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THE IMPACT OF HEMP SHIV ON CEMENT SETTING AND HARDENING: THE INFLUENCE OF EXTRACTS AND STUDY OF THE INTERFACE

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ABSTRACT

The need for efficient building insulation with low environmental impacts materials has led to a growing market for hemp lightweight concretes. However, a deeper understanding of the interactions between hemp particles and the binder taking place during setting and hardening process is needed to fulfill the requested industrial specifications. In this paper, the effects on the cement setting of shiv and its corresponding water extracts are investigated. Various analyses taken together show that these extracts delay hydration and consequently lower the mechanical properties of the cement. An analysis of the chemical composition of shiv water extracts provides some indication of the identity of the molecules responsible of the deleterious effects. The development of a new methodology combined with the use of ^{13}C labeled plant material enables close monitoring of the physicochemical phenomena occurring at the interface of plant aggregate and cement.

KEYWORDS:

Hemp; Cement; Retardation; Interface; Concrete

INTRODUCTION

Shiv (also called woody hemp core) corresponds to fragments of the central section of dried hemp stalk (*Cannabis sativa*) (Fig. 1.a). It is generally considered a by-product of long fiber and seed production and so far, it has been used mostly as animal bedding or mulch (Karus and Vogt, 2004). With regards to its chemical composition, shiv is comparable to wood, but presents a much lower density due to its porous microstructure (Fig. 1.b). Because of its low bulk density (110 kg/m^3), shiv is used as a natural aggregate to produce hemp lightweight concretes (HLCs) (Fig. 1.c). HLCs are made of shiv, water and a mineral binder. According to the application (wall building and roofing, among others), HLCs densities range between 200 to650 kg/m^3 and have interesting thermal and acoustic properties (Gle et al., 2011, Arnaud, 2000, Arnaud and Gourlay, 2012). Finally, these materials present a small ecological footprint thanks to plant particle CO_2 storage (Boutin et al., 2006). HLCs demonstrate however some drawbacks, compared to conventional hydraulic concrete. In particular, the measured mechanical properties are low (Arnaud and Gourlay, 2012) and a slow or "false" setting is often observed onsite. These problems are generally worse when HLC is produced only with a hydraulic binder like cement. This type of HLC is comparable to wood cement concretes but differ by their lower densities (700 to1200 kg/m^{3}for wood cement concrete). Various studies have reported the same kind of problem as above when cement is mixed with wood(Semple and Evans, 2000, Govin et al., 2005) or other lignocellulosic residues like wheat straw (Soroushian et al., 2004), oil palm (Hermawan et al., 2001) or bagasse (Bilba et al., 2003). Extractives products, which correspond to easily solubilized molecules (e.g. monosaccharides, fatty acids or phenolic compounds), are thought to play a major role in the setting and hardening process (Hachmi and Moslemi, 1989). Moreover, due to the high alkalinity of cement, degradation of lignocellulosic compounds can occur and products can be released and also impact on the setting (Vaickelionis and Vaickelioniene, 2006). Setting impairment caused by these molecules (extracts and/or degradation products) can be explained by various phenomena like adsorption on hydrated or non-hydrated

cement particles, ionic complexation or the formation of a thin barrier around cement grains by precipitation (Jolicoeur and Simard, 1998), but the general mechanisms and its dynamic are still poorly understood.

In order to circumvent setting problems occurring when plant aggregates are mixed in cement paste, different strategies have been developed (Jorge et al., 2004). For example, lignocellulosic residues can be pretreated by solvent extraction or a coating process. Enhanced carbonation can also be performed through the addition of lime and CO_2 injection, and similarly, set accelerators can be added to cement. However, certain of these attempts can be expensive or not directly applicable onsite, moreover, some of them lead to a partial loss natural insulation capacity (due to an increase of density). Despite all the work done so far, further improvement is necessary for HLCs to fulfill the specifications requested by industrial and final customer. One approach toward this goal is a better understanding of the physicochemical influence of shiv on the binder. To this end, two complementary approaches were used in this study: first, the impact of water extracts on setting and hardening was investigated in terms of setting time, hydration rates and mechanical performances. Second, the interface between shiv and cement paste were studied because it constitutes a key point of the mechanical performances of the concrete.

In Europe and more specifically in France, most HLC binders used by building professionals are composed of a mix between lime and hydraulic binder. Nevertheless, we decided to focus our study on cement only because cement constitutes a good model for hydration reactions that are responsible for early strength. Further studies currently being carried out on mix of cement and lime will later complete the understanding of the full setting phenomenon of classic HLC binders.

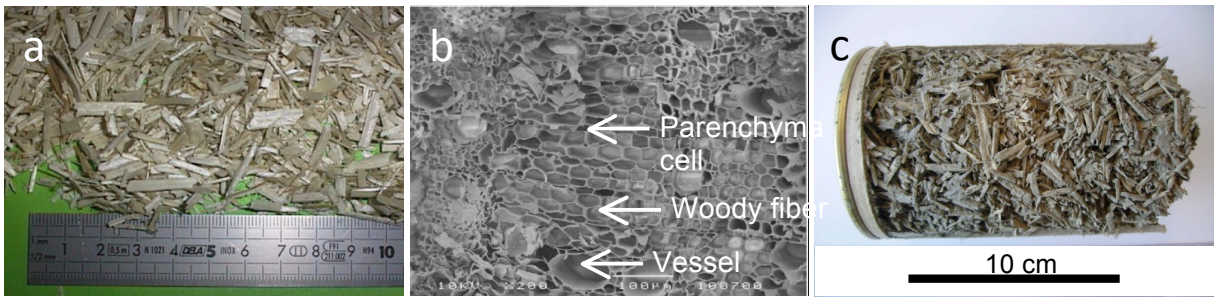

Figure 1 - a: Photograph of raw shiv particles; b: SEM micrograph showing shiv micro-porosity, due to the organization of the different types of plant cells; c: photograph of a hemp cement concrete sample (formulated for wall application)

EXPERIMENTAL

Raw materials

A Portland cement CEM I 42.5 R-HS (Schwenk) was employed as binder for this study.

The shiv used here originates from hemp grown in UK. Plants have been harvested before maturity, dew-retted, and then, transformed with hammer mill.

Chemical analysis of water extracts

The water extracts were prepared by mixing shiv (S) and water (W) with a S/W weight ratio of 0.1. After 24 h, the extracts were filtered (300µm) and analyzed as described below.

The amount of soluble protein was determined colorimetrically with the microscale Bradford reagent from Sigma-Aldrich. The standard used was bovine albumin serum. The Protein concentration was based on UV absorbance at 595 nm.

The amount of soluble lignin was determined directly from the liquid extracts by UV spectrometry at 280 nm. The absorption coefficient used for calculation was 20 for 1 $g.l^{-1}$ of lignin.

Ash content was estimated by incinerating the lyophilized extracts in a muffle furnace at 500 °C for 3.5 h. Ashes are then weighed.

Carbohydrate analysis: acid hydrolysis of 10 mg samples was performed with $H_2SO_4$and the released monosaccharides were separated by high performance anion-exchange chromatography (Dionex) as described by Beaugrand et al. (Beaugrand et al., 2004).

Procedures for analyzing cement/water extract mix

Cement setting monitoring is realized by Vicat test, according to standard *NF EN 196-3:2009* with a manual Vicat apparatus (Maurice Perrier & Cie) in triplicate. Water (reference) or half-strength extracts (diluted with water) are used to hydrate cement with a liquid (L) to cement (C) ratio (L/C) of 0.33.

Hydrates production monitoring: Cement was mixed, with water extracts (or distilled water as reference) at L/C= 0.5. The obtained mix was then poured into eight plastic bags (V≈6 ml) corresponding to eight hydration stopping times (20 min, 1 h, 3h, 7h, 1 day, 3 d, 7 d, 28 d). At each time, sample was frozen in liquid nitrogen and then freeze dried during 48 h. Finally, samples were finely ground to be analyzed by Fourier Transform Infrared spectroscopy (FT-IR) and Thermo-gravimetric Analysis (TGA).**FT-IR** was performed in middle infrared with the "Nicolet 6700" spectrometer with pressed KBr pellets. **TGA** was made with the Hi-Res Thermo-gravimetric TGA 2950 Analyzer (TA Instruments) on approximately 25 mg of sample powder. All experiments were conducted from 20°C up to 800 °C (heating rate of 10 °C/min) under dynamic nitrogen atmosphere.

Mechanical tests: Specimens (L/C = 0.33)have been produced and test according to the British standard *BS EN 196-1:2005*.,except for the following conservation modifications: specimens were first preserved in their mould in a climatic room controlled (20 °C ; 50 % relative humidity).After 3 days of setting, they were demoulded and kept in the same conditions until the test date (7, 14, 28, 60 or 90 days).The flexural strength and the compressive strength of the specimens were measured by using a universal hydraulic servo-controlled compressive testing machine (INSTRON 1273).

Interface analyzing procedures

In order to observe the interface between the shiv and cement paste, a new methodology is suggested: a shiv particle (or pellets of shiv powder) is placed on a 20 cm square glass, then, a bottomless mold is attached to the glass and filled up with cement paste. Once the cement paste has set, the device can be turned upside down to observe the interface through the glass (Fig. 6).

Pellets are produced by compressing 200mg of plant powder (shiv or flax stalk, 200 µm ground) under 1tonne of pressure for 3min. The obtained pellets have a diameter of 14mm and 1.8mm thickness.

Extractive migration monitoring: Based on the same principle described above, a device was made by placing a flax pellet at the center of 14 mm diameter plastic tube (10 cm long) as shown on Fig. 2. Each side of the tube was then filled with cement paste (freshly mixed with distilled water) and closed with stoppers. After three days, the device was frozen in liquid nitrogen and then opened to be freeze dried for 48 h. Each resulting cylinder was cut into 1 mm thick slices, from the pellet to the outside (Fig. 2). Slices were then ground and analyzed by TGA to determine the rate of potential portlandite ($Ca(OH)_2$) content (based on a reference tube without pellet), as well as by mass spectrometry to measure the carbon isotopes content as described below.

The pellets used here were made of powder of flax enriched with carbon-13 (^{13}C), (This flax has been homogeneously labeled carbon 13 by developing it in an atmosphere enriched with ^{13}C carbon dioxide). By doing so, carbonaceous extracts which migrate from the pellets can be monitored using the measured ^{13}C in the sample, because this enables its differentiation from the carbon coming from the cement.

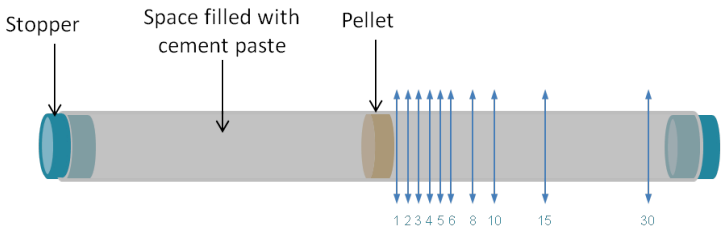

Figure 2 - Schematic representation of the device designed for the extracts migration monitoring ; double blue arrows indicate the analyzed slices and the numbers underneath correspond to the distance from the pellet (in mm).

RESULTS AND DISCUSSION

Preliminary experiments on HLC mix based on cement (Fig. 1.c) (Arnaud and Gourlay, 2012) display a very low cohesion between shiv particles and the cement matrix. This indicates that cement paste did not realise normal setting. The two following sections attempt to clarify which phenomena are responsible for the particular observed physical state of the cement paste.

Thus, the effect of shiv water extract on cement setting and mechanical characteristics was first investigated. The use of water extracts is relevant because the component dissolved from the shiv is directly supplied to the cement together with the hydrating water; it constitutes then a simple way to evaluate the net contribution of the soluble aggregates components on the cement paste changes. To go one step further, we then analyzed the physicochemical interactions taking place at the interface between plant aggregate and the cement paste.

Impact of water extracts on cement setting and hardening

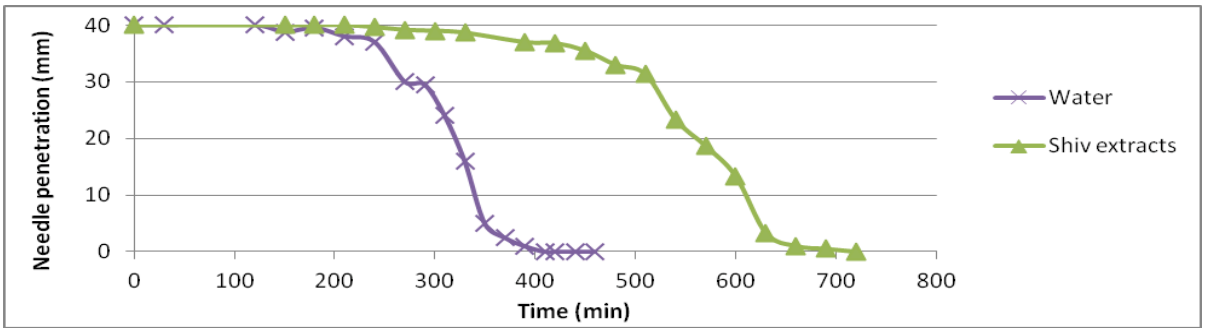

Figure 3 - Depth of Vicat needle penetration into the cement paste (made with water or shiv water extracts) as a function of time. The height of the mold was 40 mm.

The setting time measurement determined by means of the Vicat needle for cement mixed with water (reference) and with shiv water extracts is shown in Fig. 3. Initial and final set times of the reference (with pure water) are seen to occur at 240 min (needle penetration = 36 mm) and 400 min (needle penetration = 0.5 mm) respectively. It can be observed that setting is dramatically delayed when cement is mixed with shiv water extracts. In fact, they create a delay of more than five hours at the end of setting. Most set retardation seems to occur during the latency state (dormant period); this could be explained by an effect of the extracts on the dissolution of the initial phases and/or on nucleation of hydrates.

It can be pointed out that this delay is considerable, even though the shiv proportion (compared to cement) used to produce water extracts is significantly lower (approximately one-tenth, in mass) than the proportion used in a conventional HLC mix formulation (C2P, 2006).

Results given by the Vicat needle measurements clearly show that shiv water extracts act as a strong cement retarding agent. To go further, TGA was used in order to investigate if this delay continues at longer term and if it is related to changes in hydrates proportion.

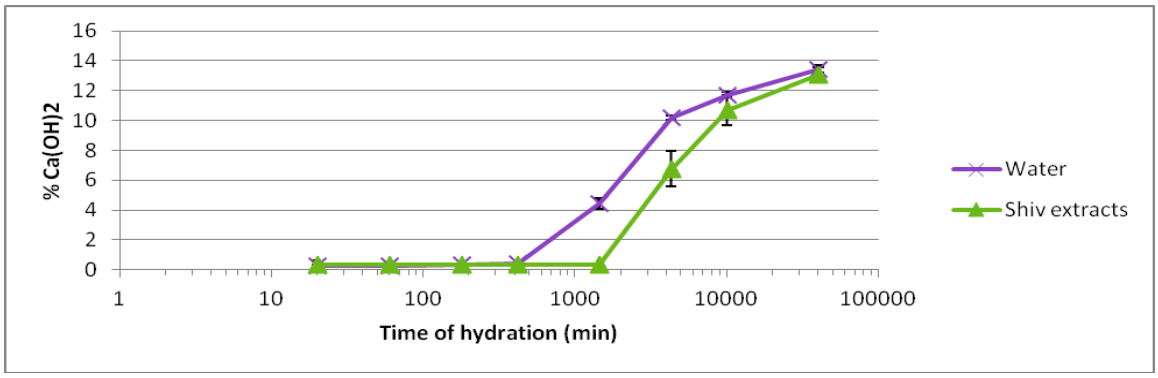

Figure 4 - Evolution of Portlandite content in cement mixed with water and with shiv water extracts.

Shiv water extracts have a strong impact on Portlandite content when mixed with cement (Fig. 4), since there is no measurable Portlandite after one day of hydration (same results have been obtained for CSH content – data not shown). However, final Portlandite content (after 28 days) is approximately the same for the reference and cement mixed with water extracts. This last result indicates, in those conditions, a simple setting delay rather than an irreversible effect on cement hardening process.

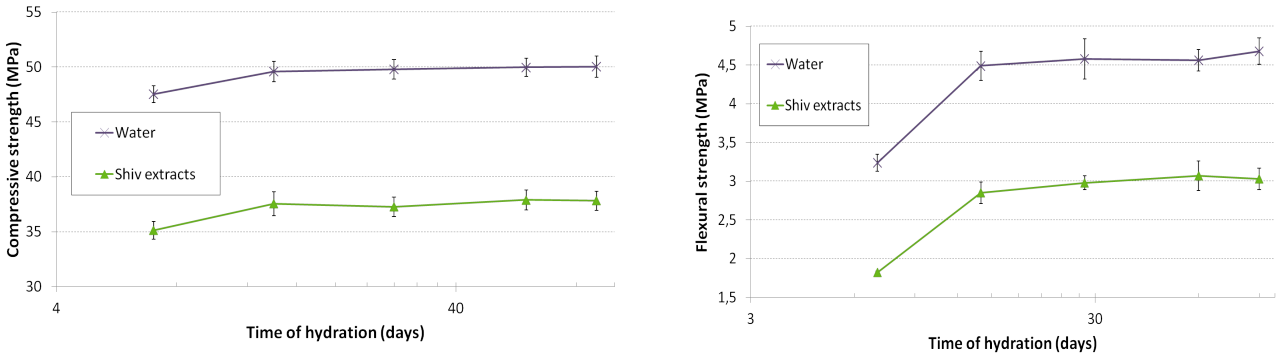

Figure 5 - Change in compressive strength (a) and flexural strength (b) of neat cement mixed with water and with shiv water extracts.

To evaluate the impact of water extracts of shiv on mechanical properties both compressive and flexural strength have been test on cement paste with extracts. The compressive strength of the reference cement paste mixed with water is 49.8 MPa after 28 days of curing (Fig. 5.a), which is a normal value for a cement grade 42.5. Shiv water extracts lead to a significant drop in compressive strength for both short term and long term (about 25% decrease after each curing period). Moreover similar results have been found for flexural strength (Fig. 5.b).

Even though same amount of hydrates has been measured after 28 days, lower mechanical performances are observed with water extracts at this curing time. This could be explained by two hypotheses. Unlike samples produced for hydrates measurement, mechanical samples were not tightly isolated from the air. Hence, higher water evaporation yield could have occurred due to the setting delay, which can lead to a depletion of water for reaction, and so, to a lower final amount of hydrates. However, it also cannot be ruled out that, even if the same amount of hydrates was present, those hydrates present a different structural arrangement from the reference, which impairs the mechanical performance.

Table 1 - Chemical composition of water extracts of shiv. Extracts content is represented in percent of dry weight of shiv used for extraction. Proportion of each componentis represented based on the extracts content (in %).

Extracts content	*Sugar*	*Lignin*	*Protein*	*Ash*	*Others*
4.41	16.54	14.81	0.91	35.90	31.85

Chemical analyses were carried out on the shiv water extracts to investigate which class of molecules might be responsible of the effects on the cement described above.

Table 1 shows the amount of total extracts according to the dry shiv weight as well as the proportion of each component. A large part of the extract is ash, which could come from the plant constitutive minerals or from soil dust (soil residues, fertilizers) that were not removed during the defibration process (Bag et al., 2011). Even though this mineral fraction could be responsible for a slight delay, since it has been demonstrated that zinc, lead or phosphates can impact the setting and hardening process (Olmo et al., 2001), the strongest set retarding agents are in general organic compounds. In the same way, lignin and more importantly sugar have been described as impairing cement setting (Bilba et al., 2003, Thomas and Birchall, 1983), but the quantities measured here for those molecules do not seem to be high enough to explain all the effects on cement described previously. Moreover, the comparison of chemical composition of water extracts of three different shivs displaying different impacts on cement, shows that the main chemical difference corresponded to uncharacterized molecules (data not shown). In fact, after an extensive quantification of the main class of the plant cell wall derived molecules, about 30% in mass of shiv extracts remain to be identified. These unknown components may be constituted by molecules initially present in the sap of the vascular system of hemp, and are chiefly molecules from plant metabolism (primary or secondary). Also, xylem sap was shown to contain low molecular weight inorganic compounds and organic substances including hormones, amino acids, sugars, oligo and polysaccharides as well as organic acids(Satoh, 2006), some of them being described as accelerator (e.g., oxalic acid) or retardant (e.g., citric acid) in cement setting (Govin et al., 2005, Moschner et al., 2009, Singh et al., 2003).

Macroscopic study of the cement/plant interface

The first section demonstrated a detrimental effect of hemp water extracts on cement paste setting and hardening, such as delay in setting and hydrates production and lower compressive strength. These findings on hemp confirm and complete the effects previously described for other plant aggregates (Govin et al., 2005). To go beyond the effect of extracts, experiments were carried out on shiv particles and powder to study the interface with the cement matrix.

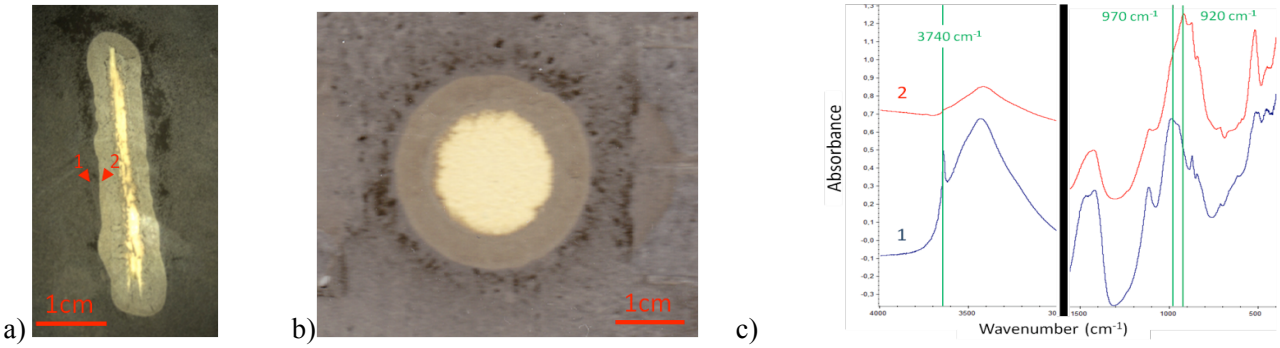

Figure 6 - Photograph taken after 3 days of hydration for cement paste with two kinds of plant aggregate inclusion: (a) one particle of shiv, arrows 1 and 2indicate sampling points for FT-IR analysis (c); (b) pellet made of shiv powder.

Thanks to the new device previously described, the interface between the shiv and the cement matrix can be observed after 3 days of hydration. Fig. 6.a shows a brighter halo of cement surrounding one particle of shiv with a well-defined limit. To study the cement paste on both sides of this limit, samples were taken (see the arrows in Fig. 6.a) then analyzed by FT-IR (Fig. 6.c). Cement inside the halo (sample 2), unlike sample 1, does not present peaks corresponding to hydration products (CSH at970 cm^{-1} and $Ca(OH)_2$ at 3640 cm^{-1}) but still presents a high peak at 920 cm^{-1} for C_3S phase. This proves that the cement matrix in the halo corresponds to non-hydrated cement. This result is extremely significant if we consider the limited space between the shiv particles in a conventional hemp concrete (Fig. 1.c), which could then contain unset cement with poor binding properties.

Particles of shiv have an irregular shape, which does not allow easy quantification of the halo phenomenon. To overcome this problem, standardized cylindrical pellets were produced by compressing shiv powder then analyzed using the same test as for the particle (Fig. 6.b). The same kind of halo (verified by FT-IR – data not shown) surrounds the pellet in similar proportions to those observed for the particle.

The hydration inhibition capacity of pellets made from reference shiv powder and pellets made from powder that was previously washed (4 times) has been compared. This test aims to confirm the effect of water extracts shown in the first section and quantify their contribution to the hydration inhibition capacity of hemp aggregates.

When shiv powder has been previously washed, the pellet still displays a non-hydrated cement area but two times smaller than the halo produced by the reference. Thus, water extracts are responsible for the major part of the non-hydrated halo observed. The existence of this area seems to demonstrate that, close to the pellet, local concentration of extracts is high enough to lead to an irreversible effect.

Moreover, cement paste displays high alkalinity (pH>12). Polymers can thus suffer degradation leading to the release of molecules which differ from simple water extracts. And this can explain the remaining effect observed with pre-washed shiv pellets. This hypothesis is supported by the following fact: when the FT-IR spectras obtained with pellets before and after immersion on cement are compared, a disappearance of peaks is observed (Fig. 7). Peaks at 1740cm^{-1} and 1243cm^{-1} may be attributable either to pectins or acetyl groups of xylan. Thus, it can be assumed that when plant aggregates are immersed into cement, degradation of pectin or hemicelluloses can occur, releasing products which can diffuse into the cement matrix and have the observed deleterious effect on cement setting.

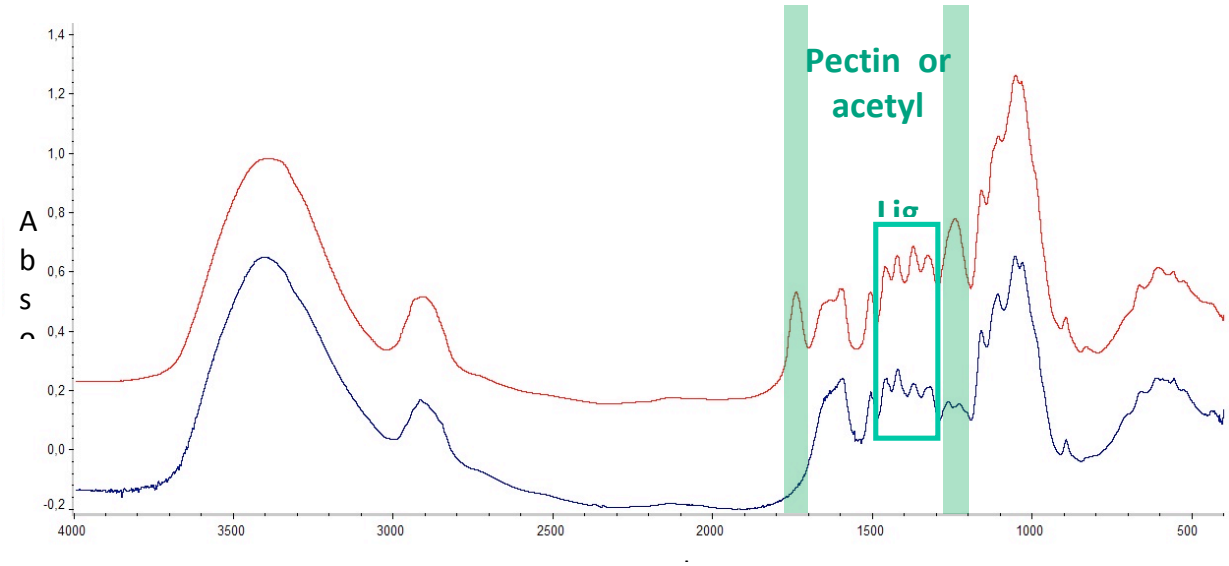

Figure 7 - Comparison of FT-IR Spectra of shiv powder in pellet from before (a) and after (b) 3 days of immersion into cement.

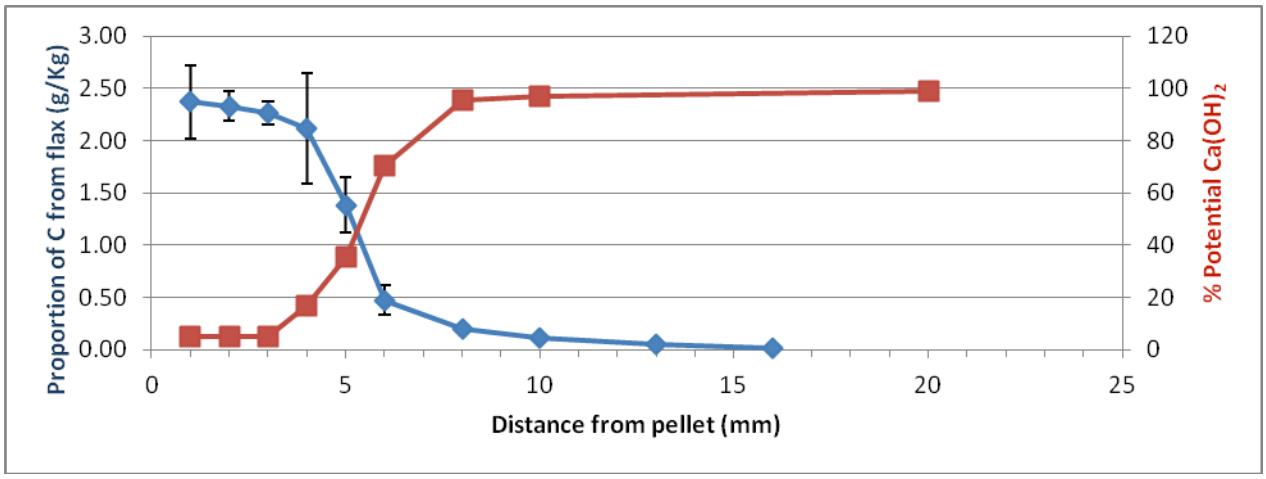

Figure 8 - Effect of the migration of carbonaceous extracts (diamonds) on the production of Portlandite (squares).

Previous results showed that extracts are involved in the non-hydrated cement halo surrounding plant aggregates; therefore, diffusion throughout cement paste of those extracts was monitored. To do so, pellets were made with a powder of ^{13}C labeled flax. The use of flax is justified not only because of its availability in the laboratory, but also because its tissue organization is similar to hemp (woody core and peripheral long fiber). After verifying that the pellets presented the same non-hydrated halo and in a similar proportion to that obtained with hemp pellets, it was possible to determine the diffusion of carbonaceous extracts through sampling at an increasing distance from the pellet (Fig . 8) using the device described in Fig. 2.

The first three points of the curve correspond to the sample taken inside the non-hydrated halo. The fourth point corresponds to the limit of the hydrated cement area, with a corresponding sudden drop of extract quantity. The relative homogeneity of carbon quantity measured first in millimeters can be explained by a nearly isolated tank delineated by hydrated cement (corresponding to the halo) where mobility continued to exist over a longer period (until liquid water departure). No additional carbonaceous extracts were detected beyond 16 mm.

To complete this analysis, extracts diffusion curve has been compared to the potential Portlandite production rate curve measured against distance from pellet (Fig. 8). From this cross examination, the existence of three areas can be suggested:

- A first area, close to the pellet (0 to 3 mm), where cement almost never sets at all, because of the excess of extracts (irreversible effect or drying effect due to considerable delay)
- A second area (3 to 14 mm), where setting is delayed proportionately to the quantity of extracts
- Beyond this area, extracts are virtually absent, allowing cement to set normally.

Altogether, our data strongly supports the hypothesis that the formation of these three areas and their change over time results from the combination of cement paste setting and extract migration. In fact, these two phenomena interact with each other, because the more the extracts migrate, the more the setting is delayed, and in return, the more the setting is delayed, the longer the extracts can migrate. This suggests an interactive competition between these simultaneous phenomena.

CONCLUSIONS

Delayed or even "false" settings have been regularly reported onsite or in laboratories during the manufacture of hemp lightweight concretes using cement binder. To analyze and identify the phenomena responsible of these problems, interactions between the cement matrix and extracts in water of shiv in the one hand, and shiv in the other hand have been characterized.

This research clearly shows that the components extracted from shiv by water have deleterious effects on cement setting and hardening: first, they act as strong retarding agents that lead to lower amount of hydrates up to 28 days of curing. Secondly, the long-term decrease of mechanical performances caused by water extracts, can be explained by drying effect or non optimal structuring of hydrates.

A new methodology is also described in this paper that allows a direct visualization of the cement/aggregate interface and also a precise monitoring of carbonaceous extracts migration and level of setting in this key location. This combination of techniques has permitted to define three areas (from the pellet to the outside): the non-set area, the delayed set area and the normal set area.

Outgoing works aim to study the influence of the shiv and water extracts used in this paper on setting and hardening of other kinds of binder generally used to manufacture hemp lightweight concretes (e.g., slaked, quick or hydraulic lime). Moreover, different treatments of shiv are also studied to improve the mechanical properties of hemp lightweight concretes.

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REFERENCES

Arnaud, L. Year. Mechanical and thermal properties of hemp mortars and wools: experimental and theoretical approaches. *In:* Third international symposium bioresource hemp and other fibre crops, 2000 Germany: Wolfsburg.

Arnaud, L. & Gourlay, E. 2012. Experimental study of parameters influencing mechanical properties of hemp concretes. Construction and Building Materials, 28, 50-56.

Bag, R., Beaugrand, J., Dole, P. & Kurek, B. 2011. Viscoelastic properties of woody hemp core. Holzforschung, 65, 239-247.

Beaugrand, J., Cronier, D., Thiebeau, P., Schreiber, L., Debeire, P. & Chabbert, B. 2004. Structure, chemical composition, and xylanase degradation of external layers isolated from developing wheat grain. Journal of Agricultural and Food Chemistry, 52, 7108-7117.

Bilba, K., Arsene, M. A. & Ouensanga, A. 2003. Sugar cane bagasse fibre reinforced cement composites. Part I. Influence of the botanical components of bagasse on the setting of bagasse/cement composite. Cement & Concrete Composites, 25, 91-96.

Boutin, M.-P., Flamin, C., Quinton, S. & Gosse, G. 2006. Étude des caractéristiques environnementales du chanvre par l'analyse de son cycle de vie.

C2p 2006. Règles professionnelles d'exécution d'ouvrages en béton de chanvre. *In:* RP2C, C. R. P. C. C. (ed.).

Gle, P., Gourdon, E. & Arnaud, L. 2011. Acoustical properties of materials made of vegetable particles with several scales of porosity. Applied Acoustics, 72, 249-259.

Govin, A., Peschard, A., Fredon, E. & Guyonnet, R. 2005. New insights into wood and cement interaction. Holzforschung, 59, 330-335.

Hachmi, M. H. & Moslemi, A. A. 1989. Correlation between wood-cement compatibility and wood extractives. Forest Products Journal, 39, 55-58.

Hermawan, D., Subiyanto, B. & Kawai, S. 2001. Manufacture and properties of oil palm frond cement-bonded board. Journal of Wood Science, 47, 208-213.

Jolicoeur, C. & Simard, M. A. 1998. Chemical admixture-cement interactions: Phenomenology and physico-chemical concepts. Cement & Concrete Composites, 20, 87-101.

Jorge, F. C., Pereira, C. & Ferreira, J. M. F. 2004. Wood-cement composites: a review. Holz Als Roh-Und Werkstoff, 62, 370-377.

Karus, M. & Vogt, D. 2004. European hemp industry: Cultivation, processing and product lines. Euphytica, 140, 7-12.

Moschner, G., Lothenbach, B., Figi, R. & Kretzschmar, R. 2009. Influence of citric acid on the hydration of Portland cement. Cement and Concrete Research, 39, 275-282.

Olmo, I. F., Chacon, E. & Irabien, A. 2001. Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement. Cement and Concrete Research, 31, 1213-1219.

Satoh, S. 2006. Organic substances in xylem sap delivered to above-ground organs by the roots. Journal of Plant Research, 119, 179-187.

Semple, K. & Evans, P. D. 2000. Adverse effects of heartwood on the mechanical properties of wood-wool cement boards manufactured from radiata pine wood. Wood and Fiber Science, 32, 37-43.

Singh, N. K., Mishra, P. C., Singh, V. K. & Narang, K. K. 2003. Effects of hydroxyethyl cellulose and oxalic acid on the properties of cement. Cement and Concrete Research, 33, 1319-1329.

Soroushian, P., Aouadi, F., Chowdhury, H., Nossoni, A. & Sarwar, G. 2004. Cement-bonded straw board subjected to accelerated processing. Cement & Concrete Composites, 26, 797-802.

Thomas, N. L. & Birchall, J. D. 1983. The retarding action of sugars on cement hydration. Cement and Concrete Research, 13, 830-842.

Vaickelionis, G. & Vaickelioniene, R. 2006. Cement hydration in the presence of wood extractives and pozzolan mineral additives. Ceramics-Silikaty, 50, 115-122.