A chemical, morphological and mineralogical study on the interaction between hemp hurds and aerial and natural hydraulic lime particles: Implications for mortar manufacturing

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HIGHLIGHTS

- Microstructure at the interface between hemp hurds and lime in mortars.
- Delayed hardening of the lime due to the presence of hemp.
- High amount of vaterite after three months due to lack of water for the matrix.
- Need of further studies on the reactions between $Ca(OH)_2$ and hemp organic compounds.

ARTICLE INFO

ABSTRACT

Mixing hemp with aerial or natural hydraulic lime gives rise to mortars with improved flexibility and insulation but with peculiar microstructure compared to lime-aggregate mortars. The chemical–mineralogical and morphological investigation carried out here shows that hemp absorbs most of the water present in the matrix, causing superficial deposition and scarce adhesion of the lime to the hemp. This also delays the hardening process, as demonstrated by the high content of portlandite, vaterite and calcium silicates found after three months of curing. Some modifications to the production and curing procedures are suggested to improve the microstructure and final performance of hemp-lime mortars.

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1. Introduction

Mortars are among the most used and diffused building materials in new and old constructions all over the world. Although only three basic components (i.e. binder, aggregate and water) are needed to produce this composite material, a huge variety of mortar types are possible, due to the existence of binders and aggregates with different chemical, mineralogical and textural features. The variability of properties and characteristics typical of composite materials, achieved by adjusting the component types and proportions, is a distinctive feature of mortars, for

example compared to natural stone. As a consequence, mortar is a versatile composite material with multiple uses in construction.

Furthermore, mortars are often made with additional components, called additives and admixtures, which modify the properties or improve already existing characteristics of the material [1]. The use of admixtures is an ancient practice in the field of construction, as indicated by Vitruvius in *De Archirectura libri decem* (15 BC). In particular, the addition of fibres (e.g. animal hairs, vegetable fibres) to mortars is an ancient and effective method of improving flexibility, adhesion and strength of mortars [2].

With a world production of 214,000 ton [3], hemp is one of the 10 major primary plants grown as source of bast fibres (i.e. fibres obtained from the exterior part of the stem) and hurds (i.e. inner woody part of the stem, also called shives), used for various

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industrial purposes, such as: textiles, cordage, panelling, biofuel, paper, plastic composites and building materials. In particular, the hemp hurd, which in the past was discarded (only fibres and seeds were used [4]), is now of great interest for the unique properties that confers to building materials. For example, the use of hemp-based mortar leads to a reduction of 12–17% in energy consumption in buildings [5]. Hemp-based mortars are also efficient CO_2-sequestering agents, thanks to the ability of both hemp bast fibres [6] and lime of absorbing CO_2 from the atmosphere (during crop and hardening, respectively). Furthermore, the use of hemp in the place of a stone aggregate allows the production of mortars with a very low bulk density (i.e. lightweight mortar), which makes them suitable for specific building applications (e.g. filling, rendering, etc.).

However, the formulation of a mortar composed of only lime and hemp hurds involves important changes of the main characteristics (i.e. chemistry, mineralogy, texture) and properties (i.e. hygric and mechanical behaviour, durability) of a typical mortar. In recent decades, the importance of studying hemp-lime-based mortars to understand the influence of the presence of hemp both at microscopic and macroscopic level is being taken into consideration. The hygric, mechanical and thermal properties of hemp-based blocks have been investigated [5,7–10]. However few studies relate the macroscopic properties of these peculiar composite materials with the microstructural characteristics at the interface between the matrix and the vegetable fibre [11–13] and still many unanswered questions remain about the interaction between such different components when they are mixed together.

In this work, we have studied the interaction between hemp hurds and three types of lime (natural hydraulic and aerial in form of powder and as a putty) from chemical, morphological and mineralogical perspectives. Morphological and chemical investigations of both fresh and dry hemp hurds were carried out to evaluate the differences between these two hurds, depending on the initial amount of water. Moreover, investigations on the lime particle size distribution and specific surface area and microscopical observations of the mixes have been performed to evaluate the adhesion of the lime particles to the hemp hurds. Finally, a mineralogical study has been carried out to evaluate if the contact of the matrix with hemp hurds somehow modifies the hardening process of the limes (mineral phases consumed and formed).

2. Materials and methods

2.1. Materials

The hemp, whose commercial name is Cannhabitat®, is produced by AgroFibre, Euralis (Cazeres, France) and was supplied by the Cannabric enterprise (Guadix, Granada, Spain; www.cannabric.com). Plants are usually collected at the end of summer and dried on site. The hemp hurd, which is the part of the plant used for construction purposes, is cut to elongated and flat particles of size in the range of 2–25 mm (Fig. 1). Both fresh (i.e. green, not dried) and dry hurd particles were investigated although only the dry hemp hurds were mixed with lime, as usual in construction.

Three different types of lime were selected for this study: a hydrated lime in the form of dry powder (CL90S [14]) produced by ANCASA (Seville, Spain); a hydrated lime in the form of putty stored under water for 2 years (CL90S PL), produced by ComCal (Barcelona, Spain); and a natural hydraulic lime (NHL3.5 [14]) produced by Socli, Italcementi Group. The lime:hemp:water dosage by volume was 3:5:2.5 for the limes in the form of a powder (CL90S and NHL 3.5). This dosage was chosen with the objective of producing suitable mixes for application as rendering materials. In the case of the lime putty (CL90S PL) the same volume of lime but a lower amount of water were used, since this lime already has 6% wt. of supernatant water. The difference in the water content was calculated considering the differences in the bulk density between the powdered (~540 g/L) and the putty (~1205 g/L) lime. In total, 30 samples of $4 \times 4 \times 16$ cm were cured for three months under average conditions of $T = 17$ °C and RH = 75%. The mixes were named as: AL-dh (aerial lime CL90S + dry hemp); AP-dh (aerial lime putty CL90S PL + dry hemp); NHL-dh (natural hydraulic lime NHL 3.5 + dry hemp).

2.2. Study of the limes

X-ray fluorescence (XRF) was used to analyse the chemical composition of major and minor elements of the limes, by means of a Bruker S4 Pioneer X-ray fluorescence spectrometer with wavelength dispersion, equipped with a goniometer that analyses crystals (LIF200/PET/OVO-55) and a Rh X-ray tube (60 kV, 150 mA). Measurements were performed in a vacuum with a rotating sample. Semiquantitative scanning spectra were obtained using Spectraplus® software. Before the analysis, the lime powders (~5 g) were dispersed in KBr, deposited in an aluminium cup and then pressed at 10 ton to obtain a pressed pellet (40 mm sample disc).

The mineral phases of the three lime types were identified by X-ray diffraction (XRD) analysis, using a Panalytical X'Pert PRO MPD diffractometer, with automatic loader. Analysis conditions were: radiation Cu Kα (λ = 1.5405 Å), 3–60° 2θ explored area, 45 kV voltage, 40 mA current intensity and goniometer speed using a Si-detector X'Celerator of 0.01° $2\theta/s$. The identification and semi-quantification of the mineral phases (portlandite, calcite and calcium silicates) was performed using the X-Powder© software [15]. In particular, the identification of calcite indicates that a partial transformation of the lime occurred; therefore XRD analysis was used not only to identify mineral phases in the limes but also to control their prior carbonation during sample preparation.
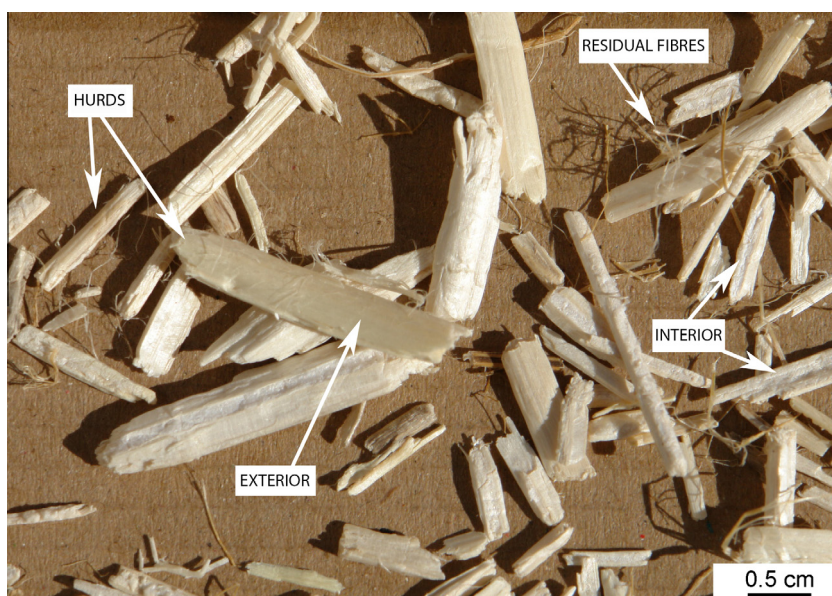

Fig. 1. Dry hemp hurds. Interior and exterior indicate the concave and convex surfaces of the hemp hurds, respectively.

The specific surface area (SSA) of the limes, determined with the BET [16] method, was measured by using the N_2 Adsorption technique, by means of a Micromeritics 3000 Tristar equipment, which worked under continuous adsorption conditions, at a temperature of 77 K. Before the measurements, the lime samples were outgassed at 10^{-3} Torr and 110 °C for 4 h, by means of a Micromeritics Flowprep.

The lime particle size distribution was analysed by means of a Mastersizer 2000LF from Malvern Instruments, which measures particles in the range of 0.02–2000 μm. Lime samples were dispersed in ethanol and sonicated for 20 s before the measurement.

Prior to the analyses, the lime in the form of putty (CL90-S PL) was oven-dried for 8 h at 40 °C. This temperature was high enough to reduce the lime to dry powder, at the same time delaying carbonation (the ideal T for the carbonation process is 15–20 °C [17]) during sample preparation.

2.3. Study of the hemp hurds

The chemical composition of both fresh and dry hemp hurds was analysed by means of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FT-IR), using a JASCO 6200 spectrometer, which performed 100 scans per measurement, in the range of 600–4000 cm^{-1} and at a resolution of 2 cm^{-1}. Data were acquired by the SPECTRA MANAGER v2 software and interpreted following Le Troëdec et al.'s work [12]. The advantage of the use of the ATR method is that the hemp hurd particles did not need any preparation before the analysis.

Finally, the structure and surface morphology of both the fresh and dry hemp hurds were observed by means of environmental scanning electron microscopy (ESEM), by using a Philips Quanta 400 microscope that worked at a fixed temperature of 2 °C. Small pieces of hemp hurds (~5 mm) were directly put in the chamber, without needing to be previously dried and sputter coated. Both the concave (external) and convex (internal) surfaces of the hemp hurds were observed (as indicated in Fig. 1). Before observation, the microscope chamber was purged 5 times at a range of pressures between 2.5 and 5.5 torr, which correspond to relative humidity of approximately 50% and 100% (at $T = 2$ °C), respectively. Once equilibrium was achieved, pressure was fixed at 4 torr (RH ~ 80% at $T = 2$ °C) and 3.5 torr (RH ~ 70% at $T = 2$ °C) for the observation of fresh and dry hemp hurds, respectively. The former have a water content of 10% of the total weight, which explains why the RH established during observation was higher in this case. During observation, relative humidity was never decreased below 70% or 80% to avoid modifying the structure of the hurd particles.

2.4. Study of the interaction between hemp and lime particles

The adhesion of lime particles to the hemp (in the hardened mixes) was analysed by means of ESEM, using the same working conditions as those described above.

To investigate the chemical compounds formed from the interaction between lime and hemp, ATR FT-IR analyses were performed on both the hurds and the matrix of each mortar mix, at the same working conditions as those described above after three months since mortar production. The FT-IR spectra of the mineral phases were interpreted by means of the RRuff database, which is available online (rruff.info).

Table 1
Chemical and mineralogical composition and specific surface area (SSA, in m²/g) of the three types of lime, determined by X-ray fluorescence (XRF), X-ray diffraction (XRD) and N_2 adsorption analyses. Port = portlandite; Cal = calcite; CS = calcium and di-calcium silicates; LOI: loss on ignition; – = absent; * = 5–10%; ** = 40–50%; *** = 90–95%.

Chemical composition			
	CL90-S	CL90-S PL	NHL3.5
%			
Na_2O	0.06	0	0.04
MgO	0.47	1.2	2.62
Al_2O_3	0.10	0.28	0.1
SiO_2	0.23	0.92	8.35
CaO	73.86	93.34	65.68
Fe_2O_3	0.04	0.23	0.57
K_2O	0.02	0.02	0.34
P_2O_5	0.05	0.01	0.03
TiO_2	0.02	0.02	0.05
S	0.55	0.19	0.35
LOI	24.84	3.42	6.19
Mineral phases			
Port	***	***	**
Cal	*	*	*
CS	–	–	**
SSA			
	13.82	29.52	9.26

Finally, the mineral phases formed after three months of curing were studied by means of XRD analyses, at the same working conditions as those described above. For this analysis, only the matrix was sampled, trying to avoid the residual fibres (i.e. very fine fibres proceeding from the wall of the hemp hurd).

3. Results and discussion

3.1. Chemical, mineralogical and morphological study of the limes

The aerial limes (CL90S and CL90S PL) show a high degree of purity, due to the high amount of calcium (>70%, expressed as CaO) and portlandite (>90%), found by XRF and XRD (Table 1), respectively. Differences in the amount of CaO, MgO and S between the two aerial limes are due to the different outcrops of the limestone used for lime production. In particular, the difference in MgO content indicates that the original limestone used for producing the lime putty (CL90S-PL) was richer in this compound, probably dolomite, with respect to that used for the production of the dry hydrated lime (CL90S). In the same way, differences in the CaO amounts indicate different initial contents of calcite in the original limestone. Neither dolomite nor calcite proceeding from the limestone can be determined, since these phases decomposed during burning of the limestone, undertaken during lime production. Indeed, the small amount of calcite (5–10%) found by XRD in the three limes (Fig. 2) was a result of their prior carbonation due to air exposure during sample handling and preparation. Since calcite derives from the carbonation of portlandite, it is possible to state that both the aerial limes were initially composed of 100% of portlandite, whilst the natural hydraulic lime (NHL 3.5) was initially composed of 50% portlandite and 50% calcium ($CaSiO_3$) and di-calcium (Ca_2SiO_4) silicates. Moreover, a higher amount of MgO was found in the natural hydraulic lime compared to the aerial ones, as Mg comes from the clay present in the raw material used for NHL3.5 lime production.

The lime putty (CL90S PL) has the highest specific surface area (SSA, in Table 1) due to the storage of this lime under water, which induces a reduction of the particle size over time [18]. Indeed, this lime presents a bigger amount of nanometric portlandite crystals, which are also slightly smaller in size (0.04 < ∅ < 0.3 μm, Fig. 3), compared to the aerial lime in the form of powder (CL90S, 0.09 < ∅ < 0.8 μm, Fig. 3). The latter is mostly composed of micrometric particles of size in the range of 1–20 μm. The natural hydraulic lime, in spite of being characterised by the lowest SSA, presents the highest volume of nanoparticles and the lowest of microparticles among the limes (Fig. 3). Notwithstanding, the particle size distribution measured by LASER also depends on the shape of particles (e.g. elongated, rounded, etc.), which needs to be fixed for data interpretation. In the aerial lime all particles have a hexagonal shape (of portlandite); the presence of small amount of calcite particles in the aerial lime is not likely to modify the particle size distribution because the calcite formed mainly presents tabular shape (although also scalenohedra and rhombohedra precipitate) and similar size (from hundreds nm up to 1 μm) compared to the lime particles [19]. In the natural hydraulic lime, instead, particles with undefined shape are also present (calcium silicates), therefore an error can be introduced during data interpretation. For this reason, during particle characterisation, it is fundamental to perform other complementary studies, such as the determination of specific surface area that is considered a more accurate parameter to evaluate the reactivity of a lime, compared to the particle size [20].

3.2. Chemical and morphological study of the fresh and dry hemp hurds

ATR FT-IR spectra show that the hemp hurd is composed of cellulose, hemicellulose, lignin, pectin, waxes and water (Fig. 4).
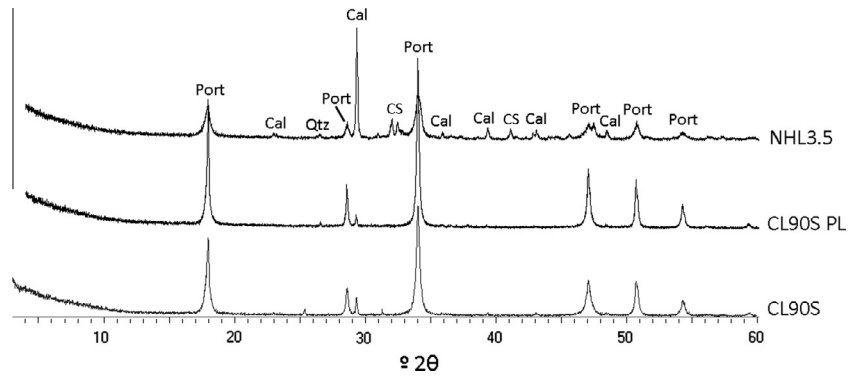
Fig. 2. X-ray diffraction patterns of CL90S, CL90S PL and NHL3.5 limes. Port = portlandite; Cal = calcite; CS = calcium silicates; Qtz = quartz.
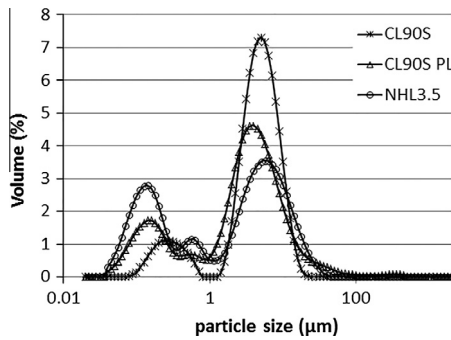

Fig. 3. Particle size distribution curves of CL90S, CL90S PL and NHL3.5 limes, in which the volume (in %) is represented as a function of particle size (in μm).

These chemical compounds were identified comparing the transitions in the spectra with those described for hemp by Le Troëdec et al. [12]. As shown in Fig. 4, there are no differences between the FT-IR spectra obtained for fresh and dry hemp particles, apart from the higher water content in the former, as indicated by a lower transmittance (i.e. higher absorbance) of the band centred at around 1600 cm^{-1} (O–H bending).

By means of ESEM, it has been observed that the convexe (external) surface (Fig. 5a and c) of the hemp hurd is smoother than the concave (internal) one (Fig. 5b and d) although this difference is more visible in the dry (Fig. 5c and d) than in the fresh hemp (Fig. 5a and b). However, the latter shows more impurities

(described by Le Troëdec et al. [12] as waxes and oil) on both surfaces (Fig. 5c and d). The peculiar honeycomb structure shown in Fig. 4d was observed both in fresh and dry hurds. Also some residual fibres (Fig. 5b) and broken pieces of the hurd skin (Fig. 5d) have been observed.

Finally, tracheary elements (i.e. elongated, rigid and lignified cells of the xylem) were recognised due to their typical structures: annular (Fig. 6a), scalariform (Fig. 6b), reticulate (Fig. 6c) and pitted (Fig. 6d) [21]. These forms were all recognised in both fresh and dry hemp hurds.

Our observations coincide with the general description of the permanent tissues (i.e. tissues consisting of mature cells with a definite shape and size, not able to divide further) composing the hemp hurd: a superficial epidermis, constituted by small fibres and impurities of waxes; an internal woody part called xylem, which is lignin rich and made by many vascular tracheary elements that have the function of transporting water and minerals to the plant; and the centre of the stem, which is composed by cellulose pits and has a honeycomb structure [13].

3.3. Morphological and mineralogical study of the interaction between lime particles and hemp hurds

The pore structure and the adhesion between the matrix of the three mixes and the hemp hurds were studied after three months of curing by observing the cross section of a hurd, by means of ESEM (Fig. 7). As shown in Fig. 7a–c, the internal pore structure of the hurd is not modified by the presence of lime particles (i.e. it is not filled by lime), which only adhere to the epidermis. This adhesion is higher in
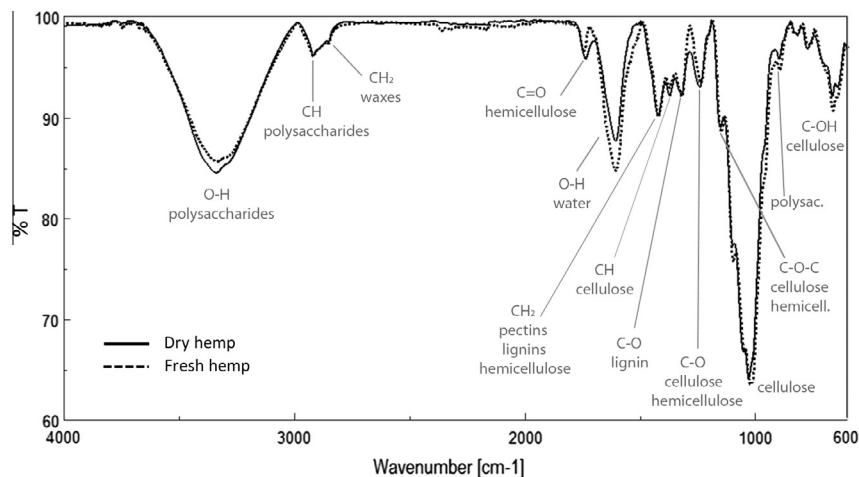

Fig. 4. ATR FT-IR spectra of the fresh and dry hemp hurds. The wavenumber (in cm^{-1}) is plotted versus the transmittance (*T*, in %).
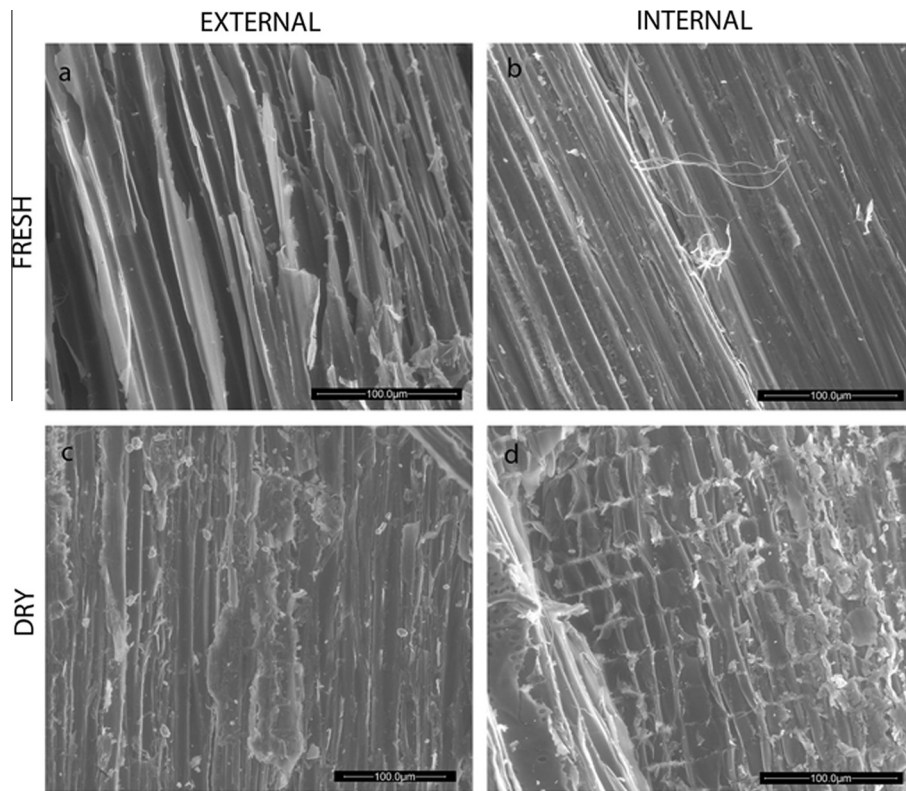
Fig. 5. ESEM images of the convexe (external, a and c) and concave (internal, b and d) surfaces of fresh (a and b) and dry (c and d) hemp hurds.
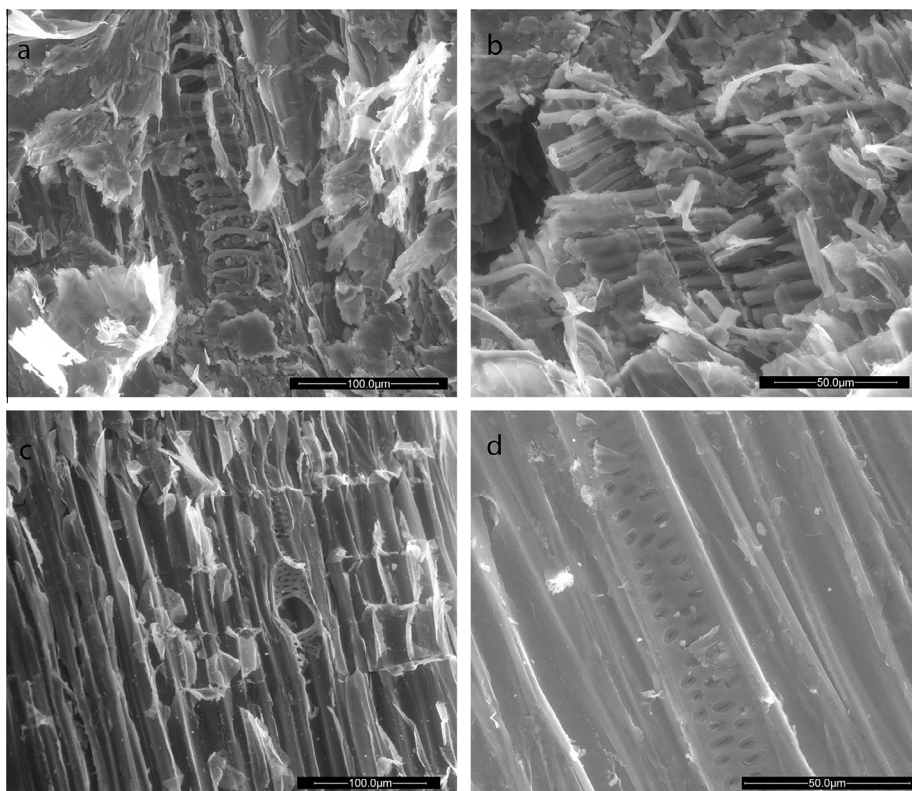

Fig. 6. ESEM images of the tracheary elements of the fresh hemp hurds: spiral (or annular, a), scalariform (b), reticulate (c) and pitted (d).

AL-dh (Fig. 7a and d) and AP-dh (Fig. 7b) than in NHL-dh mix (Fig. 7c). It has also been observed that, when the matrix is in contact with the concave (internal) surface of the hurd, the adhesion of lime particles is improved (Fig. 7d). The higher roughness and the honey-comb structure of this surface (Fig. 5d) are likely to increase the adhesion of the lime particles to the hurd wall.

Since the lime is composed by nano- and micrometric particles (Fig. 3), these are expected to fill the porous structure of the hurds, whose channels and pores are much bigger in size (up to 50 μm, Fig. 7a) than the lime particles. Nevertheless, the overall adhesion is poor and in none of the samples have the lime particles reached the interior of the hurds (pores and channels, Fig. 7a–c). We believe that the high water absorption ability of hemp [10,13,22] has hindered the penetration of lime particles into the channels of the hurds. These, in fact, are mainly composed of cellulose (50% of the chemical composition of the plant [3]), whose interactions with water molecules (by hydrogen bonding to hydroxyl groups) are stronger than those between a porous solid (in this case lime particles) and water [23]. These strong interactions are likely to induce water migration from the lime paste to the porous structure of the hurds during mixing of these two components. Thus, the hemp absorbs most of the water from the matrix and it also releases this water very slowly over time, in agreement with the NMR study on the water transfer in hemp-lime mixes, carried out by Faure et al. [24]. As a result of this, the matrix is drier compared to that of typical lime–aggregate–mortars. Consequently, with decreasing amounts of water, lime particles are driven to deposit onto the more superficial zone of the hurds, unable to fill their channels. The presence of an insufficient amount of water in the lime paste would also explain the poor adhesion of the lime particles to the hurds, as observed by ESEM (Fig. 7), and the powdered aspect of the matrix observed macroscopically in the hardened mixes. To reduce water absorption by the hemp, it might be helpful to use fresh hurds instead of dry ones, since the former already have 10% more water with respect to the latter. In this way, more water may be available in the paste and a stronger adhesion of the matrix to the hurds could be achieved. Another possibility is to maintain a moist curing environment to ensure higher humidity in the samples. In a similar way, Colinart et al. [10] attributed the low

consistency of hemp-lime-based mixes to dry curing conditions. Le Troedec et al. [12], instead, assumed that the poor adhesion of a mineral matrix to hemp hurds is due to an interface incompatibility that they reduced by pre-treating the hurds chemically.

By comparing the mineralogy of our hemp-based mortars to that of lime-aggregate mortars after similar curing times [25], it is evident that the insufficient amount of water in the matrix also delayed the hardening process in the former, which both in aerial and natural hydraulic lime occurs in presence of capillary water (i.e. the carbonation reaction proceeds by a solution mechanism and its rate is controlled by the dissolution of lime [20,26]). The XRD analysis carried out after 3 months since hemp mortar production demonstrated that only between 40% and 60% of the lime reacted (represented by [†††] in Table 2 and Fig. 8), which is low compared to carbonated lime pastes and lime-based mortars [24,27]. The greatest amount of unreacted portlandite (~60%) was found in the AP-dh mix, which was made with the lime putty (CL90S PL, Table 2 and Fig. 8). Moreover, in the natural hydraulic mix (NHL-dh), about 40% of calcium silicates were found, which means that only 10% had reacted (Table 2 and Fig. 8). The hydration of C_2S (di-calcium silicates) is known to be slower than that of C_3S

Table 2
Mineralogical composition (%, by weight) of AL-dh (air lime CL90S + dry hemp), AP-dh (air lime putty CL90S PL + dry hemp) and NHL-dh (hydraulic lime NHL 3.5 + dry hemp), determined by means of X-ray diffraction analysis. Port = portlandite; Cal = calcite; Vat = vaterite; CS = calcium and di-calcium silicates; cell = cellulose; tr = traces; – = absent; [†] = 5–10%; [††] = 15–20%; [†††] = 40–60%.

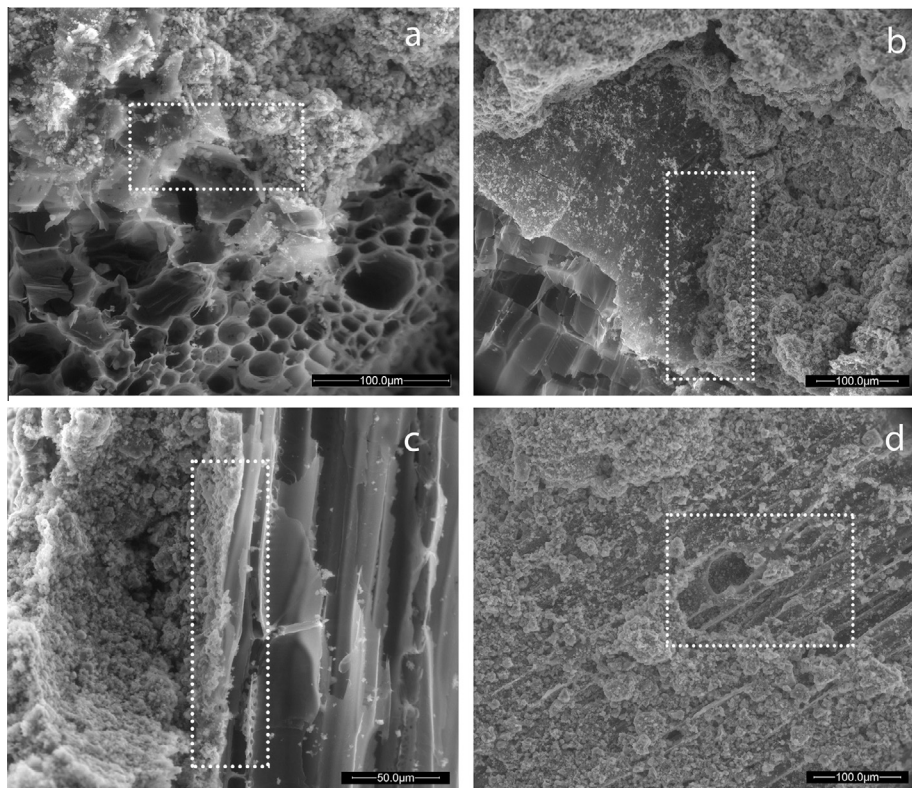|	Port	Cal	Vat	CS	Cell
AL-dh	[†††]	[†††]	[††]	–	tr
AP-dh	[†††]	[††]	[††]	–	tr
NHL-dh	[†]	[†††]	[††]	[†††]	tr

Fig. 7. ESEM images of the adhesion between the matrix and the external (a–c) and internal (d) surfaces of hemp hurds in AL-dh (air lime CL90S + dry hemp, a and d), AP-dh (air lime putty CL90S PL + dry hemp, b) and NHL-dh (hydraulic lime NHL 3.5 + dry hemp, c). Dotted rectangles show the contact zone between the two components.
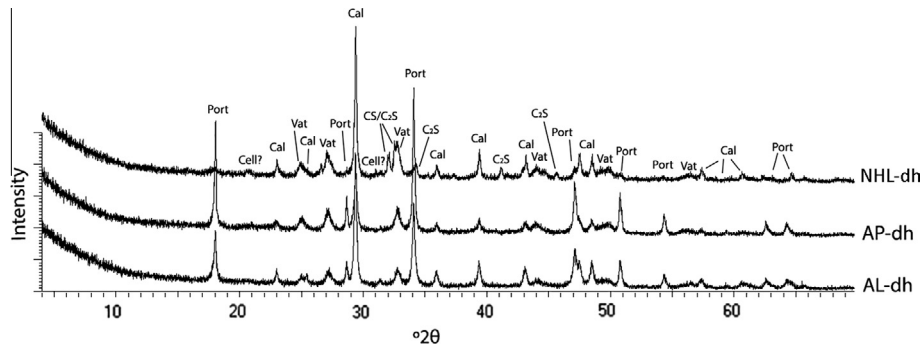
Fig. 8. X-ray diffraction patterns of AL-dh (air lime CL90S + dry hemp), AP-dh (air lime putty CL90S PL + dry hemp) and NHL-dh (hydraulic lime NHL 3.5 + dry hemp). Port = portlandite; Cal = calcite; Vat = vaterite; CS = calcium and di-calcium silicates; Cell = crystalline cellulose (? = possibly).
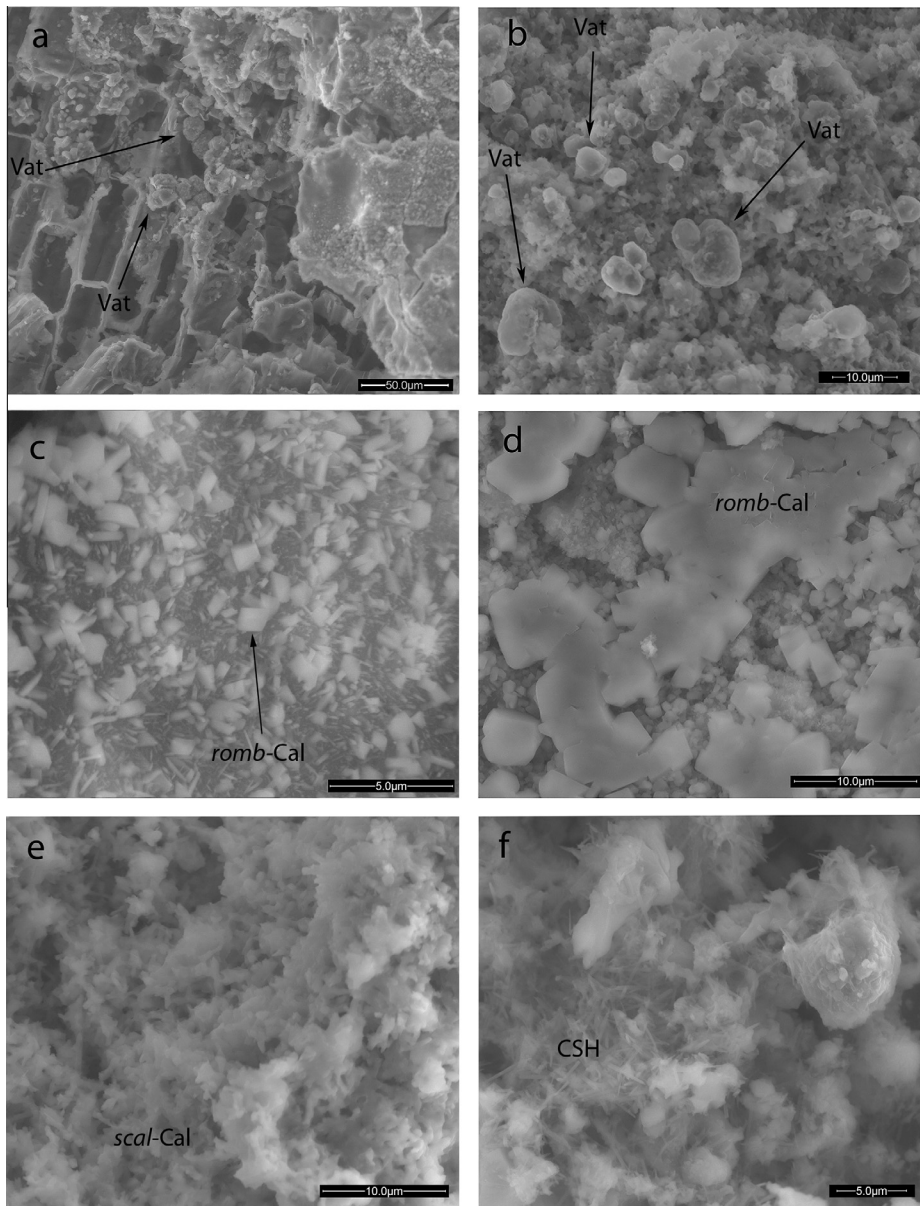

Fig. 9. ESEM images of the phases found in the matrix of AP-dh (air lime putty CL90S PL + dry hemp, a–e) and NHL-dh (hydraulic lime NHL 3.5 + dry hemp, f). The morphologies indicated are: framboidal particles of vaterite (Vat), calcite rhombohedra (*romb*-Cal) and scalenohedra (*scal*-Cal), and needle-like calcium silicate hydrates (CSH).

(tri-calcium silicates), starting from 28 days onwards [28]. However, a larger amount of C_2S might be expected to be hydrated after 90 days. This may indicate that also the hydration reaction is somehow delayed by the presence of hemp in the natural hydraulic mix.

After three months of curing, both calcite and vaterite precipitated in the three mixes, due to carbonation of lime, as found by means of XRD analysis (Table 2 and Fig. 8). Calcite is the most abundant calcium carbonate polymorph in AL-dh and NHL-dh mixes (40–45%), whilst about 17% of vaterite was found in all mixes. Only in AP-dh, was a lower amount of calcite found (~20%). The presence of such a high amount of vaterite in the mixes three months after their production might seem unusual considering that vaterite is a metastable phase that precipitates as a precursor in conditions of high supersaturation and transforms into calcite in few hours or days [29,30]. However, it is known that the vaterite-calcite polymorph transformation occurs by a dissolution/precipitation mechanism [30], which means that it can only occur in presence of water. If, as we assumed, not enough capillary water was present in the matrix from the start, this polymorph transformation might have been delayed or hindered and this would explain the high amount of vaterite found in the matrix of the mixes. Moreover, the low amount of water in the mixes would justify also the condition of supersaturation at which vaterite is likely to form [30].

The two peaks at ~22° and ~32° 2θ in the X-ray diffraction patterns (Fig. 8) may correspond to the diffraction of different sets of planes of the cellulose crystalline structure [31,32] of small residual fibres that could be present in the matrix. As in other vascular plants, indeed, cellulose chains are disposed both in an exactly defined crystalline network (crystalline zones) and in a disordered and less compact structure (amorphous zones) [3].

Observations of the matrix of the mixes were also carried out by means of ESEM to investigate the morphology of the mineral phases formed. In the aerial lime mixes, especially in AP-dh, carbonates with different morphologies have been observed: framboidal spheres of vaterite (2–10 μm in size, Fig. 9a and b) resembling those described by Adreassen [29] and Nehrke and Van Cappellen [33]; and calcite crystals with typical rhombohedral (1–10 μm in size, Fig. 9c and d) and scalenohedral (~2 μm in size, Fig. 9e) habit. Whilst vaterite and scalenohedral calcite crystals were also observed in AL-dh (Fig. 7d), rhombohedral calcite was only found in AP-dh mix. The morphology of calcite precipitated at a temperature between 20 and 30 °C is normally the scalenohedral one [34], especially under excess of Ca^{2+} ions [19]. However, when all the Ca^{2+} ions are consumed, rhombohedra precipitate after scalenohedra dissolution and this transformation is favoured at high RH [35]. Therefore, the presence of rhombohedra only in AP-dh mortar indicates that the lime putty retained more water in the matrix
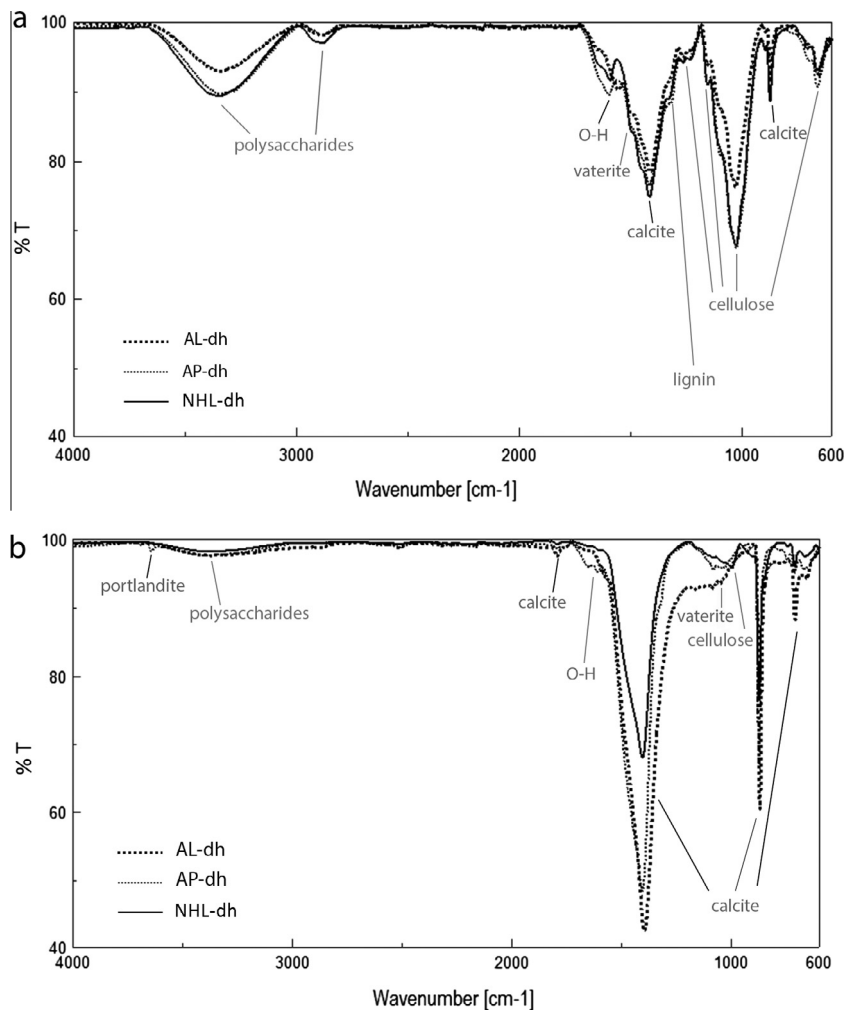

Fig. 10. ATR FT–IR spectra of the hurds (a) and the matrix (b) of AL-dh (air lime CL90S + dry hemp), AP-dh (air lime putty CL90S PL + dry hemp) and NHL-dh (hydraulic lime NHL 3.5 + dry hemp). The wavenumber (in cm^{-1}) is plotted versus the transmittance (T, in %).

with respect to the dry-hydrated one, due to the higher specific surface area of the former (Table 1).

In the NHL-dh mix, instead, typical needle-like calcium silicate hydrated (CSH) phases were observed (Fig. 9f).

3.4. Chemical study of the interaction between lime particles and hemp hurds

The ATR FT-IR spectra of the hemp hurds and the matrix collected from the three mixes after three months of curing are shown in Fig. 10. Some bands of the spectra obtained for the hemp hurds (Fig. 4) are still recognisable in Fig. 10a, mainly cellulose and lignin. Some of the other infrared transitions of these compounds are overlapped by the bands of calcite (Fig. 10a). The band at ~ 2850 cm^{-1} corresponding to the CH$_2$ stretching of waxes [12] was not identified in Fig. 10a. However, this cannot be related to reactions with the Ca(OH)$_2$ of the matrix, because waxes are soluble only in organic, non-polar solvents [22]. Since waxes are present on the surface of the hemp hurds as impurities (Fig. 5c and d), it is possible that they were scratched out when the hurd surface was cleaned, prior to the FT-IR analysis. The band at ~ 1730 cm^{-1}, characteristic of hemicellulose, disappeared in the FT-IR spectra of the hurds (Fig. 10a), as a result of the presence of lime water, which can be used as treatment to remove hemicellulose [12].

In the spectra of Fig. 10b bands characteristic of cellulose were identified, possibly due to the presence of small residual fibres in the matrix.

Both in the spectra of the hurds and those of the matrix (Fig. 10), some characteristic bands of vaterite were identified [35]. However, the abundance of the calcite polymorph meant it was not possible to distinguish all the infrared transitions of vaterite, due to the strong overlapping of the bands of these two polymorphs [35].

As shown in Fig. 10b, the content of portlandite is higher in AP-dh mix, as also determined by XRD analysis (Table 2 and Fig. 8).

4. Conclusions

This work represents a step forward in the research of peculiar composite materials such as hemp-based mortars. The study of the microstructure, chemistry and mineralogy of hemp mortar has contributed to the understanding of the macroscopic properties of this material, especially in relation with the hardening process. Furthermore, this study has highlighted that all the divergences from the usual features found in a mortar made with lime and stone aggregate are due to the presence of hemp hurds (especially regarding drying behaviour and hardening). Indeed, few differences related to the type of lime were found.

Firstly, the matrix does not fill the big pores and channels constituting the hemp hurds and only a superficial deposition was observed. Moreover, a poor adhesion exists between the matrix and the surface of the hemp hurds. This is almost independent on the lime type (a slightly higher adhesion was found in mixes made with aerial limes) and in part caused by the smooth external surface of the hemp hurds.

Secondly, mixes showed a delayed hardening, considering that large amounts of portlandite and calcium silicates were found in aerial and natural hydraulic lime mixes, respectively, after three months of curing. Moreover, an unusually high amount of vaterite was also found in all mixes after three months, demonstrating a delayed transformation of this metastable polymorph into the stable one (i.e. calcite).

The reason for these main findings (superficial deposition, poor adhesion, slow setting and presence of vaterite in the matrix) is inferred to be an insufficient amount of water available to the matrix of the mixes from the start. This assumption is supported by the ability of hemp hurds to absorb large amounts of water over a long time. Given that the fresh hemp hurds already have a certain amount of water in their porous structure, using fresh hemp instead of dry for the production of hemp-lime-based mixes could lead to a lower and slower absorption of water during mixing and at the beginning of the setting process. On the one hand, this would ensure a greater amount of capillary water in the matrix, which would enable the hydration of calcium silicates and the transformation of the metastable vaterite into the stable calcite. On the other hand, the use of fresh hemp could reduce the already poor adhesion of the matrix to the hurd, given the smoother surface of the fresh hurds compared to the dry ones, as observed here (Fig. 4a and c). Another risk of using fresh hemp involves the volume reduction that the hurds may undergo as they dry slowly over time.

Alternatively, other production or curing procedures might be considered. In relation to this, we have demonstrated that, although the hemp was previously wetted, this method was not efficient enough to reduce the hemp water absorption in the mix. Therefore, maintaining a higher relative humidity (e.g. spraying frequently) during curing of mixes might ensure a greater amount of water available to the matrix. Maintaining a higher relative humidity, however, may slow down the CO$_2$ diffusion through the mortar matrix, therefore, spraying should not be undertaken continuously and should be limited only during the first days after application. Besides, a forced-saturation of the hurds under vacuum prior to the mixing with lime might be a way to reduce the water absorption by the hurds once in the mix. These precautions would change not only the consistency of the hemp-lime-based mixes but also their hygric behaviour (i.e. water absorption and drying).

Further investigations on the morphological and mineralogical characteristics of hemp-lime-based mortar mixes made with fresh hurds or with other elaboration methods and curing conditions are needed to verify the reduction of the hurd water absorption and the increase of the amount of water available to the matrix, which would both improve the consistency and the hardening of hemp-lime-based mixes. Further studies are also needed to fully understand whether the structure and chemical composition of the hemp hurds are modified by the interaction with the lime, depending on pH and concentration conditions.

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References

[1] prEN 16572. Draft BS EN 16572, Conservation of cultural Heritage - Glossary of technical terms concerning mortars for masonry, renders and plasters used in cultural heritage. BSI London (UK), 2013.
[2] Henry A, Stewart J. Mortars, renders and plasters. In: Martin B, Wood C, editors. English heritage, practical building conservation. Farnham (UK): Ashgate Publishing Limited; 2011. p. 64–5.
[3] Faruk O, Bledzki AK, Fink H-P, Sain M. Biocomposites reinforced with natural fibres: 2000–2010. Prog Polym Sci 2012;37:1552–96.
[4] Esmail AM. Cannabis Sativa: an optimization study for ROI. Massachusetts Institute of Technology; 2010.
[5] Tran Le AD, Maalouf C, Mai TH, Wurtz E, Collet F. Transient hygrothermal behaviour of a hemp concrete building envelope. Energy Build 2010;42:1797–806.
[6] Pervaiz M, Sain MM. Carbon storage potential in natural fiber composites. Resour Conserv Recy 2003;39:325–40.
[7] Collet F, Bart M, Serres L, Miriel J. Porous structure and water vapour sorption of hemp-based materials. Constr Build Mater 2008;22:1271–80.

[8] Elfordy S, Lucas F, Tancret F, Scudeller Y, Goudet L. Mechanical and thermal properties of lime and hemp concrete ('hempcrete') manufactured by a projection process. Constr Build Mater 2008;22:2116–23.

[9] Arnaud L, Gourlay E. Experimental study of parameters influencing mechanical properties of hemp concretes. Constr Build Mater 2011;28:50–6.

[10] Colinart T, Glouannec P, Chauvelon P. Influence of the setting process and the formulation on the drying of hemp concrete. Constr Build Mater 2012;30:372–80.

[11] Valadez-Gonzalez A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ. Effect of fiber surface treatment on the fiber–matrix bond strength of natural fiber reinforced composites. Composites Part B 1999;30:309–20.

[12] Le Troëdec M, Peyratout CS, Smith A, Chotard T. Influence of various chemical treatments on the interactions between hemp fibres and a lime matrix. J Eur Ceram Soc 2009;29:1861–8.

[13] Nozahic V, Amziane S, Torrent G, Saïdi K, De Baynast H. Design of green concrete made of plant-derived aggregates and a pumice–lime binder. Cem Concr Compos 2012;34:231–41.

[14] BS-EN 459-1. Building Lime. Part 1: Definitions, specifications and conformity criteria. London: BSI, Standards Publication; 2010.

[15] Martín Ramos JD. XPowder. A software package for powder X-ray diffraction analysis. Lgl. Dep. GR 1001/04, 2004.

[16] Brunauer S, Emmett PH, Teller J. Adsorption of gases in multimolecular layers. J Am Chem Soc 1938;60:309.

[17] Sánchez-Moral S, Luque L, Cañaveras JC, Soler V, Garcia-Guinea J, Aparicio A. Lime pozzolana mortars in Roman catacombs: composition, structures and restoration. Cem Concr Res 2005;35:1555–65.

[18] Rodriguez-Navarro C, Hansen E, Ginell WS. Calcium hydroxide crystal evolution upon aging of lime putty. J Am Ceram Soc 1998;81(11):3032–4.

[19] Cizer O, Rodriguez Navarro C, Ruiz-Agudo E, Elsen J, Van Gemert D, Van Balen K. Phase and morphology evolution of calcium carbonate precipitated by carbonation of hydrated lime. J Mater Sci 2012;47:6151–65.

[20] Van Balen K. Carbonation reaction of lime, kinetics at ambient temperature. Cem Concr Res 2005;35:647–57.

[21] Dickison WC. Integrative plant anatomy. San Diego: Harcourt/Academic Press; 1980, ISBN 9780122151705.

[22] Bledzi AK, Gassan J. Composites reinforced with cellulose based fibres. Prog Polym Sci 1999;24:221–74.

[23] Hay JN, Laity PR. Observations of water migration during thermoporometry studies of cellulose films. Polymer 2000;41:6171–80.

[24] Faure P, Peter U, Lesueur D, Coussot P. Water transfers within hemp lime concrete followed by NMR. Cem Concr Res 2012;42:1468–74.

[25] Arizzi A, Cultrone G. The influence of aggregate texture, morphology and grading on the carbonation of non-hydraulic (aerial) lime-based mortars. Quart J Eng Geol Hydrogeol 2013;46:507–20.

[26] Moorehead DR. Cementation by the carbonation of hydrated lime. Cem Concr Res 1986;16:700–8.

[27] Arandigoyen M, Bicer-Sismir B, Alvarez JI, Lange DA. Variation of microstructure with carbonation in lime and blended pastes. Appl Surf Sci 2006;252:7562–71.

[28] Lanas J, Perez Bernal JL, Bello MA, Alvarez Galindo JI. Mechanical properties of natural hydraulic lime-based mortars. Cem Concr Res 2004;34:2191–201.

[29] Andreassen JP. Formation mechanism and morphology in precipitation of vaterite-nano-aggregation or crystal growth? J Cryst Growth 2005;274:256–64.

[30] Schmidt M, Stumpf T, Walther C, Geckeis H, Fanghänel T. Phase transformation in $CaCO_3$ polymorphs: a spectroscopic, microscopic and diffraction study. J Colloid Interface Sci 2010;351:50–6.

[31] Zhao H, Kwak JH, Zhang ZC, Brown HM, Arey BW, Holladay JE. Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis. Carbohydr Polym 2007;68:235–41.

[32] Park S, Baker JO, Himmel ME, Parilla PA, Johnson D. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulose performance. Biotechnol Biofuels 2010;3:10.

[33] Nehrke G, Van Cappellen P. Framboidal vaterite aggregates and their transformation into calcite: a morphological study. J Cryst Growth 2006;87:528–30.

[34] García-Carmona J, Gómez Morales J, Rodríguez Clemente R. Morphological control of precipitated calcite obtained by adjusting the electrical conductivity in the $Ca(OH)_2$–H_2O–CO_2 system. J Cryst Growth 2003;249:561–71.

[35] Sato M, Matsuda S. Structure of vaterite and infrared spectra. Zeitschrift für Kristallographie 1969;129:405–10.