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Impact of Bio-Aggregates Properties on the Chemical Interactions with Mineral Binder, Application to Vegetal Concrete

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Abstract

Plant concretes were developed and are currently used as filling material in a timber frame. Their properties are strongly related to the bio-aggregates characteristics. In addition, since hemp shiv, the reference bio-based aggregate, has a limited availability, it is necessary to consider alternative bio-aggregates largely and locally available. Thus, this paper focused on identifying and understanding mechanisms of interaction between different bio-aggregates and mineral binders. To address this issue, the first objective was to determine the properties of five hemp shives and two alternative bio-aggregates for vegetal lightweight concrete: corn and sunflower bark particles. The study of the chemical interactions between bio-aggregates and a pozzolanic binder was conducted on model pastes mixed with filtered solutions containing bio-aggregates extractives. The mechanical properties of the paste, as well as their hydration and their mineralogical evolution were studied. In the last part, the mechanical behavior of vegetal concretes was assessed. The results highlight a strong relation between the mechanical behavior of pastes and concretes and the extractive content of the different tested bio-aggregates. Finally, pastes appeared as a relatively good model to predict the behavior of concretes by following their early age performances: setting delay and 3-day mechanical strength.

1. Introduction

The building sector is responsible for major environmental impacts: construction accounts for about 40% of CO₂ emissions in developed countries, 37% of energy consumption and 40% of waste produced (Deshayes 2012). Consequently, the design and characterization of innovative eco-friendly building materials has become a priority. The incorporation of bio-based raw materials

could be a response to this environmental challenge since they are renewable, mainly by-products of local crops, and carbon neutral (Cherrett *et al.* 2005; Maalouf *et al.* 2016; Pretot *et al.* 2014). Over the last fifteen years, these environmental benefits have contributed to the development of a specific building material called “hemp concrete”. This composite combines a mineral binder and a plant aggregate: hemp shiv, i.e., the ligneous by-product resulting from the mechanical extraction of technical fibers from hemp stalk. Many studies have underlined the great interest of the hygrothermal properties of bio-based materials (Bourdot *et al.* 2017; Collet and Pretot 2012; Rahim *et al.* 2014; Ratiarisoa *et al.* 2016). Use of bio-aggregates reduces the thermal conductivity of many materials because of the high porosity of hemp shives (Bennai *et al.* 2018; Bourdot *et al.* 2017; Rahim *et al.* 2016), while moisture exchanges with the air around the material could enhance indoor comfort.

Nevertheless, hemp bio-based materials can have variable mechanical properties in accordance with drying process (Benfratello *et al.* 2013), curing conditions and time of demolding (Pavía *et al.* 2015), nature of the binder matrix (Balčiūnas *et al.* 2013; Dinh 2014; Stevulova *et al.* 2013), composites design (Balčiūnas *et al.* 2013), or hemp shives characteristics (Arnaud and Gourlay 2012; Stevulova *et al.* 2012). Hemp shives characteristics can be length or nature of shives, including with hemp shives in compliance with the requirements of the label hemp aggregate of “Construire en chanvre”, meaning “Build with hemp”. Indeed, the replacement of hemp type by another can generate mechanical performance differences up to a factor 10 (Niyigena *et al.* 2018). In addition, stiffness problems

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with crumbling can be observed with mineral binder (Sinka *et al.* 2014).

According to the literature, these observations could result from chemical interactions between water-soluble compounds of the plant aggregates and mineral species of the binder. Several researchers showed a negative impact of hemp or other lignocellulosic particles on the setting and the early hardening of cement paste. Diquélou *et al.* (2015) studied the short term interaction between hemp and flax shives with a cement matrix and showed a halo of non-hydrated cement surrounding hemp particles. The formation of hydrates appears to be inhibited in composites combining bio-aggregates and a pozzolanic binder (Dinh 2014) or Portland cement (Diquélou *et al.* 2015) involving a deficit about 20 to 25% in compressive strength (Diquélou *et al.* 2015; Ratiarisoa *et al.* 2016). Several mechanisms were proposed to explain the action of lignocellulosic compounds with numerous parameters but observations differed as reviewed by Magniont and Escadeillas (2017). At early age, it should be a migration of extractives into the paste inducing the inhibition of the formation of some hydrates: a decrease in C-S-H and undetected calcium hydrates. The alkaline degradation of bio-aggregate particles induces the release of calcium carbon dioxide, which could be responsible for the carbonation of portlandite. Consequently, a deficit in portlandite can be highlighted. Distinct ways of action were summarized by Magniont and Escadeillas (2017): trapping of calcium ions present in the binder solution by plant components, formation of a thin adsorption layer on the surface of cement grains, poisoning of the nucleation sites by adsorption on the first $\text{Ca}(\text{OH})_2$ and C-S-H hydrates, formation of calcium carbonate.

These short term chemical interactions are significantly influenced by the nature of the inhibitory molecules, the concentration of plant extracts, the nature of the binder, the production process of plant aggregates, the storage condition of bio-aggregates and the part of the plant involved. The species responsible for the deleterious effect could be water-extractives of lignocellulosic particles or even products of the alkaline attack of the particles by the cement or lime-based matrixes (Diquélou *et al.* 2015; Govin *et al.* 2005). These early age impacts could have direct consequences on medium term performances. However, other long-term interactions between plant particles and binder could occur, affecting the performances of the concrete. Until now, few studies have been made on these phenomena in bio-aggregates based materials. In the context of the development of plant concretes, one of the challenges would be proposing a straightforward characterization test to qualify the level of interaction with the mineral matrix inducing acceptable or unacceptable mechanical strength.

In addition, although hemp has been considered as the reference for bio-aggregates based building materials, its availability is limited. Therefore, it is necessary

to consider other bio-aggregates largely and locally available. Some alternative bio-aggregates, such as flax shives (Rahim *et al.* 2015), rape straw (Rahim *et al.* 2016), lavender stalks (Ratiarisoa *et al.* 2016) etc. have been studied. This paper proposes to focus on bark particles from sunflower and corn stalks, both selected for their large availabilities in South-West part of France. Corn is the second most cultivated cereal in France, generating large quantities of by-products: 5.2 tons of stalks in 2015. Sunflower is grown for its seeds to produce vegetal oil with about 614 000 ha cultivated nationwide. 230 000 tons of by-products were produced each year due to this agricultural crop. In comparison, only 17 000 t/year of hemp by-products are available (Laborel-Préneron *et al.* 2018).

Therefore, the present study aims to characterize five sources of hemp shives and to evaluate the potential of two other agricultural by-products (corn and sunflower bark particles) as alternative bio-aggregates for vegetal lightweight concrete. The paper focuses on the extractives, which could interact with the mineral binder. The extractives could play a role in the stiffness of pastes and thus in the mechanical behavior of bio-aggregate based concretes. The first part of the study focused on the plant particles characterization. According to the recommendations of RILEM Technical Committee 236-BBM (Amziane *et al.* 2017), bulk density, particle size distribution and water absorption capacity were determined on different bio-aggregates. Because of the variability of hemp properties due to their nature, five hemp shives are studied. Two other aggregates largely and locally available, as replacement of hemp are characterized: bark particles extracted from corn and sunflower stalks. In a second part, the impact of the water-soluble components extracted from the different bio-aggregates on the binder paste setting and hardening mechanisms was investigated.

The identification of water-soluble substances being far from obvious, the objective of the article is to evaluate if the quantity of water-soluble substances easy to measure, the hydration delay or the decrease in the mechanical strength of model pastes, can be a reliable indicator regarding interactions and the impact on the mechanical strength of hemp concrete. The mechanical performances were studied through compressive strength and explained by the hydration and hardening mechanisms of the lime-metakaolin binder from XRD, TGA and calorimetric measurements. Finally, the mechanical performances of the associated bio-aggregate concretes were compared and a discussion was conducted to link the results obtained on bio-aggregates, model pastes and plant concretes.

2. Materials and methods

2.1 Materials

(1) Bio-aggregates

Different hemp shives from five strains were character-

ized to observe the influence of their properties on the mechanical behavior of hemp concretes. The samples are presented in Fig. 1. They are denoted as H1 (KANABAT), H2 (Agrofibre), H3 (CVF), H4 (Standard Lézoux) and H5 (ISOcanna, CESA). Corn and sunflower bark particles, denoted as Co and S, are also evaluated and compared to hemp shives. Alternative aggregates result from the combination of a preliminary stage of grinding of the entire stalk and a second phase of separation of the pith from the bark using a tilted conveyor belt and a blowing system. The bark particles under 1 mm were then eliminated by sieving.

(2) Mineral binder and admixtures

The binder is composed of 70% by weight of metakaolin and 30% by weight of aerial lime. Metakaolin is a pozzolanic admixture produced by flash calcination of kaolinite at 700°C, produced by ARGECO Développement Co. in France. It is mainly composed of quartz, silicon and aluminium oxides with an amorphous silicoaluminat mineralogical form. The latter phase is responsible for the pozzolanic activity of metakaolin, which reacts with calcium hydroxide $[Ca(OH)_2]$ to form C-S-H gel, calcium aluminate hydrates $[C_4AH_{13}]$ and $[C_3AH_6]$ – hydrogarnet and calcium alumino-silicate hydrates $[C_2ASH_8]$ – straetlingite (Rojas and Cabrera 2002). The flash metakaolin has a lower water demand than traditional rotary metakaolins, leading to a better workability of composites (San Nicolas *et al.* 2013). The aerial lime is around 92% $[Ca(OH)_2]$. Two admixtures were used to improve the performance of the composite at early age: potassium sulfate, a chemical activator to encourage ettringite formation and accelerates the pozzolanic reaction, and a superplasticizer to improve the workability.

2.2 Methods of aggregate characterization

The physical characterization of hemp shives was realized according to the RILEM Technical Committee 236-BBM recommendations on bio-based materials (Amziane *et al.* 2017).

(1) Bulk density

The material was dried at 60°C until constant mass (variation less than 0.1% between two readings at 24 h). The sample of hemp shiv was put in a cylindrical container of 28.3 cm in height and of 12 cm in diameter (Fig. 2A). The quantity of the material was adjusted to be half the volume of the container. The cylinder was then upend ten times. The volume was marked by a cardboard and measured with water. The test was repeated 3 times.

(2) Dust content

Dust is defined as particles with length or width lower than 0.5 mm. 5 samples of 50 g were sieved mechanically with 315 mm diameter sieves for 30 minutes.

(3) Particle size distribution by image processing

The image analysis method used a scanner and “ImageJ” software, which is an open source image processing program designed for scientific images. This method was carried out on bio-aggregates samples of 3 to 6 g each, in order they include at least 2000 identified particles. A scanner was used in order to acquire 8-bit gray scale image at 600 DPI resolution. Particles were laid on a transparent paper on the glass of scanner and covered by a dark background in order to obtain the maximum contrast. Before scanning, the particles were arranged in such a way that they did not touch or overlap one another. Images were analyzed using the ImageJ software

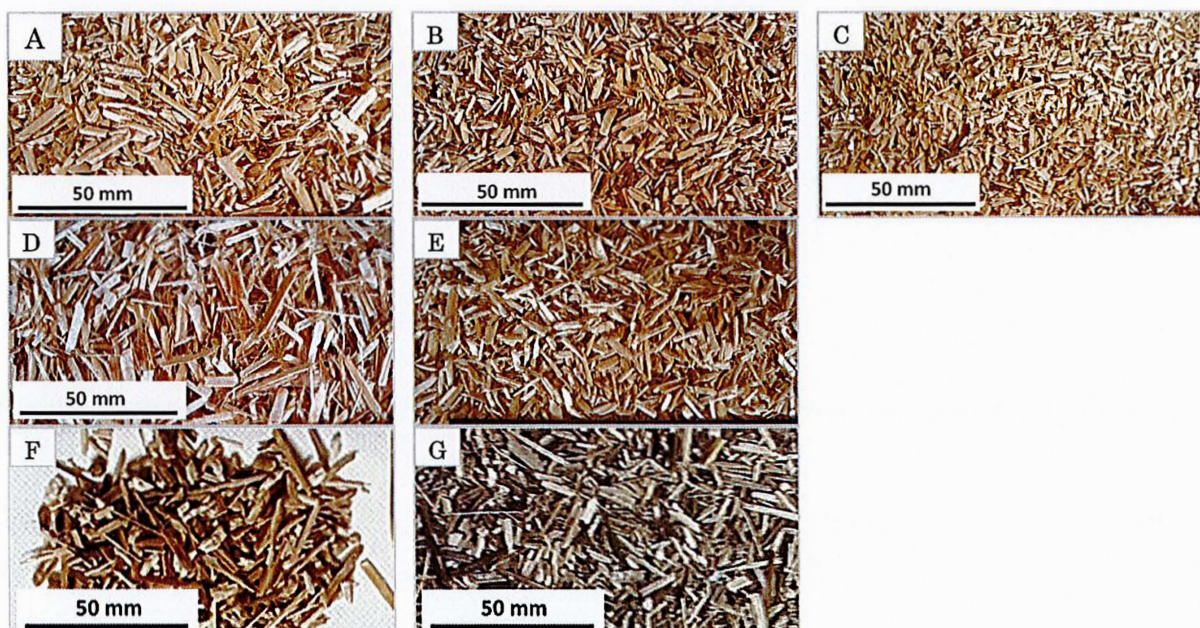


Fig. 1 Photographs of the five studied hemp shives: H1 (A), H2 (B), H3 (C), H4 (D), H5 (E); corn Co (F); sunflower S (G) bark particles.

Table 1 Mixing sequence of paste.

Step	Action	Mixing time (s)	Speed (rpm)
1	Introduction of the binder and potassium sulfate	30	140
2	Introduction of the filtrate or distilled water and superplattizer	30	140
3	Final mix	30	280

and the ImageJ “Analyze particles” tool was used to determine the hemp particle dimensions and morphological parameters such as circularity:

$$Circularity = 4\pi \frac{Surface\ area}{Perimeter^2} \quad (1)$$

(4) Initial water content and absorption

Aggregates were dried at 60°C until a constant mass (change in mass of the sample less than 0.1% over 24 h). The initial water content W_0 is calculated with the following equation:

$$W_0 = \frac{M_0 - M_D}{D} \times 100 \quad (2)$$

where M_0 the initial mass of aggregates (g) and M_D the mass of the dry aggregates (g).

Three dried samples were put in synthetic permeable bags (with square mesh around 1 mm²) and immersed in water. The gain in mass was measured after 1 min, 15 min, 4 h and 48 h: bags were placed in a “salad spinner” and wrung by 2 rotations per second for 50 s to eliminate the water adsorbed at the surface of plant particles or remaining among them. The water absorption capacity $W(t)$ in % weight is obtained by the following equation:

$$W(t) = \frac{M(t) - M_D}{M_D} \times 100 \quad (3)$$

where $M(t)$ is the mass of wet aggregates after each time of the immersion (g) and M_D the mass of dry aggregates (g).

The results presented are mean values of measurements taken on three different samples.

(5) Extractives proportion

Before the tests, samples were crushed to a grain size of

less than 1 mm (Fig. 2B). The water-soluble content, adapted from the TAPPI 204 cm-97 standard (TAPPI 1997), is determined by boiling aqueous extraction for 1 h. The content of water-soluble compounds is determined by a gravimetric method. About 1 g of raw material, previously dried, is introduced into a sintered porous crucible and placed on a hot extractor (Fibertec Tecator M1017) shown in Fig. 2C. The material immersed in 100 ml of water is boiled for 1 h. The extract is then sucked up using a vacuum tube. Once filtered, the sintered sinter is put to dry in an oven at 105°C for 24 h. The weighing of the sintered material after drying allows the determination of the overall content of water-soluble compounds of any biochemical nature. All determinations were carried out in duplicate.

2.3 Experimental methods on binder pastes

(1) Elaboration of pastes

Eight different mixes were tested and, for each mix, the test was repeated 3 times. The eight mixes differed by the nature of the mixing solution: a control paste was made with demineralized water, and the other seven pastes were mixed with the filtrate of bio-aggregates containing extractives. The filtrates were obtained after immersion of crushed particles (under 1 mm) of bio-aggregates in demineralized water for 48 h at ambient temperature. The water to particles mass ratio was 15 in order to extract high quantity of filtrates. Paste was mixed with a Controls mixer complying with the NF-EN 196-1 standard (AFNOR 2006). The binder was composed of 70% metakaolin and 30% aerial lime by weight for all pastes. The distilled water or bio-aggregate filtrate to binder ratio was 0.55. The potassium sulfate to binder ratio was 0.03 and the superplasticizer to binder ratio was 0.016. The mixing sequence is presented in Table 1.

After mixing, the binder paste was cast in 40 × 40 × 160 mm moulds complying with NF-EN 196-3 (AFNOR 2017). The samples were then demolded at 3 days, cut in three samples of 40 × 40 × 40 mm and continuously

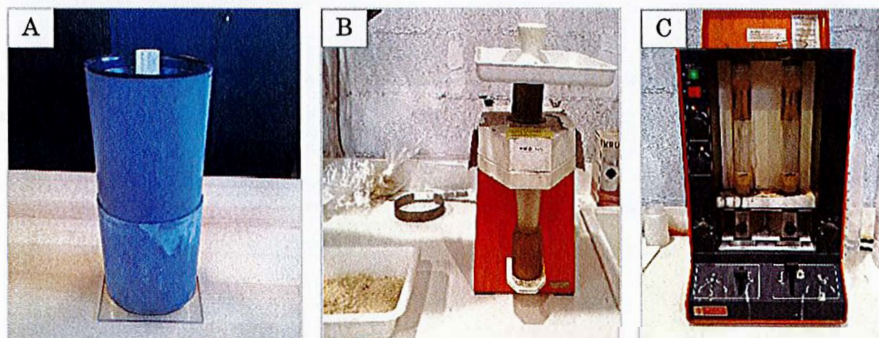


Fig. 2 Cylindrical container for raw density measurement (A), Crush apparatus (B) and Hot extractor (C).

Table 2 Mix design of studied hemp concretes.

Mix	Binder (kg/m ³)	Aggregates (kg/m ³)	W/B
HC	286	137	1.2

Table 3 Mixing sequence of hemp concretes.

Step	Action	Mixing time(s)
1	Introduction of hemp shives with 25% of water and homogenization	120
2	Introduction of supplementary 25% of water and homogenization	60
3	Introduction of anhydrous binder and homogenization	180
4	Continuous introduction of left 50% of water and homogenization	300
5	Final mix	90

cured in a room at 20°C and RH > 95% until the date of the test. The pastes are denoted as H1P, H2P, H3P, H4P and H5P for samples made from H1, H2, H3, H4 and H5 extractives respectively. The pastes based on corn and sunflower particles are denoted as CoP and SP respectively. The control paste is referenced as CP.

(2) Isothermal calorimetry

The hydration process of the pastes was studied by isothermal calorimetry using a microcalorimeter (TAM AIR model 3116). The mixing of the ingredients, previously balanced at the calorimeter temperature (20°C), was carried out manually outside the calorimeter. Heat flow due to the hydration reactions was recorded during 6 days.

(3) Compressive strength of pastes

Compressive strength tests were performed on 40 × 40 × 40 mm specimens with ages at 3, 14 and 150 days. They were conducted with a constant loading speed of 2.4 kN/s according to NF-EN 196-1 standard (AFNOR 2006).

(4) Thermogravimetric analysis

Thermogravimetric analyses were performed on the dry powdered samples, weighing around 1050–1550 mg each that passed through an 80 µm sieve. The thermal analyzer (NETZSCH STA 449 F3 Jupiter®) operates at a heating rate of 10°C/min up to 1000°C. Analyses were performed 24 h, 48 h, and 9 months. For each age, the hydration is stopped by immersion in liquid nitrogen and freeze-drying.

(5) X-Ray diffraction

The measuring system was a diffractometer (Bruker D8 Advance) using K α ($\lambda = 1.542 \text{ \AA}$) copper anticathode. The 2θ values, which ranged from 4θ to 70θ , were recorded in 0.02θ steps with an acquisition time of 0.25 s per step. Measurements were performed on crushed samples, of ages 24 h, 48 h, and 9 months passing through an 80 µm sieve. For each ages, the hydration is stopped by immersion in liquid nitrogen and freeze-drying by placing under vacuum (13.3 Pa) in a freeze dryer for 24 h.

2.4 Experimental methods on concretes

(1) Elaboration of plant aggregates-based concretes

Two concrete types were manufactured. The influence of hemp shive nature is studied using a lime binder producing “hempcrete”. The alternative bio-aggregates are employed with the alternative pozzolanic binder in order to characterize a total alternative bio based concrete.

On the one hand, hemp-concrete was elaborated with hemp shives H3, H4, H5 and a commercial lime binder. **Table 2** and **Table 3** report respectively the corresponding mix proportioning and the mixing sequence. The cylindrical test specimens ($\phi 11 \times 22 \text{ cm}$) were cast following a methodology described in the work of Niyigena *et al.* (2018). The moulds were filled in four layers manually compacted. The upper surface of each layer was scratched to help the next layer to adhere properly. To ensure a constant compacting energy, the same operator realized all the compactations and a similar fresh weight were reached for each sample.

When filled and weighted, the specimens were left in their moulds for 72 h. After removal, open-air drying took place in a test room (average conditions: 21°C and 35% RH). Finally, specimens were oven dried at 60°C for 48 h, prior to the mechanical testing.

Thereafter, the hemp concretes are referred to H3C, H4C and H5C for samples made from H3, H4 and H5 hemp shives respectively.

On the other hand, sunflower and corn bark particles were used in association with the pozzolanic binder composed of 70% by weight of metakaolin and 30% by weight of aerial lime for the design of an alternative plant concrete. Additionally, in order to improve the performance of the concrete at early age, potassium sulfate was added (2.9% by weight of binder). K₂SO₄ is a chemical activator that encourages ettringite formation and accelerates the pozzolanic reaction (Dinh 2014). Moreover, a superplasticizer was introduced in water to improve the concrete workability (1.65% by weight of binder). The total amount of water results from the addition of pre-wetting water, adjusted to the absorption capacity of plant aggregates after 1 minute, and mixing water added after the anhydrous binder. **Table 4** reports the mixing sequence applied for the concretes fabrication, while **Table 5** summarizes the mix proportioning of sunflower concrete (SC) and corn concrete (CoC).

Table 4 Mixing sequence of sunflower and corn concretes.

Step	Action	Mixing time (s)
1	Introduction of sunflower ad corn bark particles and homogenization	60
2	Introduction of pre-wetting water and homogenization	180
3	Introduction of anhydrous compounds and homogenization	180
4	Introduction of mixing water + superplastizer and homogenization	300
5	Final mix	90

Table 5 Mix design of studied sunflower and corn concretes.

Mix	Binder (kg/m ³)	Aggregates (kg/m ³)	W/B pre-wetting	W/B mix
SC	319	138	0.44	0.55
CoC	319	138	0.28	0.55

Table 6 Buk densities, dust content and initial water content of bio-aggregates.

Aggregate	Bulk density (kg/m ³)	SD	Dust content (wt%)	SD	Water content (wt%)	SD
H1	99.6	3.6	1.4	0.2	8.0	0.0
H2	154.2	0.6	1.7	0.3	9.0	0.2
H3	145.9	4.0	2.0	0.2	6.2	0.0
H4	70.3	2.8	0.7	0.2	6.9	0.1
H5	108.4	4.4	5.7	0.8	6.9	0.1
Co	120.2	1.0	3.4	0.0	10.4	0.2
S	168.2	4.5	0.7	0.1	12.6	0.0

After mixing, the mix was cast in $\phi 11 \times 22$ cm cylindrical moulds in three layers under manual vibro-compaction for 5 s. The moulds were removed from concrete samples in two phases. First, top and bottom of the moulds were turned out of the specimen 7 days after concrete pouring. 48 days later, samples were completely demoulded.

(2) Mechanical strength

The compressive strength tests on the specimens ($\phi 11 \times 22$ cm) were performed respectively after 30 and 60 days of curing for hemp concrete and sunflower/corn concrete. The tests were performed using a 100 kN capacity hydraulic press. At least three samples were tested for each formulation. The load was applied at a constant deflection rate of 3 mm/min while the unloading was realized at 6 mm/min. The following four step loading cycle was applied to samples.

Loading up to 1% of strain - unloading up to 0%;

Loading up to 2% - unloading, 0%;

Loading, 3% - unloading, 0%;

Loading, 15% (resp. 20%) for the sunflower-based (resp. corn-based) material items - unloading, 0%

The Young's modulus E of each specimen was then calculated according to a procedure named "floating modulus" from Niyigena *et al.* (2016, 2019), which is the mean value of maximum values obtained at the second, third and fourth loading steps.

3. Results and Discussion

3.1 Bio-aggregates characterization

(1) Bulk density

The bulk densities of bio-aggregates are summarized in Table 6. Hemp shives have a bulk-density in the range

of 70 to 155 kg/m³. H3 and H2 have the highest value with 146 and 154 kg/m³, respectively, whereas H4 has a low density of 70 kg/m³. H1 and H5 have similar bulk densities of 100 and 108 kg/m³, respectively. The bulk density of the corn bark particles is in the same range with a value of 120 kg/m³. The sunflower bark particles exhibit the highest bulk density of 168 kg/m³.

(2) Dust content

Dusts are particles with a diameter lower than 500 μm . Table 6 summarizes the measurements. The percentage of dust is largely variable according to hemp shiv. H1, H2 and H3 have a percentage of 1 to 2% by weight, whereas H4 has less dust, under 1% by weight, and H5 has a high percentage of dust with 5.74% by weight. Regarding the alternative bio-aggregates, corn particles present the second highest proportion of dust. On the contrary, sunflower aggregates exhibit the lowest dust content (0.66%) among the seven bio-aggregates.

(3) Particle size distribution

The image analysis method allows plotting the cumulative area of particles as a function of three morphological parameters: the mean equivalent diameter (abbreviated as EAD: equivalent average diameter), the average size assuming that particles have spherical shape, and the major and minor axes, i.e., length and width as presented in Nozahic *et al.* (2012). These size distributions of the 5 hemp shives are plotted on Fig. 3. The circularity of particles is a shape factor representing how close to a circle the shape of the particle is (it is equal to 1 for a perfect circle). This is also represented for the five hemp shives on Fig. 4.

Hemp shiv H4 displays the biggest particles, more than 80% of the particles have a length higher than 10

mm, and the highest difference between minor and major axis. This is in accordance with a low circularity. On the contrary, H3 has very close minor, major and EAD curves. Regarding the EAD curve, the cutting of the H3 shiv is regular around 2 to 3 mm. This particle size distribution results from a higher circularity compare to the other shives. H1 and H5 have greater size variability with EAD ranging from 1 to 10 mm. H2 has an intermediate particle size with EAD ranging from 1 to 7 mm. These observations are consistent with circularity. Consequently, from the histogram of the circularity of the aggregates, large differences appear between the different hemp aggregates. Circularity can be classified as $H4 < H1 < H5 < H2 < H3$.

These observations can be correlated to bulk density measurements with a low value for H4 explained by a big length and large aspect ratio of these shives, whereas for H3 and H2, the reduced size and enhanced circularity encourage the higher compactness of the bulk arrangement.

The same methodology was applied on corn and sunflower particles. The fitted curves and histograms of particle size distribution are presented in Figs. 5 and 6. On the figures, the curves and histograms are compared to extreme values of hemp shives H3 and H4. Figure 5 reveals that hemp shives present a very narrow particle size distribution in comparison with corn or sunflower

bark particles. A more adequate calibration process for these alternative aggregates could correct this point. Their circularity is also lower than for the majority of hemp particles in particular for corn particles. This result is consistent with bulk density measurement. Corn particles are more elongated. Consequently they induce a larger inter-particle porosity resulting in lower bulk density.

(4) Water absorption

The initial water contents are presented in Table 6. Initially, H2 has the higher moisture value of 9% by weight. H1 has a proportion of 8% by weight. H4 and H5 have similar initial water content of nearly 7% by weight. H3 has the lowest moisture value of 6% by weight.

After a drying procedure, the kinetics of water absorption of hemp shives and alternative aggregates were assessed and are plotted in Fig. 7. The figure presents the evolution of the water content of aggregate as a logarithmic function of time as proposed by Nozahic *et al.* (2012). Two specific parameters were determined basing on the following equation:

$$W = IRA + K_1 \times \ln(t) \quad (4)$$

where W is the water absorption, K_1 can be linked to diffusion rate of water in bio-aggregate cells with a

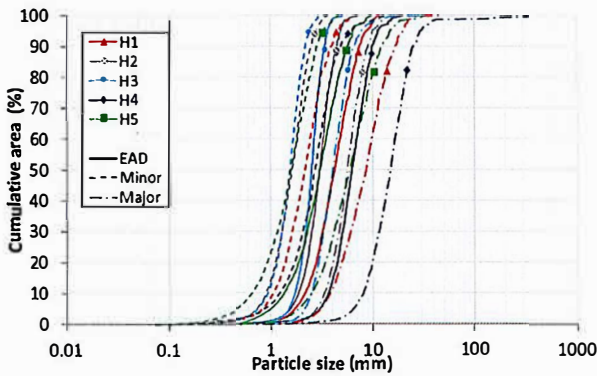


Fig. 3 Particle size distribution of hemp shives.

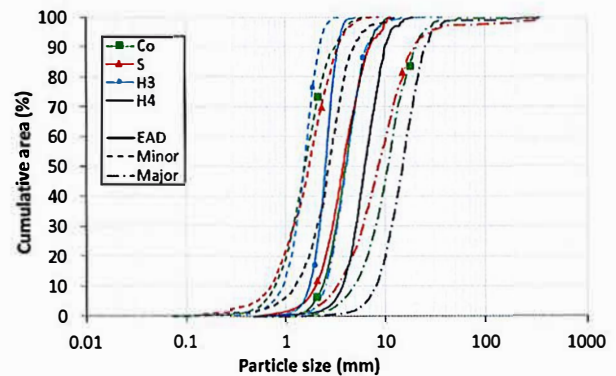


Fig. 5 Particle size distribution of corn Co and sunflower S bark particles compared to hemp shives H3 and H4.

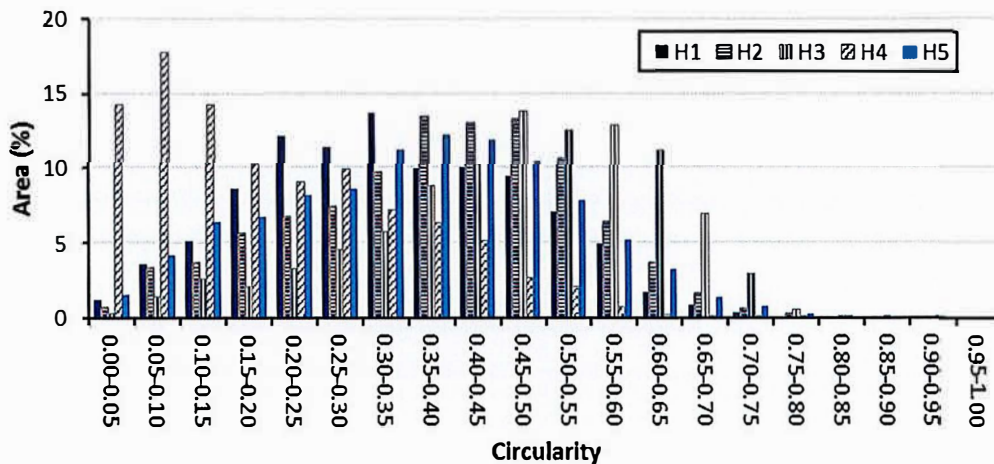


Fig. 4 Circularity of hemp shives.

Table 7 Equation of the water absorption curves.

Bio-aggregate	IRA	K_1	R^2
H1	159.2	21.91	0.98
H2	166.5	16.40	0.99
H3	190.0	15.23	0.99
H4	144.5	15.54	0.99
H5	155.2	16.41	0.99
Co	104.8	18.52	0.99
S	147.8	17.78	0.98

close relationship with the intrinsic porosity of the bio-aggregate, while IRA (initial rate of absorption) is mainly related to the external water adsorption on the surface of bio-aggregate.

To compare the results, **Table 7** presents the parameters IRA and K_1 for all the bio-aggregates. After 1 minute of immersion, the initial rate of absorption (IRA) of the different hemp shives range from 140 to 200% by weight. H4 absorbs less than the other shives with 148% by weight while H3 has the highest value of absorption at 195% by weight. This observation is consistent with the previous measurements. H4 particles are the biggest and the most elongated particles inducing a reduced specific surface and, in particular, a reduced cross section exposed to the water. This would be responsible for the lowest water adsorption and very short-term absorption in large pores when immersed in water. H1, H2 and H5 have similar IRA between 160 and 170% by weight. On the other hand, H1 has a different rate of absorption with a K_1 equal to 21.9, higher than that of the other hemp shives around 15 to 16.

The two alternative bio-aggregates present high water absorption capacity of 250 to 300% by weight after 48 h immersion. **Figure 7** evidences distinct initial rate of absorption (IRA) between the particles. After 1 minute, in the same way as hemp shives, sunflower aggregates already retain more than 150% by weight while corn particles only absorb 100% by weight. This could be a benefit for corn particles at the time of mixing with the mineral binder.

(5) Extractives proportion

In the literature, the extractives from lignocellulosic particles were identified as potential retarding agents for mineral binder hydration. They include different families of extractives as monosaccharides (i.e., free sugars), polysaccharides (Blanes *et al.* 2004) which have the ability to form strong acid-base bonds with metal-hydroxylated species present on mineral surfaces (Laskowski *et al.* 2007), peptides, phenolic compounds, terpenes, pectin which have the ability to trap Ca^{2+} ions in their polymeric structure, thus contributing to the lack of calcium close to particles and modifying the formation of hydrates, and organic acids.

In this study, 7 distinct bio-aggregates of three different plant species were characterized. The extractives content of these 7 bio-aggregates were measured and are reported in **Table 8**. The proportions are consistent with values of the literature summarized by Magniont and Escadeillas (2017).

For hemp shives, the content of water-soluble constituents varies from 5.4 to 15.0%. H1, H2 and H5 have a proportion about 5 to 7% while H3 and H4 have a higher proportion of 15.0 and 10.5%, respectively. Sun-

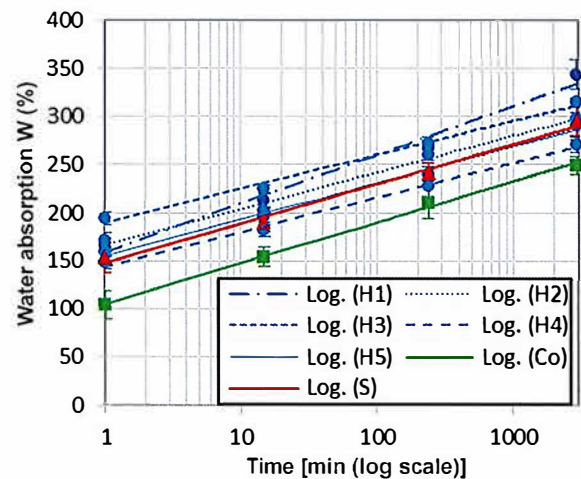


Fig. 7 Water absorption curves of bio-aggregates as a function of time.

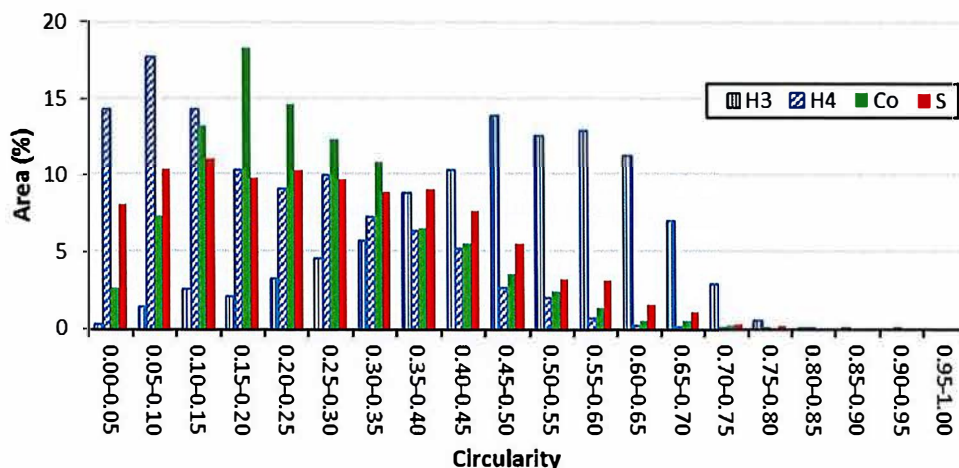


Fig. 6 Circularity of corn Co and sunflower S bark particles compared to hemp shives H3 and H4.

Table 8 Extractive proportions of bio-aggregates.

Bio-aggregate	Extractive proportions (%)
H1	6.3
H2	5.4
H3	15.1
H4	10.5
H5	6.8
Co	23.5
S	10.6

flower bark particle S has similar value as H4. However, corn bark particle has a very high value of extractives, about 23.5%. These proportions are important to note because of their supposed role in the mechanical behavior of bio-based materials.

3.2 Interactions between bio-aggregates extractives and pozzolanic binder

(1) Hydration of the model pastes

The isothermal calorimetry tests allowed exploring the impact of plant extractives on the hydration reactions and mechanisms of the binder paste. The results are

presented in Figs. 8 and 9. In Fig. 8, the heat flow curves highlight the major impact of hemp shiv extractives on binding mechanisms of the pozzolanic matrix. Indeed, a delay is observed with all kinds of hemp shiv. In addition, the heat flow intensity related to the reaction is reduced. However, the hydration reaction took place for all pastes. Two phases are noted. The first [1] corresponds to the exothermic reaction between potassium sulfate and calcium ions forming ettringite. The second [2] is attributed to the pozzolanic reaction. Thus, the results indicate an impairment of the reaction mechanisms, inducing the pozzolanic binder setting. This effect was reported in the literature during the hydration of Portland cement in the presence of wood (Na *et al.* 2014), hemp (Diquélou *et al.* 2015) or lavender (Magniont 2016). The highest negative effect of extractives is observed for H3P by the highest reduction of the heat flow intensity and retarding effect. On the contrary, extractives from H2 exhibit the less negative impact regarding hydration. The deleterious effect can be classified at 3 days as $H2 < H5 < H1 < H4 < H3$.

The isothermal calorimetry tests results of pastes with

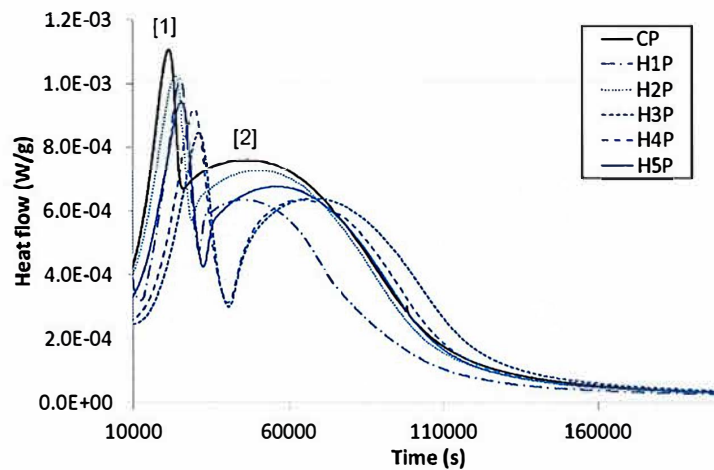


Fig. 8 Heat flow by isothermal calorimetry of control paste with distilled water and pastes containing extractives from hemp shives.

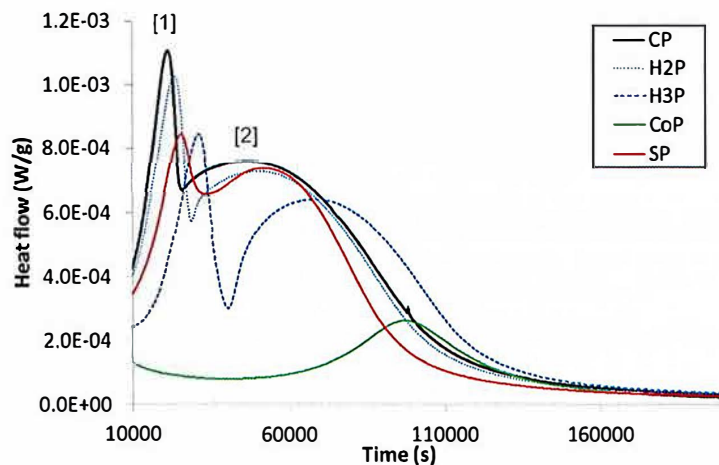


Fig. 9 Heat flow by isothermal calorimetry of control paste with distilled water and pastes containing extractives from corn particles CoP and sunflower particles SP compared to H2P and H3P.

sunflower and corn extractives are presented in **Fig. 9** and compared to extreme behavior of hemp shives, i.e., H2P and H3P. In comparison with the pastes with hemp extractives, sunflower extractives achieve an intermediary impact regarding to the hydration delay. The heat flow intensity related to the reaction [1] is reduced. However, the hydration reaction takes place and sunflower extractives appear to have a lower impact on reaction [2], not implying intensity reduction. On the contrary, pastes based on corn extractives show a dissimilar behavior than H2P to H3P. The corn extractives induce the highest impact, reflected by a delay of 27 h and a very important reduction of the heat flow intensity as well as a deep modification of the hydration mechanisms of the pozzolanic binder since one unique heat flow peak is evidenced.

(2) Mechanical performance of pastes

The compressive strengths of pastes containing bio-aggregate extractives are presented in **Fig. 10**. The results confirm that filtrate of bio-aggregates significantly influence the strength of binder pastes as previously observed by Sabathier *et al.* (2017) with water-soluble compounds from lavender and sunflower particles.

The effect of extractives can be observed after 3 days with a compressive strength value of 15.2 MPa for control CP, while, for the other pastes made with filtrates containing extractives, the strength reduction is ranging from 19 to 93%. Hemp filtrates H2, H4 and H5 as well as sunflower one have similar impact (reduction of 20 to 25%). H1 filtrate is the most affecting hemp filtrate by reducing the strength of more than 40%, while H3 filtrate induces an intermediary drop of 34%. Corn filtrate stands out with the strongest negative effect on the binder paste compressive strength at 3 days, the latter reaching only 1 MPa.

Until 150 days, the trend follows a similar pattern with the exception of the H3P whose hardening between 14 and 150 days is significantly higher than for all the other pastes.

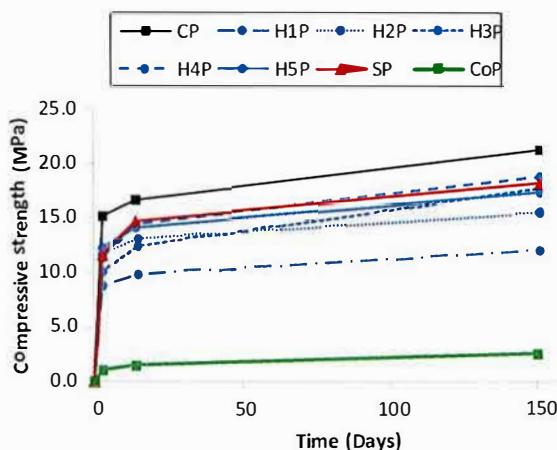


Fig. 10 Compressive strength of pastes at 3, 14 and 150 days.

(3) Impact of extractives on the hydration and hardening mechanisms of the model pastes

The short term and long term effects of plant extractives on the mineralogical composition of the model pastes were studied by XRD and TGA. TGA curves for control paste and pastes containing plant aggregates extractives after 24 h, 48 h and 9 months of curing are plotted in **Fig. 11**. 24 h and 48 h after mixing, the water-soluble fraction from the different plant aggregates has a significant impact on the pozzolanic reaction development by reducing reaction products quantity. The first peak, around 120°C, is attributed to the dehydration of C-S-H and ettringite (denoted as Et), and the second peak, at 180°C, corresponds to the dehydration of distinct products of the pozzolanic reaction, including calcium aluminium oxide carbonate hydrate, $[\text{Ca}_4\text{Al}_2\text{O}_6\text{CO}_3(\text{H}_2\text{O})_{11}]$ (denoted as Mc), and calcium aluminium oxide hemi-carbonate hydroxide hydrate, $[\text{Ca}_4\text{Al}_2\text{O}_6(\text{CO}_3)0.5(\text{OH})(\text{H}_2\text{O})_{11.5}]$ (denoted as Hc) (Frias and Cabrera 2001; Magniont *et al.* 2010). The small peak at 250°C is attributed to straelingite, $[\text{C}_2\text{ASH}_8]$ (denoted as St). A strong delay was also observed on the consumption of portlandite in pastes based on corn extractives (peak at 430°C).

In addition, differences are visible in the peak related to calcium carbonates decarbonation (mass loss between 500 and 850°C) at 24 h and 48 h. In the presence of bio-aggregates extractives (with the exception of H1 and H5) and to a greater extent in that of corn extractives, the formation of calcium carbonates is increased in comparison with the plain paste. The presence of carbonates could be related to the release of carbon dioxide induced by the alkaline degradation of hemp particles, which was responsible for the carbonation of portlandite (Govin *et al.* 2006). The thermogravimetric analyses also revealed the presence of hydrogarnet, $[\text{C}_3\text{AH}_6]$ (340°C), a usual product of the reaction of metakaolin with $[\text{Ca}(\text{OH})_2]$.

After 9 months, the gap is attenuated between control and hemp extractive pastes. Nevertheless, the content of pozzolanic products in hemp extractives pastes remains less than its content in plain paste (with the exception of H5). In the long term, pastes containing corn and sunflower present highest peak around 120°C that could be linked to the formation of delayed ettringite also visible on XRD analyses (**Fig. 12**).

XRD analyses were also performed on the different model pastes after 24 h, 48 h and 9 months. The comparison of the diffractograms, visible on **Fig. 12**, highlights the influence of bio-aggregates extractives on the mineralogical composition of the pastes from 24 h to 9 months. Concerning early age, the analyses reveal the quick formation of Mc in all the pastes (with the exception of CoP) and a conversion of ettringite, which is no more visible after 48 h. The influence of corn extractives is very clearly shown since, in CoP paste, no Mc is formed but a large peak of residual portlandite appears, allowing us to conclude to the inhibition of the poz-

zolanitic reaction. After 9 months, the results are more variable. Mc is still the main crystallized hydrate in the plain paste as well as in pastes H4P and H5P. The equilibrium of the Afm phases seems to be impacted by the nature of the extractives, since in H2P, H3P and SP, Hc

and Mc phases coexist, while in CoP, St and Hc are present. Moreover, the presence of corn and sunflower extractives seem to encourage the formation of delayed ettringite.

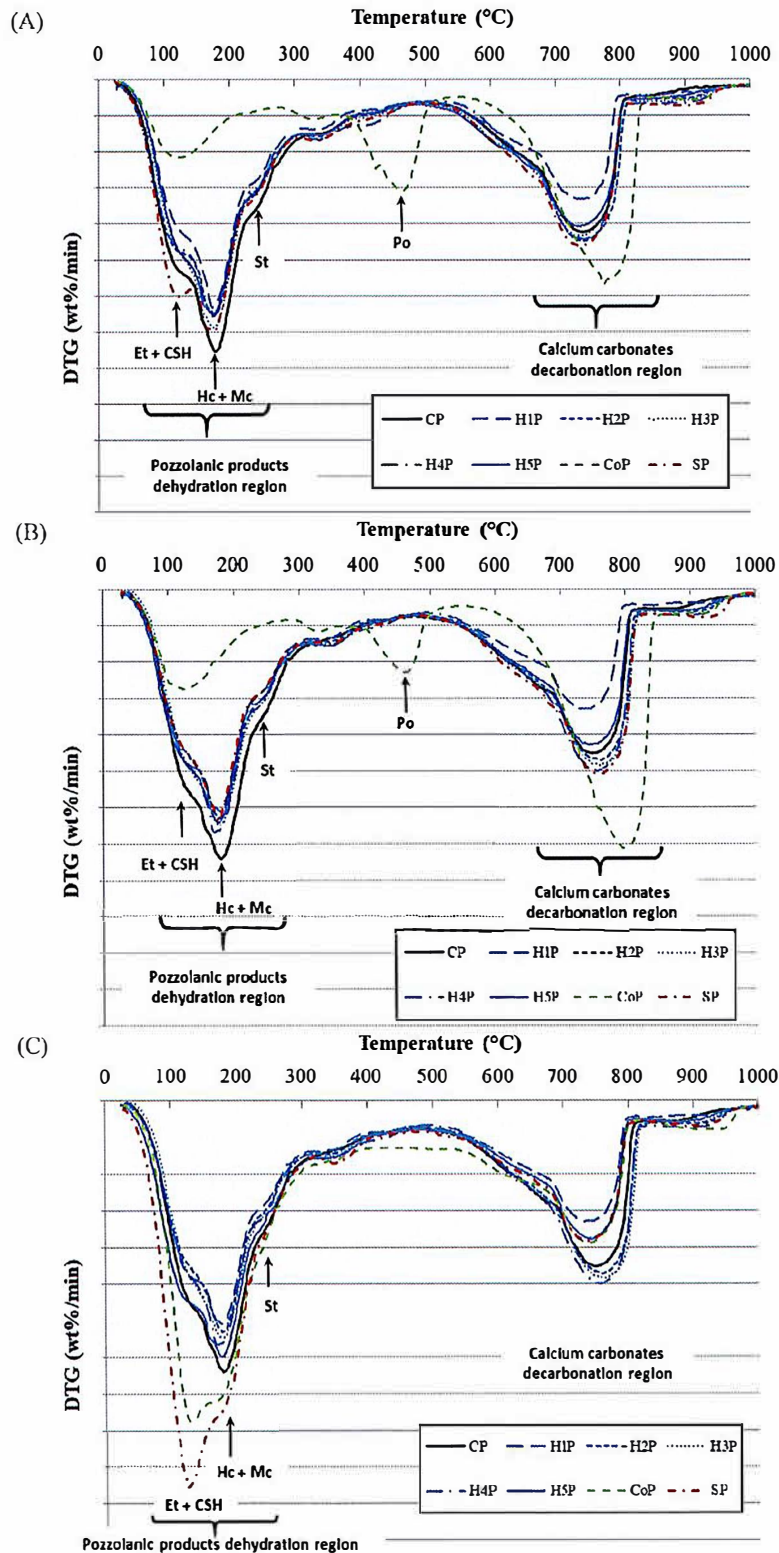


Fig. 11 Differential TGA curves of control paste and pastes containing bio-aggregates extractives after 24 h (A), 48 h (B) and 9 months (C).

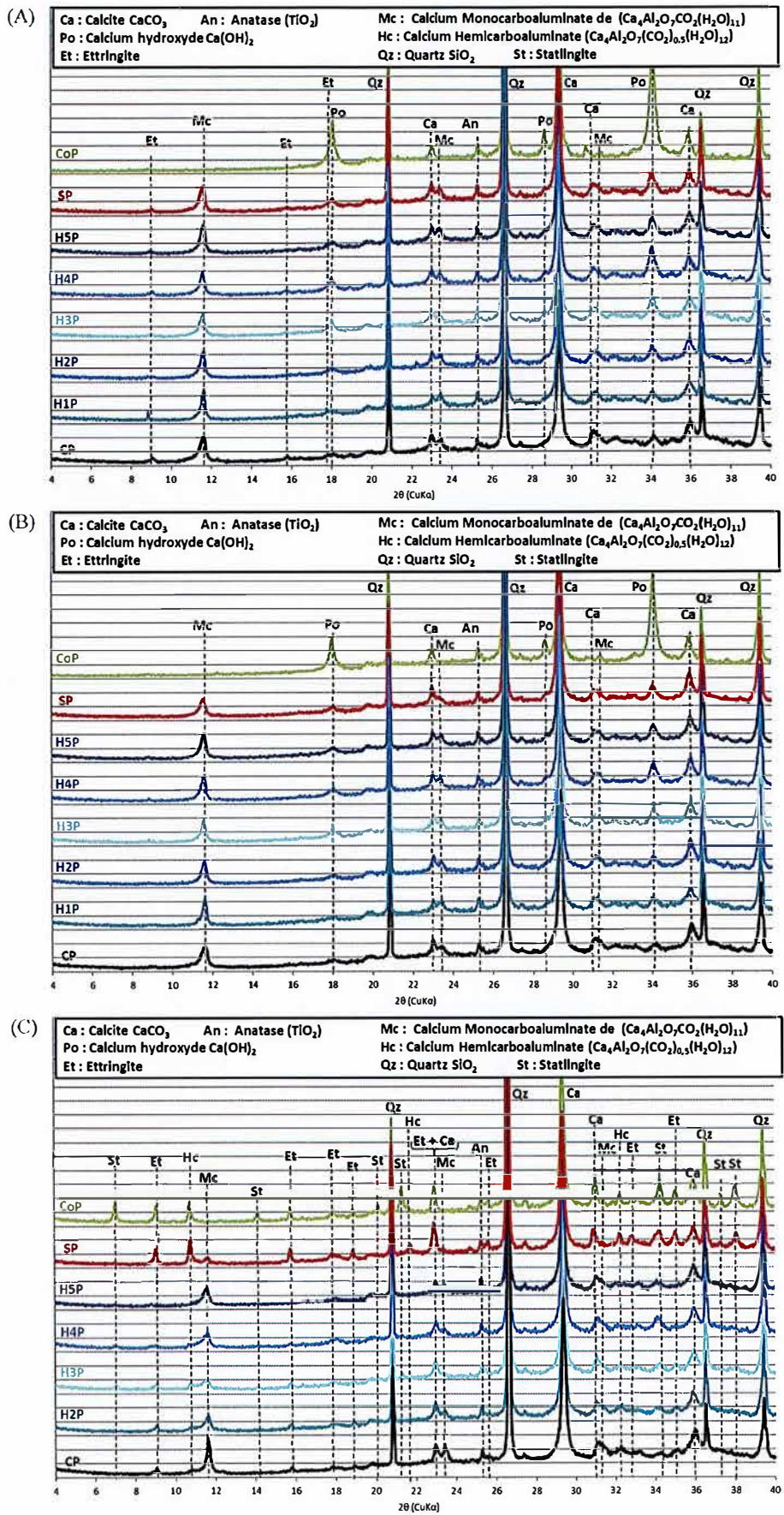


Fig. 12 XRD analyses of model pastes with different bio-aggregates extractives after 24 h (A), 48 h (B) and 9 months (C).

Table 9 Stress at strain of 1.5% ($\sigma_{\epsilon=1.5\%}$) and elastic modulus E of concretes with hemp, corn and sunflower bio-aggregates.

Mix	$\sigma_{\epsilon=1.5\%}$ (MPa)	SD	E (MPa)	SD
H5C	0.50	0.29	114.2	13.7
H4C	0.08	0.01	18.4	0.7
H3C	0.08	0.01	19.0	3.0
CoC	0.03	0.01	14.6	2.7
SC	0.13	0.02	55.1	1.8

3.3 Mechanical performances of plant-aggregates-based concrete

In order to correlate the characteristics of the bio-aggregates and, in particular, their extractives content with the performances of the composites, the mechanical compression behavior of several plant concretes made of hemp, sunflower and corn aggregates were assessed and presented in Fig. 13. This figure highlights very distinct compressive behavior between, on one hand, the composites containing the three different hemp shives and, on the other hand between the composites made of sunflower and corn particles. Two types of strain-stress curves are measured. H3C, H5C and SC vegetal concretes reach a maximum stress value after a quasi-elastic region followed by an elastoplastic phase. On the contrary, H4C and CoC specimens exhibit a continuous increase of stress, typical from a highly deformable material.

Two mechanical characteristic parameters were selected to compare quantitatively the performances of the plant concretes: the stress corresponding to a strain of 1.5% ($\sigma_{\epsilon=1.5\%}$) and the elastic modulus (E), their values are reported in Table 9. For hemp concretes, the stress corresponding to 1.5% strain and the elastic modulus vary by a factor 6 between H5C and H3C. Considering sunflower concrete, its characteristic strength is 5 times higher than the one of corn concrete. For the elastic modulus, the ratio is around 3.8. Various parameters could explain these variations, among which the mechanical strength of the binder phase, the adherence between this mineral matrix and the bio-aggregates, and especially the extractives content of the bio-aggregates. In the next part, a discussion is conducted to

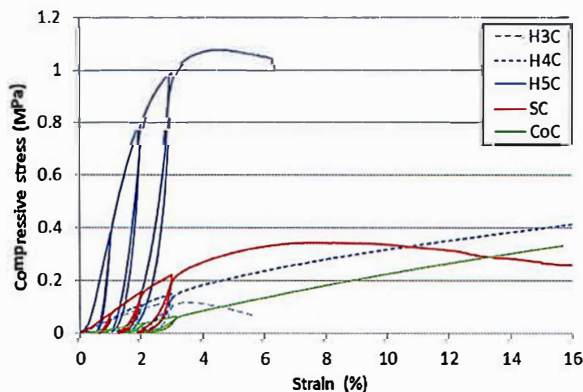


Fig. 13 Typical stress-strain curves of plant based concrete made of hemp, sunflower and corn aggregates.

link the results obtained on bio-aggregates, model pastes and plant concretes.

3.4 Discussion

Considering bulk density, dust content, particle size distribution and morphology of the seven distinct bio-aggregates studied, a wide variability has been evidenced, both between the five hemp shives and with respect to the two alternative particles of sunflower and corn. The processes of transformation, separation and/or calibration applied to the plant stalks have a predominant impact of these properties in comparison with the plant species.

The water absorption of sunflower particle is in the range of those of hemp shives. On the contrary, corn particles present a significantly reduced absorption capacity that could be linked to a hydrophobic character of corn bark.

Corn particles also stand out respecting to their extractives content, which largely exceeds those of the other bio-aggregates, including hemp shives and sunflower bark particles.

The study achieved on model pastes aimed to identify the mechanisms of interaction between these water-soluble compounds and the mineral pozzolanic binder. Extractives from all the bio-aggregates negatively influence the hydration and hardening of the binder to various extents. The hydration and indirectly setting are delayed, the compressive strength is reduced and this could be related to the limited quantity of pozzolanic reaction products evidenced by TGA analyses. We can make a correlation between the compressive strength at 3 days and the second phase [2], attributed to the pozzolanic reaction. The H1, H3 and H4 having the highest negative effect on hydration at short time induced a lowest compressive strength of pastes. In the same way, H2 and H5 have a lowest deleterious effect on mechanical strength.

Focusing on the alternative aggregates, sunflower particles (S) appear to be in the range of hemp shives, while the different analysis clearly demonstrate the higher negative impact of corn aggregates (Co) on the hardening mechanisms of the binder. The S particles have the same hydration (heat flow intensity) behavior as H2 inducing similar mechanical behavior. The highest impact of Co on the heat flow intensity, consistent with no pozzolanic products according to TGA, is well correlated with the large decrease of mechanical performances observed on the binder including corn extractives.

However, the study of hydration by the heat flow intensity does not explain all the mechanical behavior. In addition, the reduction percentage of strength is not proportional to the reduction of the heat flow intensity. The induced hydration delay exceeds 20 hours in comparison with the plain paste. This observation is in accordance with the mineralogical analyses realized after 24 h and 48 h, which evidence, for the corn paste, a

large reduction of pozzolanic products, together with a residual content of portlandite and a formation of additional calcium carbonates at early age. This inhibition, in a large extent, of the pozzolanic reaction together with the fixation of calcium ions in carbonate forms induce the reduction of the compressive strength of the paste of about 90%.

Hence, the filtrates containing the extractives showed a negative impact on the hydration and the compressive strength. The extractives content of the bio-aggregates appear as a key parameter of the reduction of the mechanical performances of the model pastes. Indeed, Fig. 14 shows the evolution of the hydration delay and of the compressive strength of the pastes as a function of the extractives content.

Considering the five hemp shives, Fig. 14A highlights an increase of the hydration delay with the extractives content that can be correctly predicted by a linear relation. Nevertheless, this relation is not valid anymore for sunflower and corn aggregates, evidencing the fact that the content but also the nature of the extractives determines the deleterious effect of plant aggregates on the hydration.

The compressive strength of the model pastes at 3 days is also directly impacted by the extractives content of the bio-aggregates (Fig. 14B), in particular above a

10% content. Below, the relation is less evident; this could be related to the variable impact of the extractives on the formation of calcium carbonates at early age. Indeed, the paste presenting a significantly lower Compressive stress S_c with only 6.3% of extractives is the HIP, i.e. the paste containing the lower quantity of calcium carbonates (Fig. 11). The same phenomenon could explain that the compressive strength of the model pastes after 150 days does not increase monotonically with the extractives content, since the inhibition of the pozzolanic reaction and the encouraging of the carbonation process conversely affect its mechanical performance. This long-term phenomenon observed on binder pastes would probably not occur in the plant concrete. In fact, in these composites with a very high open porosity (around 70%) the carbonation process is fast and facilitated.

To verify these explanations, the mechanical performances of bio-aggregates based concretes are plotted as a function of the extractives content of the considered bio-aggregates in Fig. 15. This figure allows highlighting that both compressive strength and elastic modulus of hemp concretes are negatively impacted by an increasing extractives content of the shiv. Nevertheless, the water-soluble extractives concentration does not appear to be the only impacting parameter, since, for

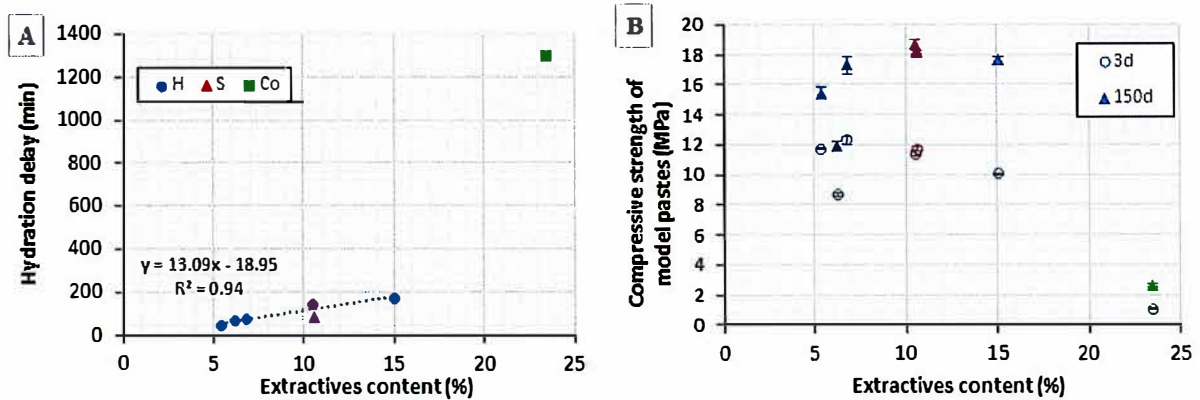


Fig. 14 Evolution of the hydration delay (A) and of the compressive strength (B) of the model pastes with the extractives content of the bio-aggregates (hemp: blue; sunflower: red; corn: green).

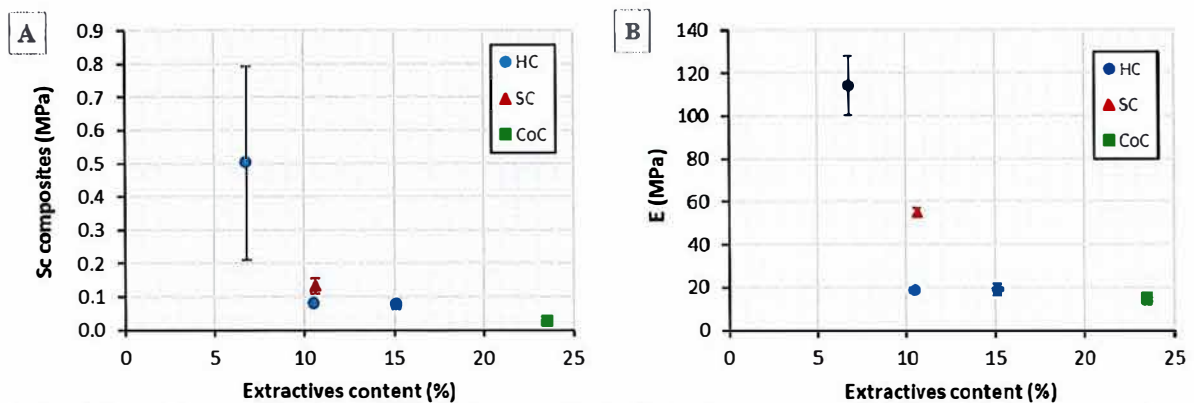


Fig. 15 Evolution of the compressive stress S_c at strain of 1.5% (A) and the elastic modulus E (B) of bio-aggregates based concretes with the extractives content of the bio-aggregates (hemp: blue; sunflower: red; corn: green).

similar extractives content, the sunflower based concrete exhibits lower performances than hemp concrete. It is difficult, however, to conclude on this point, as both composites were not designed with the same binder.

4. Conclusion

The present paper aimed to study the impact of the water-soluble components extracted from seven distinct bio-aggregates - five hemp shives and two agricultural by-products (corn and sunflower bark particles) as alternative bio-aggregates for vegetal lightweight concrete – on the hydration and hardening mechanisms of a pozzolanic binder as well as on the mechanical performances of plant concretes. Beforehand, the bark particles of the seven bio-aggregates were characterized according to the recommendations of RILEM TC 236-BBM (Amziane *et al.* 2017). Bulk density, dust content, particle size distribution, circularity and water absorption capacity were determined on hemp shives and on bark particles extracted from corn and sunflower stalks. Particle size distribution of sunflower and corn particles could be corrected through a calibration process. Corn particles present a limited water absorption capacity. This could be valorized in association with a clay matrix for example. On the contrary, corn particles stand out with higher extractives content than the six other bio-aggregates tested.

The results on pastes showed an impact of the extractives (water-soluble components extracted from the different bio-aggregates) on the compressive strength. This phenomenon was explained by their deleterious effect on the hydration and hardening mechanisms of lime-metakaolin binder explored by XRD, TGA and calorimetric measurements. Consequently, the paste could be a relatively good model to predict the behavior of concretes by following their early age performances: hydration delay and 3-day mechanical strength.

For the same plant species (i.e. hemp shiv), it was observed that the hydration delay of the model paste and the mechanical performances of the hemp concrete are directly related to the extractives content of the shiv.

Nevertheless, for distinct plant species, the extractives content does not appear sufficient to predict the performances of the vegetal lightweight concretes. The nature of the water-soluble extractives or of the products of the bio-aggregates alkaline hydrolysis by the mineral binder would also influence the final mechanical performance.

Finally, sunflower bark particles appear to be a good candidate for hemp shives substitution since their physical and chemical characteristics are close and their impact on the hydration mechanisms of the pozzolanic binder negligible.

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