Influence of the mold growth on the crystallographic composition of hemp mortar

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Abstract. The use of hemp mortar as a bio-based insulation composite is widely promoted in the construction sector in France due to its environmental and hygrothermal advantages and the availability and low price of hemp fibers. Nevertheless, the use of such materials claims the consideration of the microbiological contamination that could lead to its degradation. Molds are known for their ability to modify locally the composition of hemp mortar by decreasing the pH level. That’s why the main objectives of the present work are, first, to expose the hemp mortar favorable conditions for mold growth, secondly, to investigate the proliferation of the mold filaments inside the hemp mortar sample and, then, to analyze the crystallographic composition. Experimentally, hemp mortar samples were exposed to high level of relative humidity during one year until the mold growth. The SEM observation allowed to follow the internal growth and identify the depth of the mold growth. Finally, the composition of the contaminated hemp mortar was studied by X-ray diffraction. The obtained results reveal that molds growth occurs not only on the surface but also in the depth. Nevertheless, as the mold growth started only after one year of high humidity exposure, a good resistance of studied hemp mortar towards molds was noted. Furthermore, the mineralogical composition analysis of the contaminated samples shows that the hydrates responsible for durability remained. These results provide data to better predict the durability of hemp mortars.

1. Introduction

Today, biobased building materials are used all over the world to reduce carbon dioxide emissions and hence human impact on the planet's climate. In addition to its low carbon footprint, these are interesting building materials due to their hygrothermal, properties and the availability of raw materials [1]. Consequently, many researchers have investigated different properties of biobased materials of different nature, such as wood [2], straw [3], cork [4], jute [5] or hemp [6,7]. However, the main problem of building materials incorporating organic fibers is a lack of information about their durability. In this work, the studied material is hemp mortar, that is known for their functional performances: acoustic [8], hygrothermal [7] and mechanical [9]. Nevertheless, hemp mortars as all biobased materials representing anisotropic behavior, heterogenic microstructure and hygroscopicity. Two first parameters give the difficulty for predicting the functional performance of hemp mortars and their evolution in time. The latter characteristic is a reason for...
It provokes the structural degradation and evolution of hemp mortars’ properties [6].

Another aspect that has to be taken into account is a microbiological contamination. Though there are different microorganisms that are involved in microorganism proliferation, the mold growth is one of the most important criteria when assessing the degradation of bio-based materials [10,11]. The fungal proliferation of hemp mortar affects its microstructure and, thus, properties of the material [12]. To better understand the nature of the behavior and the durability of this biobased composite towards the fungal growth, it is necessary to study the influence of molds on the crystallographic composition of hemp mortars.

Against the subject of the microbiological durability of hemp mortars, few researchers investigated the impact of mold growth. First of all, it was suggested that mold growth affects negatively the air quality [10], as certain fungal strains produce toxins that are able to provoke different diseases such as asthma or cancer [13]. Also, molds are known for their ability to degrade lignocellulosic biomass and produce different metabolites (ethanol and organic acids) to get more minerals from environment [14]. Indeed, the consecutive decrease in pH provoked by the organic acids production gives a competitive advantage to the acid-tolerant filamentous fungi for their growth. Ectomycorrhizal fungi use this pH decrease to solubilize soil minerals and get nutrient ions [15]. In the case of saprophytic fungi, the decrease of pH level provokes an acid-catalyzed hydrolysis of holocellulose [16]. Different authors suggested the influence of mold growth on the physical and mechanical properties, as well as the microstructural integrity of building materials [17]. The decrease of mechanical properties of hemp mortars due to fungal deterioration was also confirmed by [18].

Most researchers do not focus on the influence of fungal growth on the chemical composition of hemp mortars. In fact, molds are able to modify the composition of the support that allow them to grow better. That is why, in this paper the main objectives are to identify the depth of mold proliferation in hemp mortar after one year and investigate the influence of the fungal growth on the crystallographic composition of the material. To attend this goal, different experimental procedures was conducted for two categories of samples: non-covered and covered with molds.

2. Experimental procedure

The scientific interest of this work consists in evaluation of the influence of fungal growth on the mineral composition of hemp mortars. In this section, firstly, the studied hemp mortar samples are presented in this part. Then, the experimental characterization protocols that allowed us to assess the mold growth and the mineral composition of hemp mortars are described.

2.1. Materials and conditioning

One formulation of hemp mortar was used in this study. Hemp shives of the origin from France were used to make the hemp mortar samples. The binder represents a commercial mixture developed by ParexGroup SA. It is composed of Portland cement, hydrated lime and various additions to achieve the rheology suitable for spray application. The proportions of the hemp mortar mixture used are shown in Figure 1. The mixing was done in two steps: first, the hemp shives were premixed with water for 1 minute at 140 rpm, secondly, the binder was added and mixed for 5 minutes at 140 rpm. The sample size adopted was 4x4x16 cm. After manual production, the samples were dried for 28 days under laboratory conditions (23 ± 2°C, 50 ± 5%RH). Then one sample was placed in high humidity conditions (23 ± 2°C, 97 ± 2%RH) for one year to facilitate mould growth. Another sample was kept under laboratory conditions for comparison (Fig. 2). All growing molds are the molds that are present naturally in the sample (in the hemp, environment), no inoculations were made.
2.2. Experimental methods
This paper investigates the depth of fungal proliferation in hemp mortar and its influence on the mineralogical composition of the material. After one year of exposure two categories of samples were scanned using an attenuated total reflectance-Fourier-transform infrared spectroscopy (ATR-FTIR) in order to obtain the information on the surface chemistry and confirm the presence of molds on it. It was performed with a PerkinElmer Spectrum Two spectrometer on samples. The test was conducted by studding vibratory frequencies in the middle Infrared (4000-400 cm⁻¹).
Then, scanning electron microscope (W-SEM) analyses were used to evaluate the depth of the mold proliferation and performed by using a Hitachi S-3400N device. The surface of the hemp mortar and the interface zone between cementitious matrix and hemp particles were observed. Micrographs are recorded by using secondary electrons detectors at an acceleration voltage of 15 kV, in high vacuum mode (pressure <1Pa). Previously to observations, the specimens were covered with carbon in order to improve the image quality.
Finally, the X-ray diffraction were conducted on two samples of hemp mortar at two areas (on the surface and inside). Prior to XRD crystallography analysis, hemp mortar samples of the size 4x4x16 cm³ were grinded and sieved to remove organic fibers. This step allowed us to decrease the influence of the dilution on the final result as in this case we analyze only mineral matrix. Free water was removed using the acetone. Then, the specimens were dried at 40°C in order not to modify the composition of the sample. XRD crystallography patterns were obtained using Cu Kα anode tube (λ= 1.54182 Å) radiation at 40kV and 20mA with a Bruker D8 diffractometer (Bruker, Karlsruhe, Germany) (Fig. 3). The diffractometer scanned from 5° to 60° (2θ°) in step size of 0.015° and the counting time per step was 1.2 s.

3. Results and discussion
First, validation of the presence of molds on the surface of hemp mortar samples was conducted by ATR-FTIR scanning. Figure 3 shows ATR-FTIR spectra for samples conditioned at high humidity and laboratory environment. We note the intense peaks at around 3260 cm⁻¹ that are assigned to the stretching vibration of hydroxyl an -NH groups and at around 2920 cm⁻¹ attributed to CH, methylene group stretching vibrations. Also, the vibration peak at 1750 cm⁻¹ is attributed to the C=O stretching vibrations and the peak at 1620 cm⁻¹ represents N-H vibrations. All these peaks are present only in the case of high humidity conditions and can be explained by the presence of fungi [19]. Also, we note the intense peaks at 1400 and 870 cm⁻¹ that are attributed to the deposit of calcium carbonate. In order to verify if molds...
are able to grow inside the hemp mortar the SEM analysis was conducted at different depth of the sample.

![ATR-FTIR spectra](image)

Figure 3. ATR-FTIR spectra obtained from hemp mortar samples conditioned during one year at high humidity and laboratory conditions

W-SEM observations of hemp mortar conditioned for one year in a high humidity environment were made at different depths. This allowed us to study the ability of molds to grow inside the material. Figure 4 shows the results of the W-SEM observations at the surface and at 4 mm. The presence of mold filaments on the hemp mortar surface was noted (Fig. 4-a). They are flattened, allowing better adhesion to the surface. Figure 4-b shows the presence of mold filaments at a depth of 4 mm in the hemp mortar sample. Indeed, mold growth occurs in the internal porosity of the sample. The presence of mold at a greater depth was not observed that is why the W-SEM images were not represented. The results of the W-SEM observations show the ability of mould to grow inside hemp mortars due to their internal porosity.

![W-SEM observations](image)

Figure 4. W-SEM observations of mould growth on the hemp mortar sample conditioned in a high humidity environment for one year at the surface (a) and at 4 mm from the surface (b).

In order to study the influence of molds on the mineral composition of hemp mortar, X-ray diffraction crystallography (XRD) was performed. It was carried out on two samples conditioned for one year under...
high humidity and laboratory conditions respectively. For each sample, the crystallographic analysis of the surface and the middle part of the samples was done. This allowed a better comparison of the obtained results.

The XRD patterns presented in figure 5 showed that the main mineralogical compounds of the hemp mortar are $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot26\text{H}_2\text{O}$ (ettringite), $\text{Ca}(\text{OH})_2$ (portlandite), $\text{CaCO}_3$ (calcite), $\text{SiO}_2$ (quartz), $\text{Ca}_3\text{SiO}_5$ (tricalcium silicate) and $\text{Ca}_2\text{SiO}_4$ (dicalcium silicate). Figures 5-a and 5-b represent the crystallographic analysis of the hemp mortar specimen conditioned for one year in the laboratory environment (23°C and 50% RH) in the middle and at the surface, respectively. The XRD spectrum of the middle part of the sample reveals the presence of ettringite and portlandite and low signal of calcite (Fig. 5-a). In contrary, at the surface we note the great presence of calcite and low signals of portlandite and ettringite (Fig. 5-b). It is explained by the carbonation of the mineral binder that occurs at 50% RH.

The XRD patterns of the sample conditioned at high humidity environment (23°C and 97% RH) in the middle of the sample and at the surface (Fig. 5-c and Fig. 5-d respectively) demonstrate the same pattern. The main difference is that the middle part of the sample conditioned at laboratory environment (Fig. 5-a) represents lower signal of ettringite and calcite. Also, there are signals of non-hydrated $\text{Ca}_3\text{SiO}_5$ (tricalcium silicate) and $\text{Ca}_2\text{SiO}_4$ (dicalcium silicate), which means that hydration is not completed. Indeed, the hydration of the sample at 97% RH continues because of high relative humidity, and the hydration of the sample conditioned at 50% RH was not full due to drying and the lack of water. It should also be noted that the high humidity conditioning used is not suitable for complete carbonation, with optimal values being between 50% and 70% relative humidity.

Results reveal that after one year of exposure to different conditions, both samples represent the carbonation of mineral binder at the surface. At the same time, the sample that was exposed to high humidity and mold growth demonstrates the presence of ettringite and portlandite. These two hydrates are responsible for mechanical properties and durability of the studied hemp mortar. Despite the ability of molds to grow inside the hemp mortar, it doesn’t have a great impact on the chemical composition.
4. Conclusions
In this work, the influence of mold proliferation on the hemp mortar and its durability was investigated. Also, the ability of molds to grow inside the hemp mortars was verified. In order to provoke the mold growth, hemp mortar sample was exposed for one year to high humidity conditions. Another sample exposed to laboratory conditions was used as a reference. The ATR-FTIR analysis and W-SEM observations were used to study the mold growth on the surface and inside the hemp mortar sample. The XRD scanning allowed to investigate the difference of hemp mortar samples’ chemical composition at different part.

Results revealed the ability of molds to grow inside the sample. Indeed, it was noted that molds occupy the inner porosity that is high in the case of our hemp mortar. The chemical composition analysis demonstrated the carbonation of the hemp mortar surface. At the same time, the interior part of the sample covered with molds represents the hydrates (ettringite and portlandite) that are responsible for mechanical properties and the durability. Nevertheless, the same pattern should be confirmed for the in situ conditioned hemp mortar samples.

This study provides future researchers with the sufficient refine information on the molds growth inside the hemp mortars and their influence on the chemical composition. Obtained results must be considered when studying the durability of hemp concrete under the accelerated aging protocol.

5. Conflict of interests
Non.

6. Acknowledgments
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