water absorption in hemp occurs in two steps: about half the water enters the material in a time of the order of a minute, while the second half of water slowly penetrates over a time of the order of three days. Finally, from ^{1}H micro NMR imaging we show that the first step corresponds to water entering the pith while the second one corresponds to water diffusing in the wood part of the shiv.

1. Introduction

Current environmental problems lead us to develop more environmentally friendly materials. In particular new concretes are used that contain vegetal aggregate. Hemp shives are a by-product resulting from the pulping of hemp stalks. They were originally used as animal bedding, and since the early 1990, they are also used as aggregates in hemp concrete in which the binder is often a mix of cement and hydrated lime. From a 'life-cycle assessment' perspective hemp construction materials are far more interesting: hemp is naturally produced, does not require much energy to process, does not require maintenance and consumes CO_2 to grow, making the hemp concrete a carbon-negative construction material [1]. Moreover hemp concrete has very interesting properties: it is very light, provides excellent acoustic absorption, thermal insulation and hydric regulation, and prevents condensation. The remarkable physical properties of this material are attributed to its specific multi-scale porous

structure [2]: a micro-porosity in the hemp shiv and in the mineral matrix (paste), a meso-porosity due to the presence of air in the paste and a macro-porosity due to voids in the binder-hemp packing. However, the exact mechanisms at work behind these properties are not yet well understood. In particular the thermal and mechanical properties of hemp concrete depend on moisture content so that it is critical to follow and understand the moisture transport in hemp concrete [3-4].

Although moisture transfers inside hemp concrete are known to have a significant role on their properties they are poorly understood, in particular because it is hard to have straightforward information on the water distribution inside the sample. The hygroscopic behavior of hemp was the subject of several works [5-8]. In fact it is well known that hemp can rapidly absorb large amounts of water during material preparation (up to 3 times its own weight) but the basic mechanisms of liquid water absorption are not well understood. Then, as cement needs water to hydrate, there can be a competition for water between the binder and hemp shives. This water absorption is at the origin of a lack of workability of the concrete a few minutes after the mix. It might also be at the origin of an incomplete hydration of the binder that is sometimes observed and leads to very poor mechanical properties. However it was also suggested that the incomplete hydration is due to a physico-chemical incompatibility between the binder and the plant aggregate [9]. Another explanation In that case the compression strength of the hemp concrete can drop by a factor ten as compared to the usual value when this effect does not occur. Therefore, we need to understand how water transfers between the different phases of the sample. Such information will also have some interest in other fields where hemp is used although these applications often focus on hemp fibers [10-13]. At last it was suggested that liquid water absorption has a greater influence than the vapour diffusion resistance on the moisture and heat transfers in wall components [14].

Previous works in that field are relatively scarce. Usual measurements consist to immerse some hemp in water and take it out and weigh it after different times of immersion [15]. The standard RILEM measurement is based on such an approach, with in addition a centrifugation preceding each weighing. Note that the centrifugation allows removing a part, but not all, of the free water wetting hemp shives (i.e. the water lying along the external surface of the hemp shives), and the remaining amount is unknown, so that there subsists a significant uncertainty on the effective water mass inside the hemp sample which itself forms a porous medium (see below). One study attempted to measure the capillary rise in hemp fibers [16], but it is not

clear yet whether capillarity effects play the major role in water absorption. However it was also shown that the water absorption in hemp can be influenced by surface treatments [17].

The existing knowledge on water absorption in wood may be helpful for understanding absorption in hemp. The knowledge in that field is more advanced [18] but still complex: there is a large variability in the processes depending on material type, and it appears that wood cannot simply be considered as a homogeneous porous medium in which water would penetrate as a straight front due to capillary effects. Like hemp shives, wood is composed of elongated cells called lumens (i.e. capillaries) which are connected by piths, and water may be found as constitutive, bound or free water. The constitutive water is part of the polymers that constitute the cell walls. Its removal requires high temperatures, which may also lead to the destruction of the material. The bound water is adsorbed inside the cell wall, it is linked by hydrogen bonds to the polymers that constitute the cell wall. Free water corresponds to liquid water inside the lumens. During imbibition of a wood sample, water penetrates in the lumens due to capillary forces and then diffuses in the wall cells under the effect of hydrogen bonds. The penetration of water molecules in the cell walls induces some swelling of the structure.

The question of absorption of water in hemp is complicated by the fact that hemp generally takes the form of a heap of small (centimetric) pieces stacked on each other. As a consequence this is a porous medium with two very different porosities, namely that of the packing and that of each shiv. In the present work, in order to clarify the physical processes occurring during water absorption we study the phenomena at different scales, i.e. that of the packing and that of the shiv. Moreover a simple weighing hardly makes it possible to distinguish the mass of water effectively inside the shives from that just wetting the pieces (i.e. along the external surface of the pieces). ^{1}H NMR relaxometry of water molecules, which is sensitive to the pore size will appear as a useful tool for distinguishing these different phases.

Materials and methods are first described (Section 2), then the result of the monitoring of hemp imbibition obtained by weighing an immersed sample are presented (Section 3.1). The results of NMR relaxometry (Section 3.2) are then compared with data obtained from weighing (Section 3.3), and finally the water penetration through µMRI (Magnetic Resonance Imaging) is directly observed (Section 3.4).

2. Material and methods

2.1 Materials

We mainly use a hemp "Chanvribat" provided by BCB (Balthazard & Cotte Bâtiment) Tradical, which was retted before grinding. Typical particle size is around 1 cm length and 2 mm width. Hemps from various origins were also used to compare our measurement methods with the standard one. They were obtained from three other suppliers: Planet Chanvre, Concrete LCDA, Agrofibre. Hemp shiv is obtained by removing seeds and fibers from the hemp, and the corresponding material is then cut in an industrial device. All four shives used in the present study were directly received from industrial plants and were used as such with no additional treatment. Unless explicitly pointed out, here the hemp is used without preliminary drying. We preferred to follow this approach because drying is known to affect the water absorption properties of wood materials, and the former properties are recovered only after a long time. Here, since our material has been left a long time at ambient humidity (about 50% on average) and due to the large hygroscopic time scale of such materials we consider that before each test it has reached an equilibrium initial water content of about 10% (this was checked through drying). Such materials will be referred to as dry samples. However we also looked at the impact of a preliminary drying, as will be described below.

2.2 Water absorption followed by direct weighing

This test aims at measuring the amount of water entering hemp by observing the change of apparent density of a sample immersed in water. For this measurement, hemp is suspended to a scale and immersed in water (see Figure 1). Hemp shives are compacted in a cage of 8 cm in diameter equipped with a screw (allowing the compaction). The center of the sample volume is situated around a depth of 6 cm. The resulting sample mass is 40 g for an apparent volume of 200 to 350 cm^3 depending on the imposed pressure. The compaction is such that all hemp shives are in contact with each other, and no shiv behaves loosely, but there still exist small air paths everywhere in the sample so that air escaping from hemp can easily move outside the cage. The cage is made of crossed steel bars leaving holes of about 5 mm. The sample is then suspended via a rigid bar to a scale and immersed in water. And we follow the apparent mass of the sample in time.

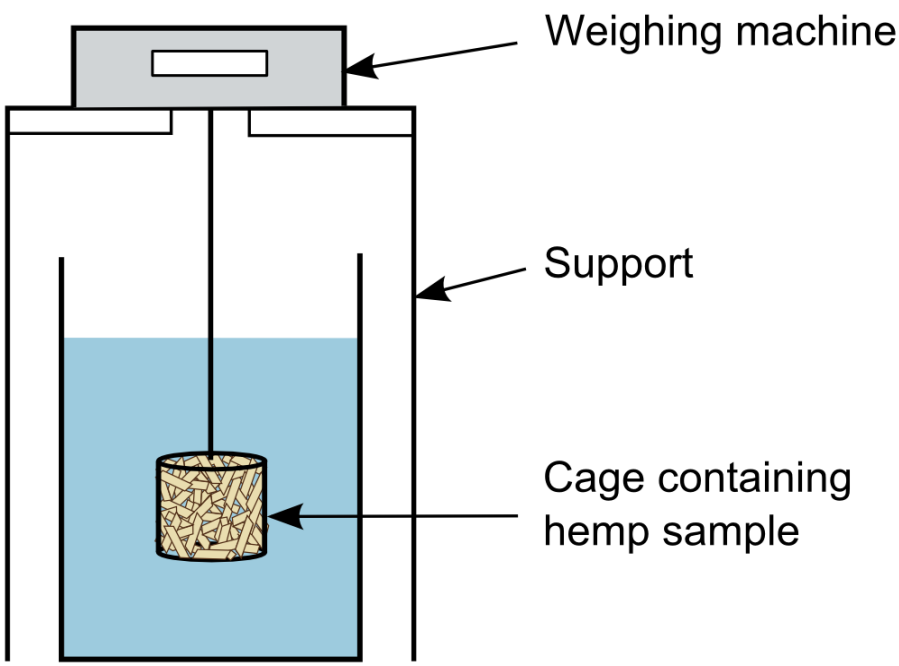


Figure 1. Scheme of the experimental setup used to monitor the water uptake of hemp shives contained in a cage.

The compacted hemp forms a porous system with large pore sizes between the hemp shives. Direct observation of the voids between hemp pieces at the free surface of the sample suggest that the typical pore size inside the medium is of the order of 1 mm, a result consistent with the typical pore size for a packing of compact objects, i.e. a few times smaller than the object size. Let us assume that the dry sample is instantaneously set up at a mean depth of $z = 6\,\text{cm}$ in water. To estimate the water penetration velocity (V) in the sample we can apply Darcy's law:

$$V = (K/\mu)\nabla(\sigma\cos\theta/R + \rho g z) \quad (1)$$

In which σ is the surface tension of water (here taken as $0.07\,\text{Pa.m}$), θ the contact angle and μ the water viscosity ($\approx 10^{-3}\,\text{Pa.s}$). Assuming a perfect wetting ($\theta = 0$) and taking a permeability $K = R^2/12$ (as for parallel cylinders of radius $R = 0.5\,\text{mm}$ and of length 4 cm) and considering that the liquid has penetrated over a distance of 4 cm, i.e. the sample radius, we find a velocity of the order of $40\,\text{cm.s}^{-1}$. That means that the water will rapidly penetrate

the large pores of the sample (between the shives), i.e. in a time of the order of that needed to fully immerse it. In the following we will assume that this penetration is finished when the other phenomena start to take place.

Now we can look at the typical velocity of penetration in the vessels of the hemp shiv, whose diameters are typically of the order of 50 µm. Using again (1) with a length of penetration of the order of 1 cm we find a velocity of the order of $2\ \mathrm{cm.s^{-1}}$, which means that the penetration through such channels should also be very fast as compared to our time of observation.

Let us now assume that the sample has been immersed and the large pores between the hemps pieces have been filled with water (mass m_{ext}). Under these conditions the apparent weight (as measured by the scale) of the cage volume is equal to the effective weight $P_{eff} = m_S g + m_W g + m_{ext} g$ minus the buoyancy force $B = \rho V_S g + m_{ext} g$, in which m_S is the mass of solid (i.e. the mass of dry hemp), m_W the mass of water which has entered the hemp shives (and replaced air volumes) since the beginning of the test (we neglect the mass of air), V_S the total apparent volume of the hemp shives and ρ the water density.

If the hemp shives keep a constant apparent volume, the evolution of the apparent weight will exactly correspond to that of the mass of water entering the hemp shives (and replacing air), i.e. m_W. If the hemp shives swell as a result of some water entrance we will have a variation of the apparent volume $\Delta V_S = m_a / \rho_a$, in which m_a and ρ_a are the mass and density of this specific water. Moreover the effective weight will now include an additional term $m_a g$, and the apparent mass will finally write: $m_W + m_a(1 - \rho/\rho_a)$.

2.3 TC RILEM protocol for water absorption

This test aims at measuring the amount of water absorbed by hemp from the change of apparent mass of a hemp sample. This protocol was performed on various hemps of different origins within the context of RILEM tests. Shives are dried at 60°C for this measurement. About 25 g of hemp are placed in a synthetic permeable bag with holes of approximately 1 $\mathrm{mm^2}$ section area and immersed 1 min in water. The bag is then removed from the water bath and put in a salad spinner which is then rotated 100 times at approximately 2 rpm. At the end

the bag containing shives is weighted and then immersed again for 15 min, 4 h and 48 h, before the same protocol of mangling then weighing is applied. The water absorption capacity of the synthetic bag is independently measured. The measurement is repeated 3 times for each hemp with a standard deviation lower than 15%. Here we only present the average value of the water mass divided by the mass of dry hemp.

2.4 NMR measurements

Here we intend to follow water absorption from the evolution of NMR signal associated with different pore size in hemp immersed in water. For these measurements, shives had to be grinded in order to enter the experimental set-up. So we first put the hemp in a rotary blade mixer during a short time which allows to get a new shiv size on the order of three times smaller than the initial value. Then this hemp is compacted in a 1 cm thick layer at the bottom of a 18 mm diameter tube and water is added until the water free surface reaches the top of the hemp packing. The initial masses of water and dry hemp are measured before introduction in the tube. In our tests the initial water to hemp mass ratio in the tube was always larger than 5, which means that hemp is in contact with more water than it can absorb, even after a long time. In the following description we consider the initial time as that associated to the first contact between hemp and water in the tube.

A Bruker Minispec MQ20 ND-Series, with a 0.5 T magnetic field corresponding to a ^{1}H (proton) resonance frequency of 20 MHz was used for NMR measurements. The probe (3 cm^3) was temperature-controlled (20°C) by circulating water. The same apparatus was used to perform both T_1 and T_2 relaxation time measurements.

In order to get the T_1 distribution, longitudinal proton magnetization decays as a result of the NMR signal relaxation were measured by means of the Inversion Recovery sequence [19], with 50 values of inversion times logarithmically distributed from 0.1 to 12000 ms. Recovery delay was chosen equal to 12 s to ensure complete relaxation of water between two measurements, which implies a measurement duration of approximately 40 min. The sample is left inside the device and the evolution of T_1 is followed during a few days after the first contact.

The T_1 distribution can then be resolved by means of ILT (Inverse Laplace Transform). Our procedure is a non-negative least square fit to the data with Tikhonov regularization, is similar to the 'Contin' method [20-21], and is described in [22]. We finally get an apparent statistical distribution of T_1, expressed in terms of signal intensity associated with each possible value of T_1. Typically such a distribution consists of several peaks situated at different T_1 values. Due to the unstable nature and known imperfections of ILT processing [22], such a distribution does not provide a precise description of an effective distribution of T_1. Two parameters of this distribution nevertheless constitute relevant physical characteristics of the sample:

(i) The positions of the peak maxima, that we will here call the T_1 values. Roughly speaking these values are related to the mobility of water molecules, and specific interactions of water with their environment (e.g. adsorption, proton exchange with other species, or magnetic interactions at nanoscale). In the particular case of water embedded in a pore cavity, within the usual hypothesis of biphasic fast exchange [23], T_1 scales as the ratio of the volume of free liquid water to the area of the water-solid interface, with a factor depending on the NMR surface relaxivity. Note that this volume to surface ratio is proportional to radius in the case of uniform spherical pores. Thus the T_1 values can be considered as reflecting characteristic pore sizes in the material.

(ii) The area beneath the part of the curve associated with a peak, which can be considered as proportional to the amount of water within a characteristic pore range.

Measurements of the transverse relaxation T_2 decays were performed thanks to the Carr-Purcell-Meiboom-Gill (CPMG) sequence. The classical sequence was adapted in order to have a varying value of echo time τ. Thus, the value of echo time is incremented at each echo by multiplying the old value of τ by a low factor. Measurements are done with a recycle delay of 12 s, with 8 scans, with 800 Pi-pulses and pulse separation varying from τ = 2.2 ms to 5 ms. The acquisition time is about 2.6 min. The relaxation time distributions were extracted using the same ILT processing as for T_1 distributions [22]. As for T_1 measurements, each NMR acquisition gives direct information on the quantity of mobile water inside the sample and the T_2 distribution. However the resulting data appeared to be rather noisy so that it is difficult to distinguish clear trends. As a consequence for most of the analysis we decided to focus on T_1 data. From T_2 data, which are obtained in a much shorter time, we could at least deduce that an amount of water of the order of the first value observed from T_1 measurements (i.e after

several tenths of minutes of imbibition) is already present inside the hemp after a time as short as 2 min.

2.5 MRI measurements

Here we intend to have information on water absorption in a hemp shiv from the evolution of the aspect of MR images. The µ-MRI experiments were performed at 17.6 T (^{1}H Larmor frequency of 750.13 MHz) on a *Bruker Avance IIIHD* spectrometer equipped with a *Bruker Micro 2.5* micro-imaging system (100 G/cm for the three axis) and a 10 mm diameter ^{1}H resonator. Acquisition and data processing were achieved with the *Bruker Paravision 6.0* software. The imaging protocol was carried out using the "Zero Echo Time" sequence (ZTE), [24]) which is particularly dedicated to materials with short transverse relaxation time (T_2*) such as porous media. 3D images were acquired with a theoretical resolution of 47 µm which took from 9 min to 1 h depending on the number of scans.

In order to follow the water absorption in one shiv, we used a NMR tube of 5 mm diameter. The shiv is chosen so that its width is around 5 mm. Thus it can be jammed in the tube at a given height with a vertical orientation of the fiber. This jamming is sufficient to avoid any displacement of the shiv even in the presence of strong vibrations possibly induced by the application of the pulsed magnetic field gradients during the measurements. Half the tube is filled with water in such a way that the lower half of the shiv is immersed in water (see Figure 2). The MRI sequence allows selecting several cross-sectional slices along the main (fiber) axis of the shiv (see Figure 2). Finally we get (see Figure 2 right) the amount of water in a slice of the sample, with mainly two zones: in hemp and in water surrounding the shiv. Since the water level in the tube decreases in time due to water absorption in hemp, the pure water regions that may be seen in the MRI images soon essentially correspond to residual water menisci left around the shiv. At some time the shiv may lose contact with the outside bottom water but we have no clear information about that.

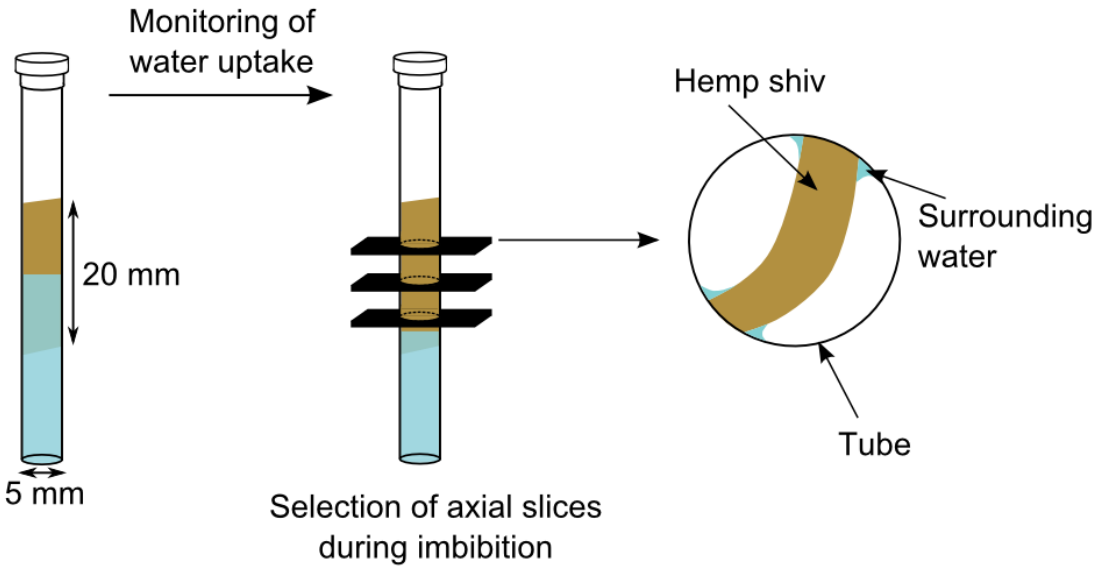


Figure 2. Experimental setup used to perform imaging on one hemp shiv (brown) partially immersed in water (blue) (left) and schematic MRI image (right) resulting from the selection of a cross-sectional slice (middle).

3. Results and discussion

3.1 Weighing of an immersed sample

In Figure 3 we represent the evolution in time of the apparent sample mass divided by the initial mass of dry hemp for such an experiment. The typical curve shape in linear scale over several tenths of hours includes a very fast increase during the first minutes followed by a very slow increase in time over several days. The overall shape of the curve is consistent with the observations reported in literature [25]. Repeating several times such a test with different initial hemp volumes we see that there is a significant variability of the result (inset of figure 3). This is due to the complex effects which occur over a short time: penetration through the porous hemp shiv network and initial imbibition of the hemp. Ideally, i.e. as assumed in the theoretical treatment above, we would need to have the two processes successively so that we could identify the initial time and initial mass at the beginning of imbibition, but since they occur more or less at the same time this is not possible. Under these conditions in the following we will just comment the shape of the imbibition curve.

Looking at the detailed evolution in a logarithmic scale we see an intermediate period (say between 1 and 10 hours) where the water mass marks a plateau and even tends to slightly decrease during a few hours before starting again to increase significantly. Such a decrease is surprising because it would a priori means that some water now leaves the hemp pores and is replaced by air, but there is no reason to suddenly invert the process of absorption. Another explanation could be that some air bubbles cannot escape easily from the cage and are jammed between (or stuck to) the particles. However such an effect should lead to a plateau of mass, and not a decrease, since it is equivalent to have no more water entrance in the hemp.

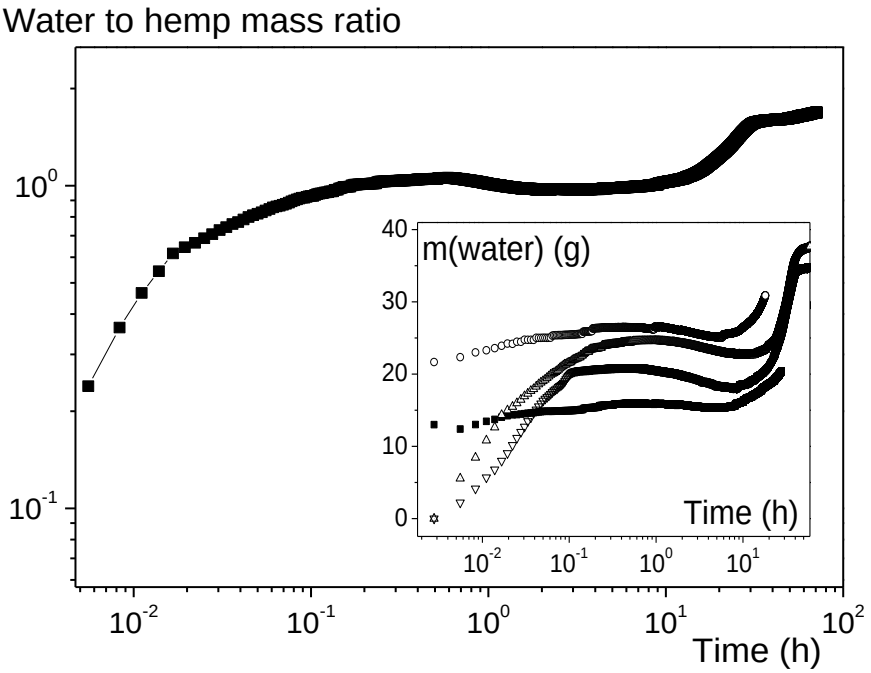


Figure 3. Water to hemp mass ratio as a function of time for hemp sample immersed in water. The inset shows the result of similar tests with different initial hemp volumes in the cage.

Another possibility would be a change of water density after absorption in the hemp. Such an effect was suggested for wood: bound water adsorbs to polymers that constitutes cell walls, and only when cell walls are saturated, liquid water fills the cells. Various investigators tried to measure the void volume fraction of wood by immerging wood in different liquids or gases (helium, benzene and water) and measuring the volume of displaced fluid [26]. Benzene was assumed not to enter microvoids in wood, unlike helium. They observed that in the case of

wood immerged in helium, the specific volume was lower than for benzene, which confirmed their hypothesis. But in the case of water, the specific volume was even lower than for helium, which means that water does not only enter microvoids. They explain this difference by a compression of water linked to the cell wall by hydrogen bondings. This compression, which corresponds to an increase of water density, might be due both to higher attractive forces in the cell wall than in bulk water and to a reorientation of water molecules. However according to the above equation such a density increase ($\rho_a > \rho$) would induce an increase of the apparent weight of the sample, and not a decrease as observed.

Finally the only explanation seems to be that there is a kind of transformation of some liquid in gas. Actually such an effect can be observed as soon as water is put in a solid container. After some time one can observe the formation of small bubbles attached to solid surfaces (see for example tap water in a glass). This results from a degassing of solubilized gases (e.g. 0_2, CO_2) at the contact with a solid surface. If the small bubbles thus created remain attached to the shives the hemp sample will appear lighter after some time, as observed in our tests (see Figure 3). Unfortunately we did not find any solution to avoid or control this effect: some air in contact with the liquid may dissolve in it during the test; and removing the ambient gas will tend to accelerate the imbibition.

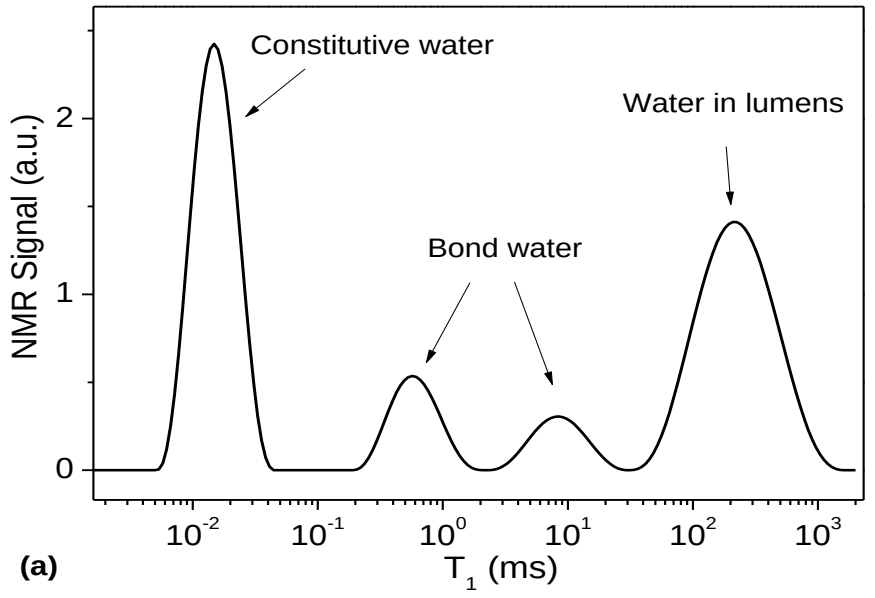
3.2 Monitoring using NMR

The weighing of an immersed hemp sample does not allow to get fully reliable data concerning the mass of water entering the pores. Therefore, we use NMR to measure the kinetics of water absorption in hemp.

3.2.1 Various types of water

As we have seen in the introduction three types of water may be considered in wood. Since depending on their environment and the interactions they develop, the spins of the water hydrogen protons exhibit different NMR relaxation times, these different types of water may exhibit different relaxation times. For example, according to Almeida [27], for Douglas fir the transverse relaxation time (T_2) of constitutive water is of the order of a few tens of

microseconds, that of bound water ranges from one to a few milliseconds, and that of water in the lumen ranges from ten to a few hundred microseconds.



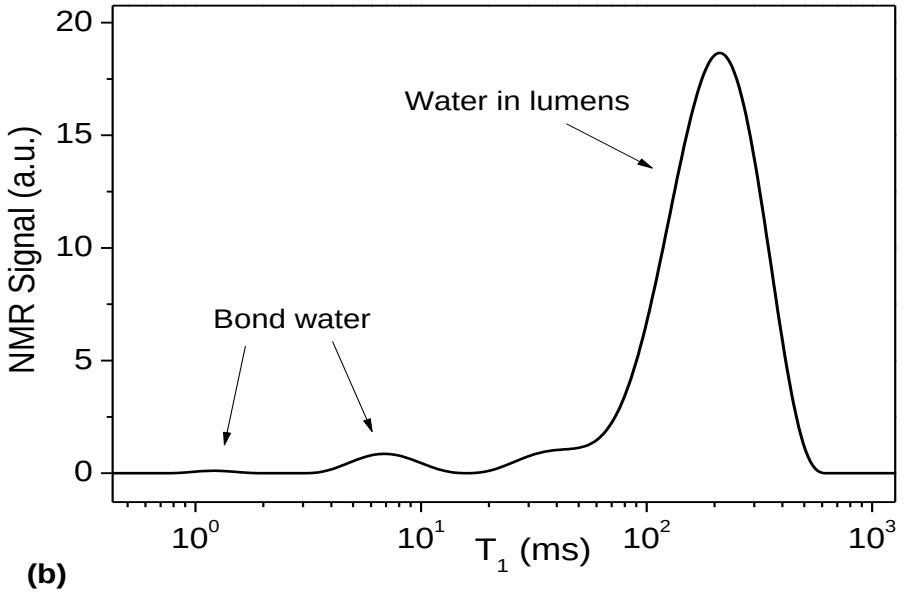


Figure 4: Distribution of relaxation times for hemp shives under ambient conditions (a) and after immersion in water for 2 min (b)

The distributions of T_1 relaxation time for dry hemp and moisten hemp (2 min immersed sample in water) are presented in Figure 4. Extrapolating the above analysis of water state in

wood to this case we can suggest that the peak associated with the smallest relaxation time corresponds to constitutive water, the two central small peaks to bound water and the right peak (i.e. the largest relaxation time) to water in lumens. It is interesting to note that even in this state (hemp under ambient conditions) the signal associated with the three states of water is significant, whereas we could have expected to have negligible water in lumens. However we cannot compare the signal intensity in these three states to that found during absorption because the absolute signal level for two different tests (and different samples), even with the same water amount, generally varies.

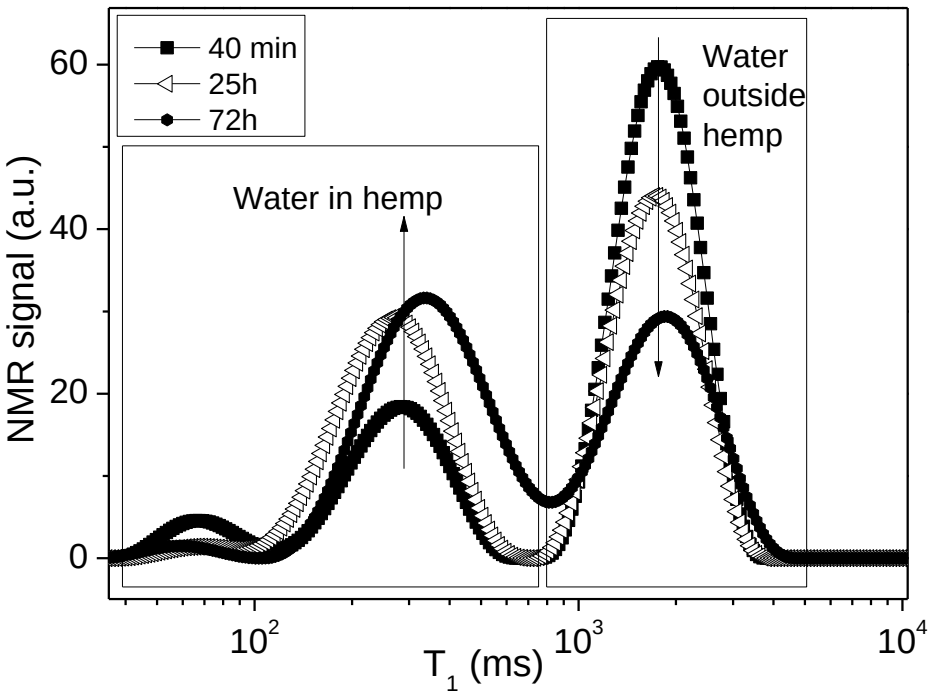
When the hemp shives have been immersed in water for a few minutes (see Figure 4b) the distribution of relaxation strongly differs from that for the "dry" sample. Here we focused on longer relaxation times so that we did not record the signal associated with the constitutive water. The main peak is now the one associated with liquid water in the lumens. We can also remark that the peak associated with the largest relaxation time for bound water has significantly increased with regards to the other peak (lowest relaxation time) for bound water. This illustrates the fact that most water has entered the lumens and a small part of it entered the cell walls but only in the largest pores of these cells.

3.2.2 Monitoring water absorption (T_1)

We now consider the situation where we have the hemp sample immersed in an excess of (outside) water for a longer time (see procedure in Section 2). The distribution of relaxation times of this system now exhibits two main peaks (see Figure 5), associated with two types of environment. The shortest relaxation time, around 300 ms, is close to the relaxation time of protons in liquid water that we observed previously in moisten hemp. Therefore, it is associated to water in the lumens. The peak corresponding to relaxation times around 2 s corresponds to water outside the hemp. At last we still have a small peak at T_1 below 100 ms which is associated to water bound in hemp, but the signal intensity associated with this water state is much smaller than that in the lumen.

As the area under each peak is proportional to the amount of water in each type of pore, we can monitor the amount of water that entered in hemp over time. In Figure 5, we can already note that the area beneath the curve part corresponding to water outside hemp seems to decrease while the area associated to water in hemp seems to increase, which corresponds to

419 the transfer of water from outside to inside the hemp shives. Note that the values of the
420 relaxation times associated with each peak slightly change during the process but such
421 changes may be attributed to a side effect of ILT processing, which can shift neighbouring
422 peaks depending on their relative amplitudes [22].
423



424
425 **Figure 5:** Distribution of T_1 relaxation times for a hemp sample put into contact with an excess of
426 water, at three times during the test.
427

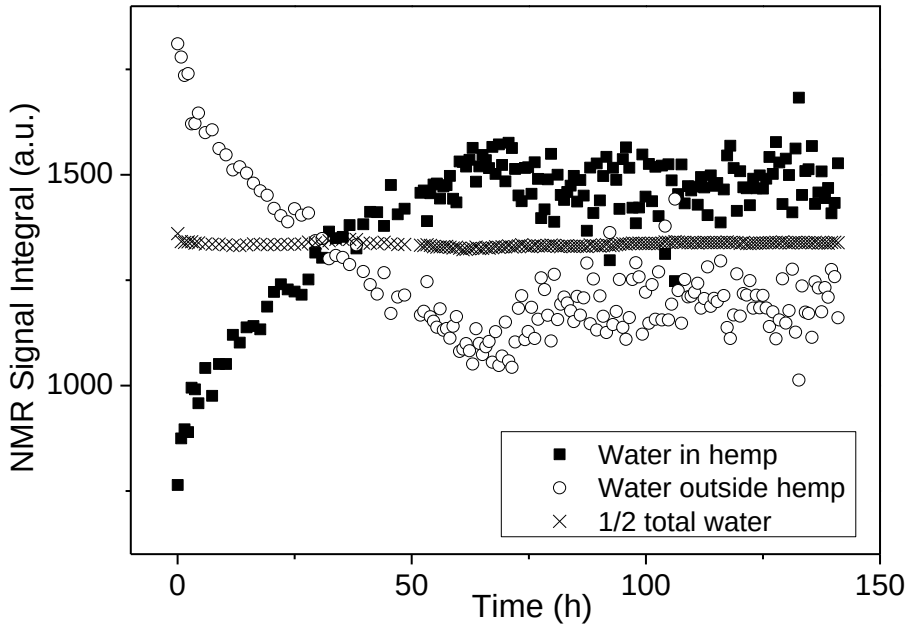


Figure 6: Evolution of the signal intensities associated to water in hemp and water between hemp particles over time. Half of the total water amount in the sample is also represented.

In Figure 6 we show the evolution of the integrated signal for water inside hemp and outside hemp. We see that the signal associated to water in hemp increases in time while the signal associated to water outside hemp decreases. The consistency of this type of measure is demonstrated through the fact that the total water amount deduced from these data remains constant (see Figure 6), as expected since the tube is closed. This in particular confirms that we effectively record the water entering hemp with this technique. We can also notice that the initial signal associated to water in hemp is ten times higher than the signal measured for dry hemp. This confirms that hemp absorbs a significant amount of water during the first measurement.

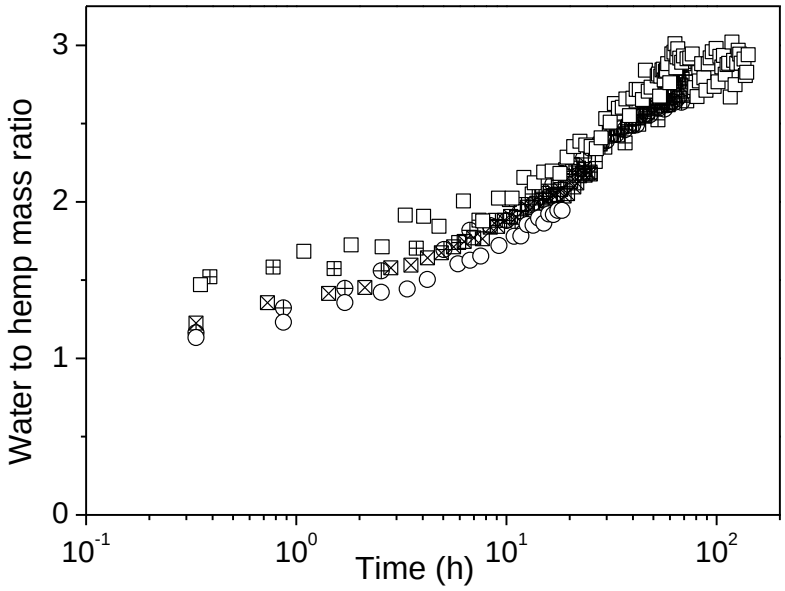


Figure 7: Water to hemp mass ratio measured by NMR for different samples (either crossed or not) either dried (circles) or not (squares). For the dried samples the water to hemp mass ratio was computed by adding to the hemp mass, and substracting from the total water mass, the mass of water lost by drying, so that the data presented here for dried and non-dried samples can be relevantly compared.

The mass of water that is added to hemp is weighted as the sample is prepared. Knowing this mass allows to calculate the effective amount of water in each phase (inside or outside hemp), and particularly to determine, for each test, the (linear) relationship between the NMR signal intensity and the water to hemp mass ratio over time. From such measurements we now have a view which is in principle not affected by any artefact (in contrast with weighing). The uncertainty on such data is about 12%, as appears from the repetition of similar tests (see Figure 7).

We also tested the impact of a preliminary drying of the sample which, as already mentioned, typically withdraws a mass of water equal to about 10% the hemp mass. It appears that this does not change the general trends of the imbibition (see Figure 7): the data obtained after drying can be transformed in data equivalent to those without drying by adding to hemp the additional mass of water associated with drying, and withdrawing this additional mass of water from the apparent water; the two sets of data appear to be similar to each other within

463 the uncertainty on such experiments. Thus it seems that drying has no more effect than simply
464 shifting the initial water mass towards a lower value but this water loss is balanced by a very
465 fast water imbibition at the beginning of the test.
466
467 We see that the hemp has initially (i.e. during the time needed for the first NMR
468 measurement) absorbed a large amount of water of about 150% of the hemp mass. Then it
469 goes on absorbing water during 3 days, until reaching a mass to hemp ratio of about 3 (see
470 Figures 7 and 8). This confirms that hemp imbibition occurs in two phases each of them
471 associated with the absorption of half the total absorbed water: one over short time, i.e. in less
472 than two minutes (as appears from T_2 measurements and weighing), and the other over several
473 days. The first phase likely might correspond to some kind of capillary imbibition in the
474 largest pores, but the entered water does not increase as predicted by a simple Washburn
475 imbibition (i.e. as $\sqrt{t}$) [28]. In the second phase the mass increase is much slower (i.e
476 approximately proportional to $t^{1/8}$). However if we consider that in phase 2 the water simply
477 penetrates in a dry region we could expect a Washburn process for the additional water mass
478 (from the penetrated amount at the end of phase 1, i.e. 1.5). And indeed the additional water
479 mass evolves as $\sqrt{t}$ (see inset of figure 8). Actually, anticipating on results of Section 5 this
480 interpretation is in disagreement with MRI observations: during phase 1 the water effectively
481 rapidly invades a first region of each hemp shiv, but during phase 2 it seems to penetrate
482 globally in another region of shiv, instead of progressively invading it from one side. This
483 suggests that in phase 2 there is a slow diffusion process through the hemp structure rather
484 than a capillary penetration.
485
486 We also remark (see Figure 8) that the data from NMR do not show a slight water mass
487 decrease between 1 and 10 h. Instead we now have a slow but regular increase, which
488 suggests that the direct mass measurement of a hemp sample fully immersed in water can be
489 affected by some artefact inducing a significant error on measurements. In the following we
490 will use the NMR data as the reference data for describing the effective water amount
491 absorbed in hemp.

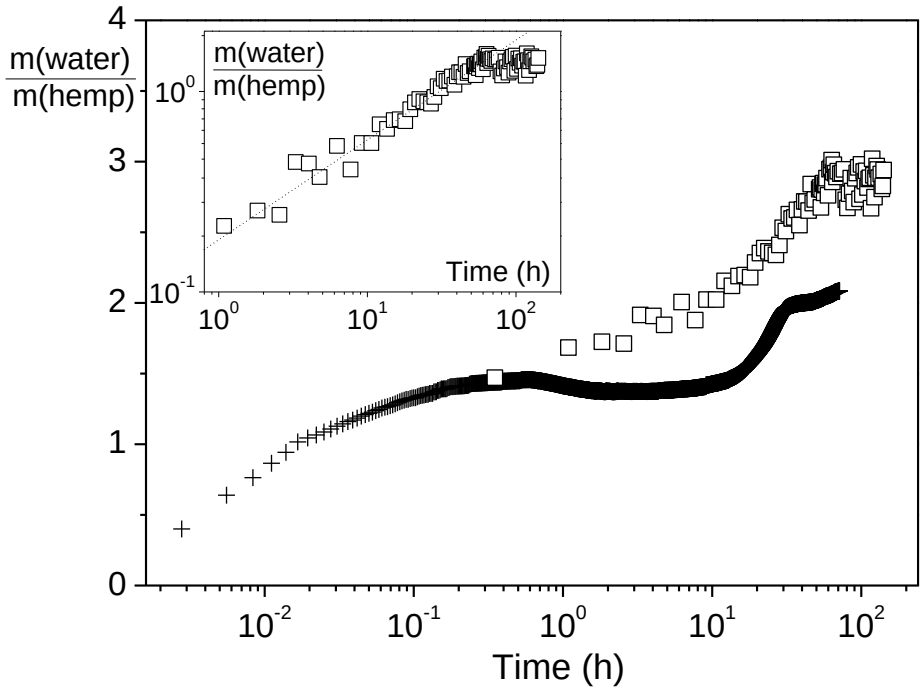


Figure 8. Water to hemp mass ratio in time as measured by T_1 relaxometry (squares) and by weighing of an immersed sample (crosses). The inset shows the additional (see text) water to hemp mass ratio in phase 2 of imbibition as a function of time in logarithmic scale. The continuous line has a slope ½.

3.2.3 Impact of sample history

Successive imbibition tests were carried out by drying the sample (put in an oven at 60°C until mass stabilization) after each test. By monitoring by NMR the successive water uptakes we see that the second imbibition is different from the first one (see Figure 9). The water mass in hemp increases faster after the first cycle (imbibition + drying), but finally reaches the same saturation level. In the next cycle the water absorption process is the same as the second one. This suggests that the structure has been irreversibly modified during the first cycle but is no more modified in the next cycles. This might be related to the observation that after the first drying (and not in the subsequent cycles) a brown layer overlays the sample, which likely corresponds to the extraction of molecules from the hemp possibly playing a role in the initial imbibition. We also could see that after the first cycle the sample volume has slightly increased so that it tends to be strongly jammed in the container in which it was initially just

packed by hand, which confirms some slight irreversible changes in the structure after the first imbibition.

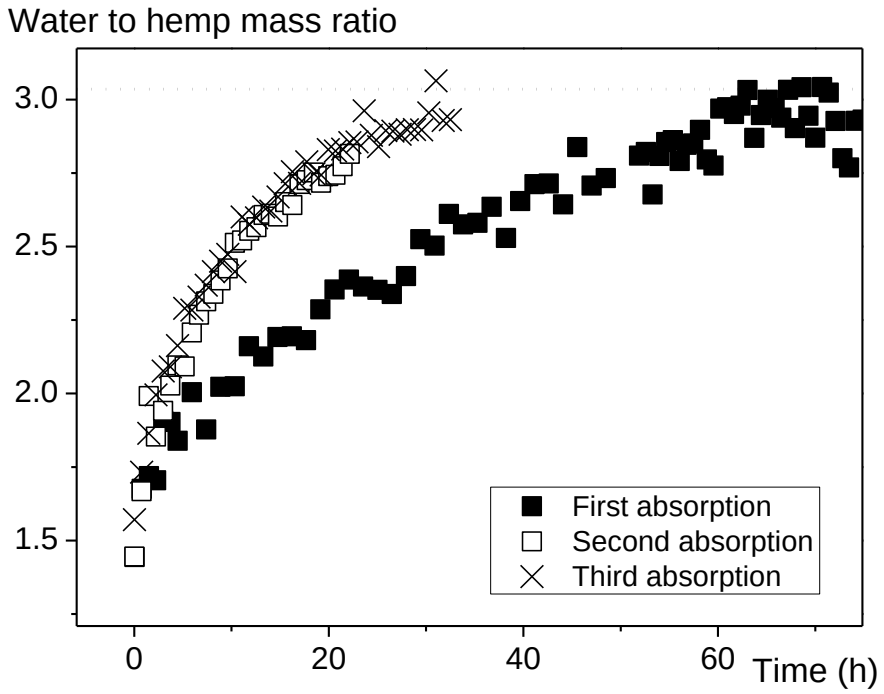


Figure 9: Results of the water absorption in hemp shives during successive imbibitions (separated by drying) measured by T_1-relaxometry.

3.3 Comparison of NMR data with data from TC RILEM method

We can now compare the results obtained from the TC RILEM method to those obtained by NMR for the four different hemps at different times during the imbibition process. Except for one material the mass found by the TC RILEM method is significantly higher than that found by NMR all along the process (see Figure 10). In fact we have a constant shift of the two evolutions, i.e. at any time during the process the water mass found by the TC RILEM method is just simply equal to that effectively entered in the hemp plus a constant term. It is likely that this term exactly corresponds to the water amount remaining at the surface of the hemp shives due to capillary effects. This would give an additional mass of water proportional to the specific (external) surface of the hemp sample, thus proportional (for a given hemp type) to the mass of hemp by a factor α, and consequently an additional term α in the representation

of m_w/m_s, in agreement with our data. This factor finally appears (see Figure 13) to vary in a rather narrow range (0.4-0.6) depending on hemp type.

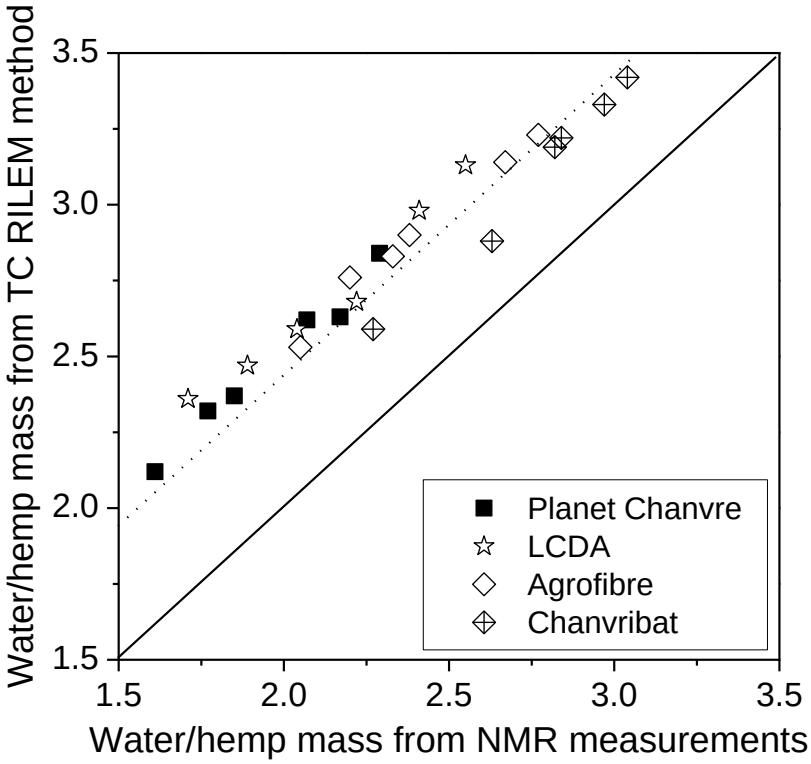


Figure 10: Water to hemp mass ratio measured by the TC RILEM method as a function of that measured by NMR measurements for different hemps at different times during imbibition. The lines have a slope 1, the continuous line would correspond to a perfect agreement between the two types of measurement.

3.4 Imaging of water absorption

In order to understand why hemp imbibition takes place in two phases with very different kinetics, a hemp shiv imbibition is directly observed using µ-MRI. We used the ZTE sequence [24] which allows detecting protons that have relaxation times as short as a few tens of microseconds. Therefore, we expect to detect both bound and liquid water. With this sequence, the signal intensity is proton density weighted, which means that it is proportional to the local amount of protons. As a consequence, roughly speaking the bright parts of the images corresponds to the zones with the highest water density.

We first attempted to get an image of dry hemp but we were unsuccessful, the signal was too low. Images could be obtained when the shiv is in contact with water. In that case the image evolution is qualitatively similar in the different slices along the shiv axis (see Figure 2). Here we focus on one of the central slice to discuss the typical trends. The first image corresponds to signal acquisition during the first four minutes of hemp imbibition. We can see that it is blurred (see Figure 11), which is likely a result of the significant evolution of the water density distribution over the time of acquisition. Indeed in MRI each information at a local scale is not simply the result of the average signal over the total time of acquisition as for several other imaging techniques, here it is based on a reconstruction by Fourier transform of the information obtained from a virtual picture obtained in the field gradient (reciprocal) space. As a consequence significant evolution of the spatial density can lead to this kind of blurring. We can nevertheless still distinguish the contour of the shiv and external water between the shiv and the tube, which are regions in which the water amount changes likely remain negligible.

In the next step, i.e. the image obtained after 18 min, the picture is better resolved, likely because as we have seen in previous measurements the absorption kinetics during that period is much slower than in the first stage. We can now clearly see the hemp shiv surrounded by water. Moreover the shiv seems to be composed of two parts. The left part is much brighter than the right part. These regions correspond to two different tissues, respectively the pith and the wood. The pith is the youngest part of the stem, it is in its centre. During the plant growth, the pith becomes wood through a lignification process. Lignin forms a three dimensional network that provides its rigidity to the cell wall. It also makes the tissues more hydrophilic. In fact, polysaccharide components of the plant cell wall are highly hydrophilic and thus permeable to water. Lignin makes it possible for the tissue to conduct water efficiently [28]. As a consequence, pith is very hydrophilic whereas the woody part is more hydrophobic. This explains that after 18 min, the pith is already very bright whereas the wood does not seem to contain much water. We can also observe some bright points in the woody part of the shiv. They are likely due to some vessels filled with water (which finally represents a small water amount). Indeed the imbibition of wood is known to take place in two successive steps. During a first stage water penetrates through some vessels due to capillary forces. Then it diffuses through vessel walls as a result of hydrogen bonding. Only when these walls are saturated water can stay in the lumens.

During the next hours, we observe a progressive brightening of the woody part. After 16 h it seems to contain almost as much water as the pith. During that period the water amount in the pith does not seem to evolve significantly. This suggests that the two successive steps in the kinetics of water absorption in hemp as observed from NMR tests results from the successive imbibition of the two different parts of the shiv: first a fast penetration of water in the pith, then a much slower penetration in the wood.

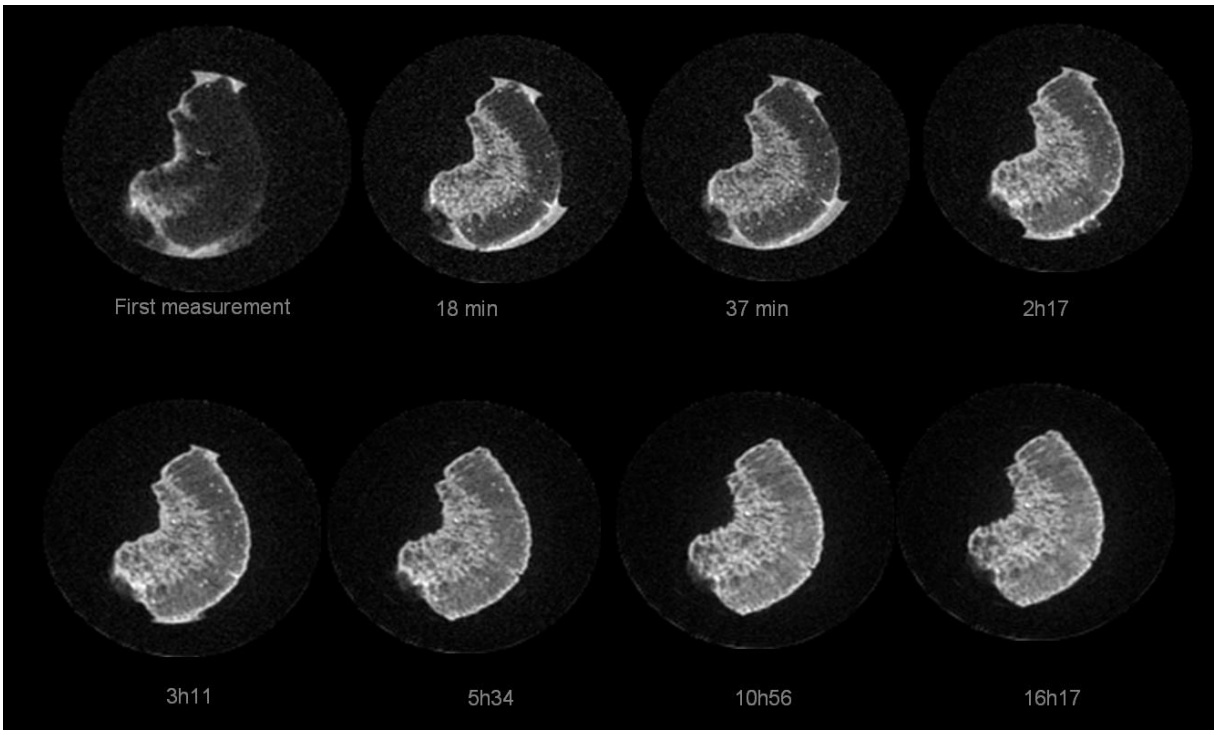


Figure 11: Evolution of the middle slice of hemp during water absorption as seen by MRI.

4. Conclusion

We have shown that following the evolution of the distribution of NMR relaxation time makes it possible to quantify the effective amount of water entering the hemp. It is more difficult to use the weighing technique to get relevant data and we were unable to understand the exact origin of some artefacts observed in that case, in particular those leading to a water mass decrease while NMR data show a continuous increase of water mass inside the hemp.

We also showed that in general the TC RILEM method significantly overestimates the effective water content inside the hemp, an effect likely due to some water remaining along

610 the hemp shiv surfaces as a result of capillary effects. It was also shown that this
611 overestimation is poorly dependent on the hemp type and does not vary in time (i.e. during
612 absorption), so that it can simply be taken into account for a better interpretation of the results
613 of such tests.
614
615 As clearly seen from NMR, water intake occurs in two steps, a fast one taking place in less
616 than two minutes, corresponding to water entering the pith, and a slow one, taking place over
617 days, corresponding to water diffusing into the woody part of the shiv. Further studies could
618 focus on how plant-related parameters (species, growth conditions...) affect the water intake.
619 The effect of additional treatment, like retting could also now be fully assessed. Finally, the
620 way this two-steps kinetics affect the setting of hemp-lime concrete can now be thoroughly
621 studied and taken into consideration in the formulation of hemp concrete relationship /
622 performance.
623
624
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626
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629
630
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