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Guillaume Delannoy, Sandrine Marceau, Philippe Gle, Etienne Gourlay, Marielle Gueguen Minerbe, et al.. Impact of hemp shiv extractives on hydration of portland cement. *Construction and Building Materials*, 2020, 244, 36 p. 10.1016/j.conbuildmat.2020.118300 . hal-02472950

HAL Id: hal-02472950

<https://hal.science/hal-02472950>

Submitted on 10 Feb 2020

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IMPACT OF HEMP SHIV EXTRACTIVES ON HYDRATION OF PORTLAND CEMENT

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Abstract

When formulating materials containing an hydraulic binder and plant particles, the setting of the binder may be slowed or prevented by the compounds extracted from the plant. In this article, a methodology is fixed to analyse three types of hemp shiv and to study the variability of the composition of extractives and their influence on the hydration of cement. Isothermal calorimetric measurements have shown that one type of shiv caused a greater delay in the setting of the cement. Analysis of free compounds extracted from the plant has shown that this shiv has a higher content of extractives, and in particular, of sugar. By using the same quantities of standard sugars, it was found that the measured sugar content could not, in and of itself, account for the delay in hydration measured in the presence of shiv. Other extracted molecules, such as phenolic compounds, also play a part in the hydration of the cement.

Keywords: calorimetry; retardation; Portland cement; vegetal; extractives; hemp, hydration

1. INTRODUCTION

With a view to reducing the environmental impact of buildings, bio-based materials are being used increasingly in building projects. In particular, this is the case with bio-based insulators, known as vegetal concrete, formulated mainly using vegetal aggregates such as shiv, made from hemp. The mechanical resistance of the material comes from the addition of a mineral binder which covers the particles. In a study on the durability of hemp concrete (hempcrete), samples corresponding to a wall formulation were made up using binders and shiv compliant with the building codes imposed by the French organisation of hemp construction [1]. With these materials, compressive strengths lower than those expected were measured and attributed to a lack of hydration of the binders due to the incompatibility of the binder-vegetal aggregate couple [2]. Similar results have been found in other works [3,4] and have been explained by the perturbation of hydration reactions of cement in the presence of molecules from the shiv. Shiv is a ligno-cellulosic material, obtained from the shredded stem of the hemp plant, and made of a mixture of cell walls and free compounds that can easily be extracted with water or organic solvents.

The plant cell walls are composed of a matrix of amorphous polymers (hemicelluloses, lignins and pectins), reinforced with crystalline cellulose microfibrils [5]. Cellulose and hemicelluloses are saccharides, commonly known as sugars. The simplest saccharide units are monosaccharides, such as glucose or fructose. Cellulose, which is the majority compound in shiv, is a polysaccharide composed solely of glucose. Hemicelluloses are polysaccharides composed of various types of monosaccharides such as fructose, xylose or mannose, but also uronic acids, which are oxidised forms of saccharides. While monosaccharides or oligosaccharides are highly soluble in water at a neutral pH (4.2 kg.L^{-1} at 20°C for sucrose [6]), hemicelluloses and cellulose are insoluble. Nonetheless, hemicelluloses can be dissolved in basic solutions [7]. Lignins, which are hydrophobic compounds formed by the polymerisation of phenolic alcohols, are not soluble in water. Finally, pectins are linear polysaccharides with varying degrees of branching, made of a linear chain of galacturonic acids. During the process of transformation of the hemp stems, during retting, the degradation of pectin under the influence of enzymes synthesised by micro-organisms allows the fibres

to be separated from the shiv. Unlike the other compounds in the cell walls, certain pectins can be extracted using water.

Numerous other molecules not found in the walls, such as polyphenols, oligosaccharides, fatty acids and terpenes, are also present in small proportions in shiv. These molecules are soluble in different solvents and are therefore extractible in the same way as pectin. Among the molecules extractible from shiv are also oligomers of hemicelluloses and lignin, along with proteins, lipids, waxes and ash [5]. These compounds are present in different proportions as a function not only of the nature of the plant matter but also of the way in which the plant was grown, any processes that it has undergone, the way in which it has been stored, etc. [3,8].

When mixing and implementing hempcrete, the extractive molecules diffuse in the mixing water and slow down the kinetics of binder hydration [9–11]. This may alter the properties of the materials – in particular, decreasing their mechanical strength [2,5,12]. Certain mechanisms of interaction between the plant molecules and the mineral phases have been identified to explain this result. They involve different types of molecules extracted from the aggregates:

- The adsorption of monosaccharides to anhydrous cement grains delays the setting by reversible physisorption [8,9,13]. For this to happen, the molecules must be charged, which is the case with monosaccharides, known as reducing sugars [14]. In a basic environment, enolate ions, negatively charged and relatively stable, are formed and can adsorb by electrostatic links to the surface of the cement grains (for the most part, positively charged), limiting access to water for non-hydrated grains.

- the capture of calcium ions [13,15–17] by uronic acids, phenolic compounds, certain polysaccharides such as pectin [7,18] or acids stemming from alkaline degradation of the saccharides [19,20] also contributes. The captured calcium ions are then no longer available to take part in hydration reactions.

- nucleation sites may be blocked by non-reducing sugars, such as sucrose or stachyose, which can form complexes in the presence of calcium ions, and affix to the hydrates [10,21]. These molecules irreversibly prevent the growth of hydrates; CSH can no longer precipitate at that site. We then speak of the poisoning of the nucleation sites [9,22,23].

- the formation of a water-impermeable hydrate barrier can be linked to the very rapid hydration of aluminates C_4AF in the presence of sugars [13,17].

These mechanisms depend on the nature and quantity of the plant molecules extracted when the vegetal concretes are being formulated. To limit the effects of the vegetal matter on binder hydration, certain studies have proposed subjecting the fibres or aggregates to a range of treatments, which may be costly [3,24–27], or adapting the formulation of the binders and their additives [28–32]. There is also a third feasible solution: to select plant materials that are compatible with the mineral binders, based on their levels of extractives. A batch of aggregates which has too high a content of extractives poses a real danger of delaying the setting of the binder, and thus altering the properties of the hardened material, and its durability.

Despite the knowledge of these interactions between plants and mineral binders and the existence of building regulations, problems of pulverization at the core of the materials are regularly reported after their implementation in buildings [33]. In order to develop the use of vegetal concretes for building insulation, it is therefore necessary to characterize the compatibility between a mineral binder and vegetal aggregates by analyzing the extractible compounds of plants. A range of extraction protocols have been used previously to study the influence of vegetal extractives on the hydration of mineral binders. The parameters used are listed Table 1 [3,4,7,11,19,23,24,34]. The immersion time, temperature, type of extraction solution and the water/vegetal ratio are parameters which vary from one study to the next, and which have a significant influence on the type and quantity of extractives measured. This variability of the extraction conditions makes it difficult to compare the results of those studies, and there is no universally accepted protocol.

Table 1. Synthesis of extraction protocols of vegetal fibres or aggregates depending on the solution, heating of the solution, the time of extraction, the liquid to vegetal mass ratio (L/V), and the quantification of total amount of extractives, of sugars and acids

| Vegetal | Solution | | | | | T°C | Time | L/V | Quantification | | |
|--|----------|---------------------|------|--------|-------------------|-----|------|-----|----------------|--------|-------|
| | Water | Ca(OH) ² | NaOH | Cement | CaCl ₂ | | | | Total | Sugars | Acids |
| Hemp fibre [7] | ★ | ★ | ★ | | ★ | | 1 h | 10 | | ★ | ★ |
| Sun flower, lavender [4] | ★ | | | | | 100 | 1 h | | ★ | | |
| Miscanthus [34] | ★ | | | | | 100 | 2 h | 5 | | | |
| Bagasse fibre, Coconut fibre, Hemp fibre, Oil palm fibre, Spruce wood, Water hyacinth [23] | ★ | | | | | 80 | 2 h | 5 | ★ | ★ | ★ |
| Hemp shiv [3] | ★ | | | | | | 24 h | 10 | ★ | ★ | |
| Wood powder [11] | ★ | | | ★ | | 80 | 24 h | 1 | ★ | | |
| Wood [19] | ★ | ★ | | ★ | | | 24 h | 50 | ★ | | |
| Lavender [24] | ★ | | | | | | 72 h | 14 | | | |

The final objective will be to set criteria for the selection of plant particles. to avoid this type of pathology. It is for this purpose that, in this study, we seek a simple method which would allow us to distinguish between different kinds of shiv on the basis of their content of extractives, and select those which have lower levels. With this goal in mind, a Portland cement is used for the study, because its setting mechanisms have already been documented and studied. Three types of shiv are chosen. The first is the shiv which we used previously in the durability study, where a lack of hydration was observed [2]. The other two shives are of different origins, and were used in an earlier study, where no problem was found with the hydration [35].

In this article, the influence of the different shives on the binder hydration time is first studied. Secondly, an extraction method is established, based on the data from previous studies. Next, once the protocol has been established, the amount of extractive molecules in the mixture is quantified. We have focused, in particular,

on sugar content, because sugars are the molecules which are most often cited as being responsible for delayed setting [3,8]. Finally, these results are discussed, and we assess the influence of the content of reducing and non-reducing sugars in comparison to that of other compounds extracted from shives on the setting of the hydraulic binder.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Types of shiv

Three types of hemp shiv were selected for this investigation, based on observations made during previous studies [2,35]. They are referred to as HS1, HS2 and HS3 (Figure 1). They come from different French hemp producers and comply with the French hemp shiv label [1]. The chemical composition of these types of shiv, presented in Table 2, was determined using the Van Soest method and French standard NF-18-122.

Photographs of the three hemp shives, their granulometry curve and their water absorption curves are shown in Figure 1 and Figure 2. These results are obtained by following the recommendations of Technical Committee 236-BBM at France's RILEM [36].

For certain tests, shives are reduced to powder using a bladed crusher, sieved to a particle size of 500 μ m and then dried for 48 hours at 105°C. HP1, HP2 and HP3 correspond to the hemp powders obtained from HS1, HS2 and HS3 respectively.

Table 2. Chemical composition of hemp shives determined by Van Soest method

| Proportion (%) | Hemp shiv 1 | Hemp shiv 2 | Hemp shiv 3 |
|----------------------|-------------|-------------|-------------|
| Cellulose | 53.0 ± 0.9 | 54.7 ± 0.5 | 54.9 ± 0.5 |
| Hemicellulose | 12.1 ± 0.9 | 11.5 ± 0.6 | 12.0 ± 0.4 |
| Lignin | 15.0 ± 0.2 | 16.8 ± 0.2 | 15.5 ± 0.3 |
| Others | 19.9 ± 2.0 | 17.0 ± 1.3 | 17.6 ± 1.2 |

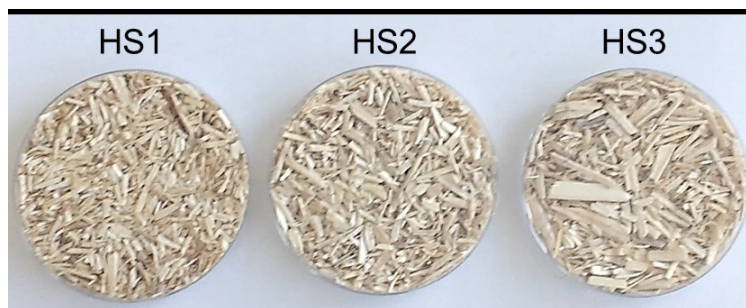


Figure 1. Aggregates of hemp shiv

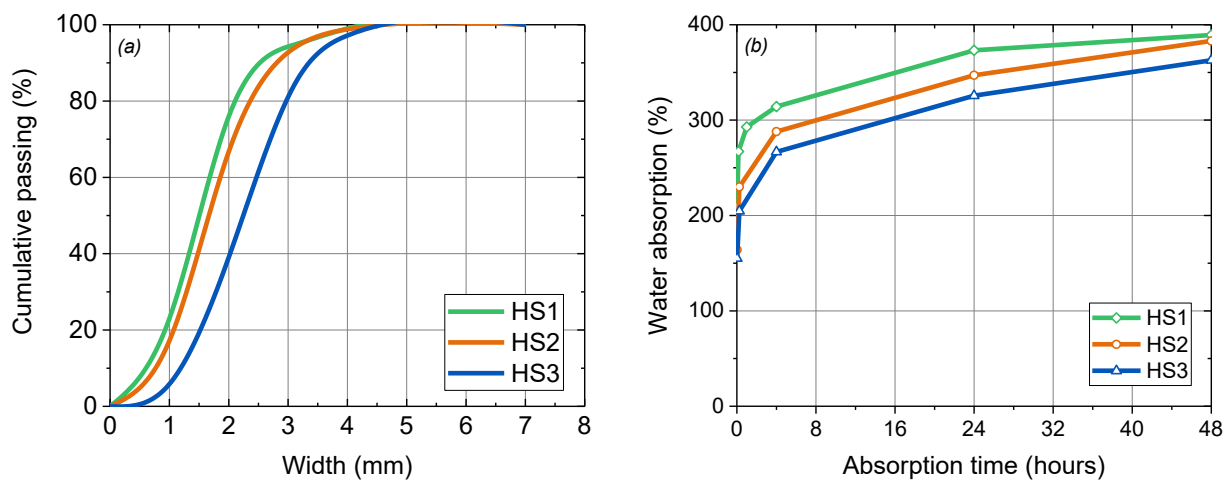


Figure 2. (a) Particle size distribution and (b) water absorption of hemp shives

2.1.2. Standard sugars

Standard samples of glucose (N° CAS 50-99-7), fructose (N° CAS 57-48-7), sucrose (N° CAS 57-50-1), xylose (N°CAS 58-86-6) and mannose (N° CAS 3458-28-4) for analysis (purity > 99.5%) are supplied by Sigma Aldrich.

2.1.3. Portland cement

Depending on the manufacturer's data, the Portland cement CEMI used for this study contains 60% of C₃S, 13% of C₂S, 2% of C₃A, 13% of C₄AF and 4% of gypsum.

2.2. Methods

2.2.1. Calorimetry

The binder hydration is measured by isothermal calorimetry at 25°C (TA Instruments, TAM AIR 8, Reference sample of Fontainebleau sand). The heat flux released and the cumulative amount of heat are measured over time in relation to a sample of sand used as a reference. The quantity of sand is adapted to the size of the sample being analysed, so that the specific heat capacities are the same in both test tubes.

The measurements are made on cement paste, cement paste containing shiv powder, hempcrete and cement paste containing standardised sugars. The composition of the different types of samples and the masses analysed are set out in Table 3. The quantity of shiv present in the samples increases when the binder-to-shiv ratio decreases.

The samples of cement containing shiv powder and the hemp concrete are made up in accordance with the hemp building regulations [1].

Table 3. Formulations of cement pastes and hemp concrete

| Sample | Pure cement paste | Cement paste + hemp powder | Hemp concrete | Cement paste + sugar standards |
|---|--------------------------|-----------------------------------|----------------------|---------------------------------------|
| Water to cement mass ratio | 0.5 | 1 | 1 | 0.5 |
| Vegetal to cement mass ratio | 0 | 0.01, 0.02, 0.05, 0.1 | 0.5 | 0 |
| Sample weight in calorimeter (g) | 4 | 4 | 8 | 4 |

2.2.2. Dosage of reducing sugars in solution

The reducing sugars extracted in the solutions are dosed by UV-Visible spectrometry after a redox reaction with dinitrosalicylic acid (DNS). DNS, which is yellow in colour, is reduced by the sugar into amino-nitrosalicylic acid (ANS), which is orange-red, absorbing light at a wavelength of 540nm (Figure 3).

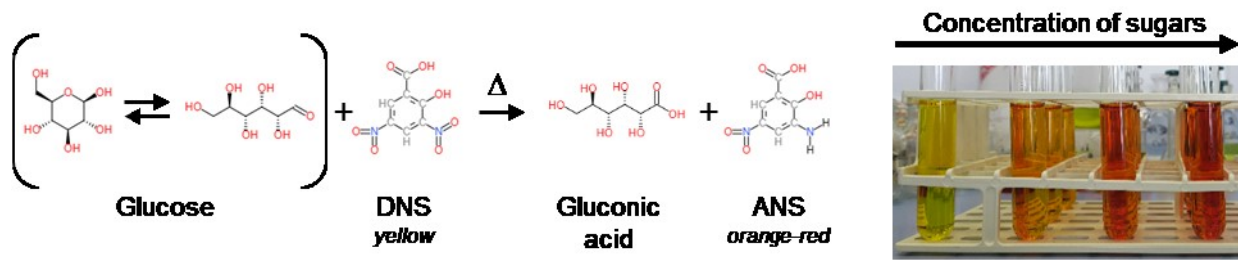


Figure 3. Oxidation-reduction reaction between glucose and DNS and picture of test tubes after reaction without glucose and an increase of sugar concentration

According to the Beer–Lambert law (eq. 1), the absorbance value at 540nm corresponds to the concentration of ANS in the solution being analysed, and hence the concentration of reducing sugars present in the initial solution.

$$A_{540\text{nm}} = \varepsilon_{540\text{nm}} l C \quad [1]$$

where:

$A_{540\text{ nm}}$: the absorbance measured at 540nm

$\varepsilon_{540\text{nm}}$: the molecular absorption coefficient of ANS at 540nm

l : the optical trajectory of the light beam

C : the concentration of ANS

The mass of reducing sugars in solution is then determined in reference to a calibration curve (Figure 4), plotted with solutions of standard sugars (glucose, fructose, xylose and mannose).

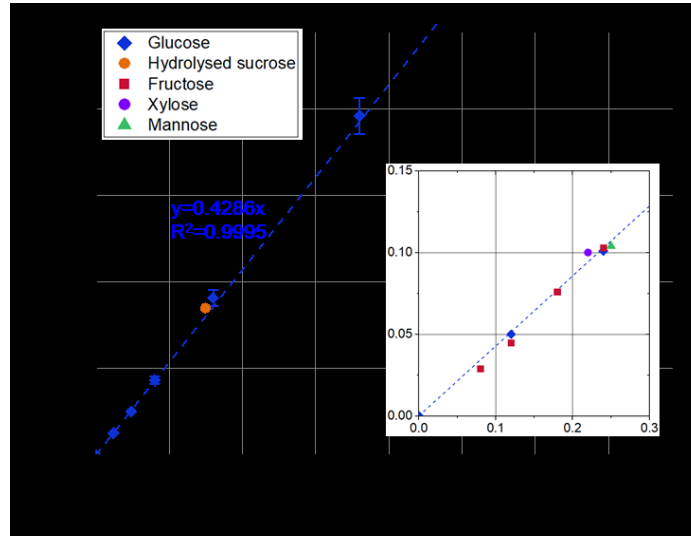


Figure 4. Calibration curve for determination of reducing sugar content by DNS

Equation 2 can be used to calculate the mass of reducing sugars extracted per gram of shiv:

$$m_{red.sugar/g} = \frac{A_{540nm} \times V_{extraction}}{S_{calib} \times V_{dosage} \times m_{hemp}} \quad [2]$$

where:

$m_{red.sugar/g}$: mass of reducing sugars in mg per gram of hemp

A_{540} : intensity of the absorbance at 540nm

$V_{extraction}$: volume of water, in mL, added for extraction

S_{calib} : slope of the calibration curve (0.4286mg^{-1} – Figure 4)

V_{dosage} : volume, in mL, of extraction solution taken for dosage

m_{hemp} : mass, in grams, of hemp added for extraction

Dosing is carried out on a volume of 1.5mL of extraction solution, to which 1mL of basic solution of DNS (10g.L^{-1} of DNS and 16g.L^{-1} of NaOH) is added. The resulting solution is heated in a water bath to 100°C for 5 minutes. After cooling and dilution by the addition of 7.5mL of distilled water, the solution is filtered with a millipore syringe filter, using a cellulose acetate membrane with $0.45\mu\text{m}$ pore size, before being analysed by UV-visible spectrometry at 540nm in a quartz cuvette with a light path of 10mm.

2.2.3. Dosage of total extracted saccharides

Certain oligosaccharides such as sucrose are not reducing, and cannot be dosed with the procedure described above. To find out the total quantity of sugar extracts, we conduct acid hydrolysis to break all polysaccharides down into monosaccharides, which can then be dosed after reacting with DNS. The formula used is then:

$$m_{red.sugar} = \frac{A_{540nm} \times V_{extraction} \times V_{hydrolysed\ neutral}}{S_{calib} \times V_{dosage} \times V_{hydrolysée\ prélevée} \times m_{hemp}} \quad [3]$$

where:

$m_{monosacc}$: quantity of monosaccharides obtained after acid hydrolysis of the extraction solution (in mg) per gram of hemp shiv

A_{540} : intensity of absorbance at 540nm

$V_{extraction}$: volume of water (in mL) added for extraction

$V_{hydrolysed\ neutral}$: volume of solution after hydrolysis and pH buffering (mL)

S_{calib} : slope of the calibration curve (0.4286 mg⁻¹) (Figure 4)

V_{dosage} : in mL, volume of extraction solution taken for hydrolysis and dosing

$V_{hydrolysed\ taken}$: volume of neutral hydrolysed solution taken for dosing (mL)

M_{hemp} : mass (in g) of hemp added for extraction.

Dosing is conducted on 20 mL of the extraction solution ($V_{extraction}$), which is hydrolysed by the addition of 5 mL of 2 mol.L⁻¹ HCl solution and heated to 100°C for 20 minutes. The hydrolysed solution is neutralised by adjusting the pH to 7 using a 2 mol.L⁻¹ NaOH solution, and made up to 50 mL ($V_{hydrolysed\ neutral}$) with distilled water. We then dose the total sugars with DNS, using the protocol described in section 2.2.2, using 1.5 mL of that solution ($V_{hydrolysed\ taken}$).

2.2.4. Statistical analysis of sugar dosage results

To check whether the differences between the results of dosages of saccharides obtained in different extraction conditions are significant, analysis of variance (ANOVA, Excel – XLToolbox, modified version of Levene's test [37]) is carried out. The ANOVA test used is sufficiently robust so that we do not need to test the normal distribution of the values in a group. It determines a probability "p" that the values in the two

groups will be statistically identical. The lower the value of p , the more significant are the differences measured in series of data. In this article, the results are considered significantly different if the probability p is less than 5% ($p < 0.05$).

2.2.5. Colorimetry

A spectrophotometer (Ci4200, X-Rite) was used to characterise the colour of the solutions of extractives. The analyses were carried out on 10mL of solution placed in an optical glass cuvette 31.6mm in diameter. The results were pinpointed in the CIELAB colour space by the coordinates L^* (luminosity) and the chromaticity coordinates: the $-a^*/+a^*$ axis from green to red and the $-b^*/+b^*$ axis from blue to yellow.

3. RESULTS AND DISCUSSION

3.1. Effect of delay on hydration of shiv

In this part, the effect of shiv on cement hydration is evaluated by isothermal calorimetry measurements. The influence of the content and then of the type of shiv is analysed.

3.1.1. Effect of shiv content

The influence of the presence of hemp shiv on the setting of a cement paste is studied by measuring the heat flow released over time from a cement paste, mixtures of cement and powder HP1 and a hemp concrete containing HS1 aggregates. The heat flows over time are presented in *Figure 5* for these various mixtures.

Whatever the sample, the addition of the samples into the calorimeter disturbs the equilibrium of the heat flows in the two chambers of the device. An exothermic peak appears which is also visible if the test tubes are empty or contain inert materials. The time taken for the heat flow to stabilise with empty tubes is between 30 minutes and 2 hours.

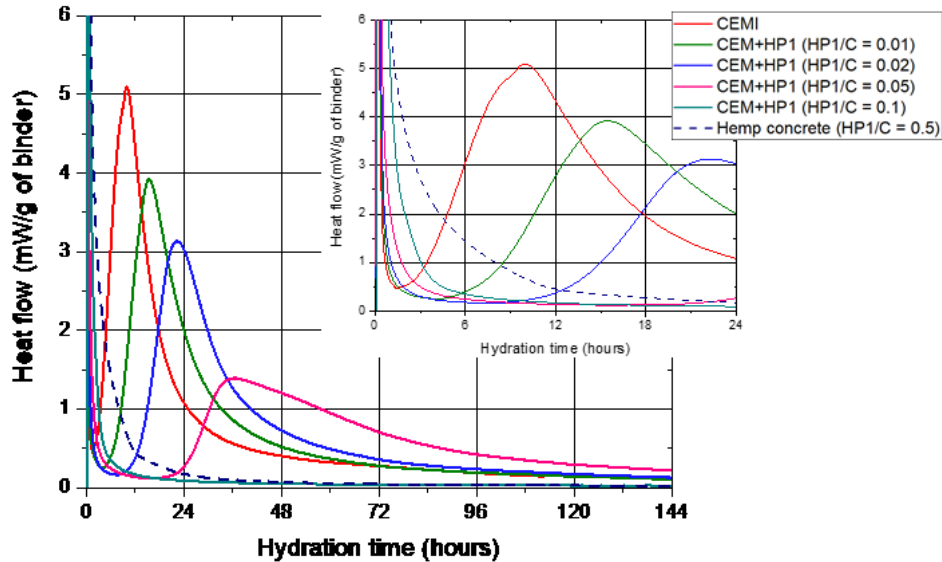


Figure 5. Heat flow for pastes of CEMI, CEMI mixed with hemp shiv powder and hemp concrete

For cement paste, the first reactions occur within the first few minutes of mixing – i.e. before the stabilisation of the heat flow. After 4 hours, the heat flow increases, which is connected to the hydration of the C_3S and the precipitation of the portlandite and the CSH phases:

The maximum of the main hydration peak is reached around 9 hours after mixing of the cement paste. The heat flow then decreases, corresponding to the deceleration of the reactions owing to the layer of hydrates formed on the surface of the anhydrated cement grains, which limits water diffusion. Thus, the hydration is slowed.

By increasing the quantity of shiv from a cement to hemp powder ratio HP/C of 0.01 to a HP/C of 0.05, the maximum of the main hydration peak shifts towards longer times – respectively 14.5 hours, 22 hours and 35 hours for HP/C ratios of 0.01, 0.02 and 0.05. The presence of shiv, therefore, causes a delay in the reactions of hydration of the C_3S in comparison to CEMI on its own. When HP/C is equal to 0.1 and for hemp concrete, no peak from the hydration of the C_3S can be seen for the first six days. In the case of cement paste containing a HP/C of 0.1, no signal variation is observed for 21 days. In certain studies where the hydration of the cement in the presence of a powerful delayer such as sucrose is characterised [10], an exothermic peak which corresponds to the hydration of C_3S is visible after 90 days monitoring.

The representation of the cumulated heat over time enables us to more closely observe the phenomena occurring over short spaces of time (Figure 6). For CEMI, the release of heat when the test tube contents are added is around 20J/g of cement. We then see a short period of dormancy, where the cumulated heat is constant. This phase corresponds to the dissolution of the cement grains in the mixing water. When the solution is saturated with ions, the precipitation of the portlandite and CSH, caused by the hydration of the C_3S , results in an increase of cumulated heat, before the reaction slows down.

Up to a value HP/C of 0.05, the duration of the dormancy phase increases in line with the quantity of shiv present. The cumulated heats converge on a value of around 350J/g of cement after 6 days.

The cumulated heats of the paste containing a HP/C of 0.1 and hemp concrete increase rapidly when the test tubes are inserted. This can be explained by the reactions of hydration of the aluminates.

Slowed by the presence of gypsum in the cements themselves, these reactions occur immediately after mixing when sugars are present in the cement paste. Indeed, the sugars catalyse reactions between gypsum and the aluminates [13,17]. Then, a dormancy phase can be seen, which lasts for the 21 days of measurement. After 6 days, the cumulated heat is much lower than that measured in cement pastes made with a HP/C varying between 0.01 and 0.05. From this, we can deduce that the rate of hydration is lower when the quantity of shiv is high.

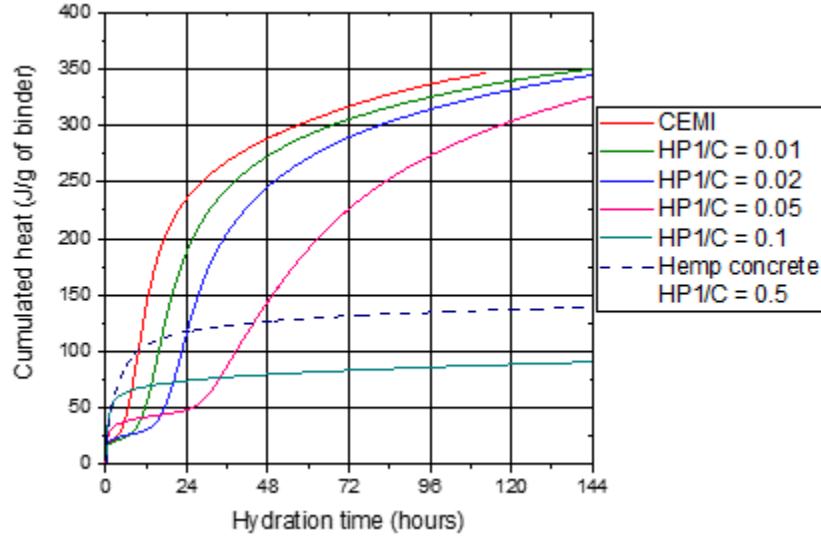


Figure 6. Cumulated heat for pastes of CEMI, CEMI with hemp powder and hemp concrete

In order to assess the compatibility between hemp particles and cement, the equation used by Pasca et al. [38] has been adapted. The CX' factor can be determined using the following equation:

$$CX' = \sqrt[3]{\frac{HR_{max} * HR_{3.5-96} * t'_{max}}{HR'_{max} * HR'_{3.5-96} * t_{max}}} * 100 \quad [4]$$

Where HR_{max} is the maximum heat flow of hemp-cement mixtures, $HR_{3.5-96}$ is the total heat released between 3.5 and 96 hours, t_{max} is the time to reach maximum heat flow. HR'_{max} , $HR'_{3.5-96}$ and t'_{max} are the values corresponding to the neat cement paste. The values obtained are reported in Table 4.

Table 4. Hemp powder – cement compatibility factor CX' for the different mixtures

| Sample | HP1/C=0.01 | HP1/C=0.02 | HP1/C=0.05 | HP2/C=0.02 | HP3/C=0.02 |
|--------------------------------------|------------|------------|------------|------------|------------|
| Hemp-cement compatibility factor CX' | 78 | 63 | 38 | 74 | 77 |

Three groups can be defined to class the hemp-cement compatibility: incompatibility if $CX' < 40$, moderate compatibility for CX' between 40 and 80 and compatibility for CX' values higher than 80 [38]. In the case of HP1 powder, the components are fairly compatible for HP/C ratio lower than 2%. For higher HP/C values, they are incompatible.

3.1.2. Effect of type of shiv

To study the influence of the nature of the shiv used on the hydration of CEM I cement, isothermal calorimetry measurements were taken on cement pastes with a HP/C value of 0.02 with the three types of shiv. This quantity of hemp powder does not correspond to that of hemp concretes and the particle size is smaller, but these conditions facilitate the homogenisation of the cement pastes necessary for calorimetry measurements and the comparison of the different types of shiv.

The results obtained are presented in Figure 7. The curves illustrating the heat flow over time recorded, for all samples, show the peak corresponding to the hydration of C_3S , where the maximum is situated at 22 hours, 15 hours and 16.5 hours, for cement pastes containing HP1, HP2 and HP3 respectively, whereas it is at 9 hours for cement on its own.

Isothermal calorimetry confirms that HS1 causes a greater modification in the binder hydration than do HS2 and HS3. This accords with the previous studies conducted with the three types of shiv [2,35], in which the mechanical strengths of the hemp concretes were found to be very different depending on the type of shiv used.

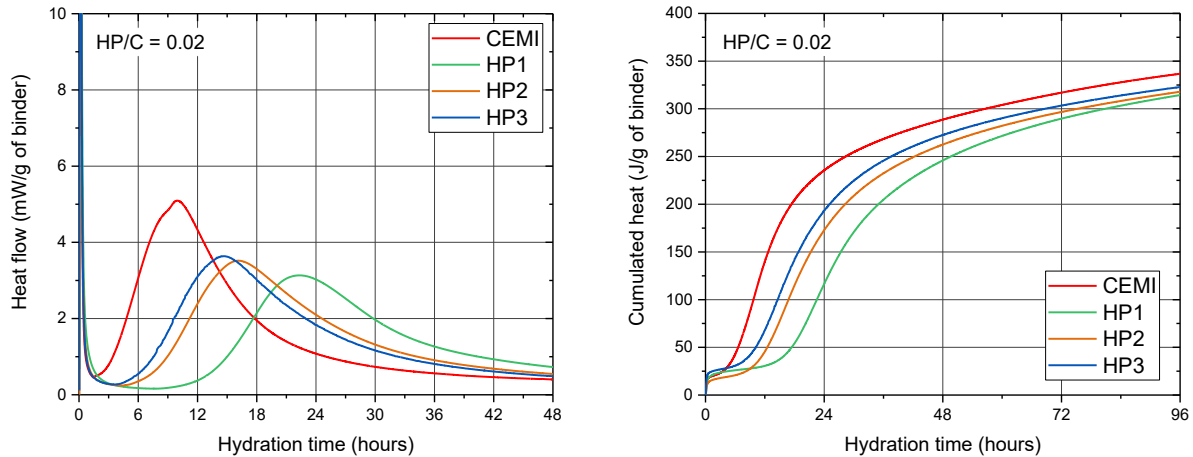


Figure 7. (a) Heat flow and (b) cumulated heat for pastes of CEMI, CEMI with HP1, HP2 and HP3 ($HP/C = 0.02$)

On the basis of these data, the CX' factors are determined (Table 4). The values of CX' confirm that HP1 is the less compatible hemp with CEMI. The values obtained for HP2 and HP3 are similar. They are in the orders of magnitude also measured for cement-wood mixtures [39].

In order to better understand these results, an analysis of the extractives from the shives – and in particular the sugars, which are liable to influence the setting of the hydraulic binders – is conducted in the next part of this study. The first step is to define the optimal conditions for extraction of the free compounds present in the shives.

3.2. Optimisation of extraction conditions

To quantify the amount of extractives and sugars present in the different shives, it is necessary to define the extraction conditions. In this section, we describe how we optimised these conditions in order to extract the maximum amount of reducing sugars in solution, whilst sticking as closely as possible to the mixing conditions. All tests are conducted on HS1 aggregates. Based on the protocols used in the existing body of literature (Table 1), various parameters influencing the extraction of molecules in solution are studied, such as the immersion time, the mass ratio of water to shiv, or the type of alkali used to reproduce the basic medium of a cement.

3.2.1. Immersion time

To evaluate the quantity of extractives as a function of immersion time, HS1 shiv is immersed in distilled water for 30 minutes, 4 hours, 24 hours and 48 hours with a W/HS ratio of 30. The quantity of reducing sugars extracted in these different time periods is presented in Figure 8-a. We observe that the quantity of molecules extracted varies as a function of the immersion time and reaches a maximum value at an immersion time of four hours. The decrease in the quantity of sugars after 4 hours is attributable to the fact that the sugars are consumed by micro-organisms, which have already been found to be present by previous studies [7]. In addition, the pH of the solution changes from 6.5 to 5 after 40 days' immersion. This decrease in pH is linked to the formation of acids due to the action of the micro-organisms, which hydrolyse the polysaccharides after having consumed all the free sugars in solution in order to continue to grow. This result was also observed in another study [7]. Dosage of the real quantity of sugars extractible from the shiv, therefore, requires us to reduce the immersion time as much as possible to avoid their being consumed by the micro-organisms.

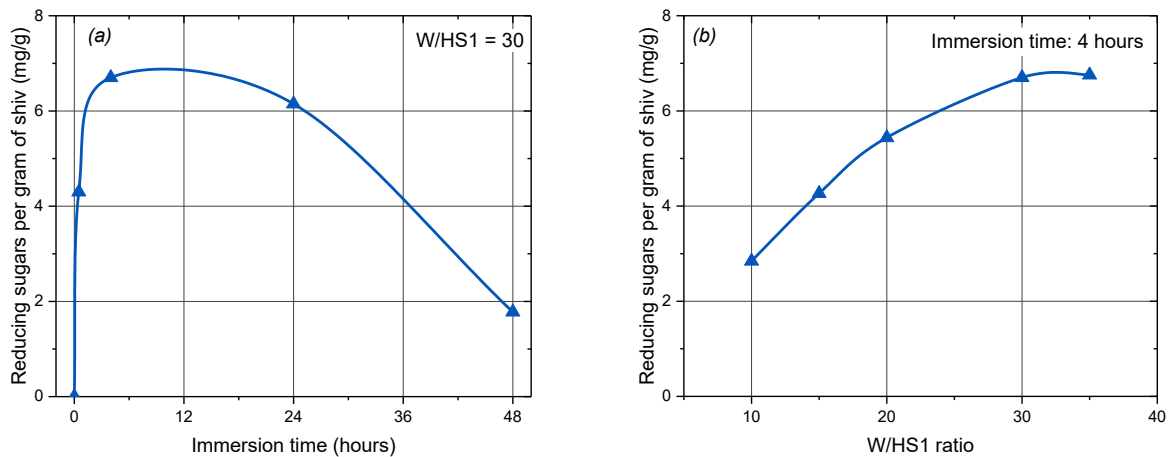


Figure 8. Amount of reducing sugars extracted from HS1 in water as function of (a) immersion time (for W/HS ratio of 30) and (b) W/HS ratio (after 4 hours of immersion)

3.2.2. Influence of the water-to-shiv ratio

To determine the water-to-shiv ratio, it is difficult to achieve conditions close to those in which a hemp concrete is mixed. Indeed, with a water/hemp shiv (W/HS) ratio of 2, and water absorption by the aggregates which reaches over 200% in the space of a few minutes, it is impossible to collect an extraction solution.

Thus, the minimum W/HS necessary in order to obtain the extraction solution is 10. The quantity of reducing sugars extracted is determined after 4 hours of extraction. The influence of the quantity of water is assessed by dosing the extracted sugars into solutions with W/HS ratios of between 10 and 35 (Figure 8-b). The quantity of reducing sugars increases as a function of W/HS, up to a maximum value when W/HS = 30. Beyond that point, the maximum quantity of extractives has been reached. It is therefore necessary to choose a high W/HS in order to extract the maximum amount of sugars. Indeed, the steeper the concentration gradient, the more the molecules diffuse from the more concentrated environment to the less concentrated one.

3.2.3. Influence of alkali for extractions in basic environments

In order to replicate the alkalinity of cement, extractions in a basic environment can be performed with solutions of soda NaOH, lime Ca(OH)₂ or a suspension of cement [11,19,40]. To monitor the type and quantity of alkaline elements, we chose to immerse the shiv samples in lime water Ca(OH)₂ (1 mol.L⁻¹) and in a solution of soda NaOH (2 mol.L⁻¹). After dosage of the reducing sugars, we observe that, in comparison to extraction in water (6.7 ± 0.4 mg.g⁻¹ of shiv), the quantity of sugars dosed is higher with the extraction in soda solution (7.7 ± 0.7 mg.g⁻¹ of shiv), whereas it is lower in the presence of lime (4.2 ± 0.1 mg.g⁻¹ of shiv). However, according to the literature, gas-phase chromatography dosages show that a larger quantity of molecules is extracted in a basic medium – notably more saccharides are extracted – whatever the alkaline agent used (extraction in NaOH and Ca(OH)₂ for Sedan [7]). Whilst the results obtained for the extraction with NaOH show the same trend, the lower quantity of reducing sugars dosed in lime water is due to the presence of calcium ions. As is the case with cement, the calcium ions are capable of forming complexes with the sugars. When this happens, a portion of the sugars is no longer available to react with DNS, and the quantity of reducing sugars is therefore underestimated. Thus, a soda solution is chosen in order to be able to dose the extracted sugars in solution with DNS.

3.2.4. Determination of the optimal extraction protocol to quantify the leachates

With the aim of quantifying the level of extractive molecules and level of saccharides extracted from different shives, the extraction protocol defined on the basis of the above results, and described below, is used for the rest of this study.

The extractions are carried out with hemp powder (HP) in order to optimise the quantity of extractives over a short period of immersion. Compared to raw shiv, immersing a hemp powder increases the exchange surface between the solid and the liquid. The use of a powder also improves the representativeness of the sample. We analyse 4g of powder from the grinding and homogenisation of 100g of shiv. In addition, the measured quantities of sugars extracted from hemp powder can be used to illuminate a discussion of the results of isothermal calorimetry obtained on cement pastes containing hemp powder (Figure 7).

A W/HP of 100 is chosen. This high value means we can optimise the extraction time at an hour. Indeed, with this ratio, the quantity of compounds extracted is 7.8 mg per gram of hemp powder, whereas after 4 hours of immersion of aggregates with a W/HS of 30, the quantity of extractives is 6.7 mg/g (Figure 8).

The extractions are carried out in distilled water at 20°C and 100°C, to assess the influence of temperature, and replicate the same conditions as those used in other studies (Table 1), and in a solution of NaOH at a concentration of 2 mol.L⁻¹ at 20°C to replicate the basic environment of a vegetal concrete.

In summary, the comparison of the extractives gained from the different kinds of shiv is based on extraction of hemp powder, in water at 20°C and at 100°C, and in a 2 mol.L⁻¹ soda solution at 20°C, for one hour, with a W/HP of 100.

3.3. Quantification of extractives from shives

The extraction protocol defined in the previous section is used to compare the different types of shiv in the study. The mass percentage of the compounds extracted from the three types of shiv is determined to begin with. As sugars are often considered to be the compounds which are responsible for significant hydration delays, the content level of reducing sugars and the total quantity of sugars are then determined. The overall methodology of the study is illustrated in Figure 9. These results are then correlated with the isothermal calorimetry analyses presented in Figure 7.

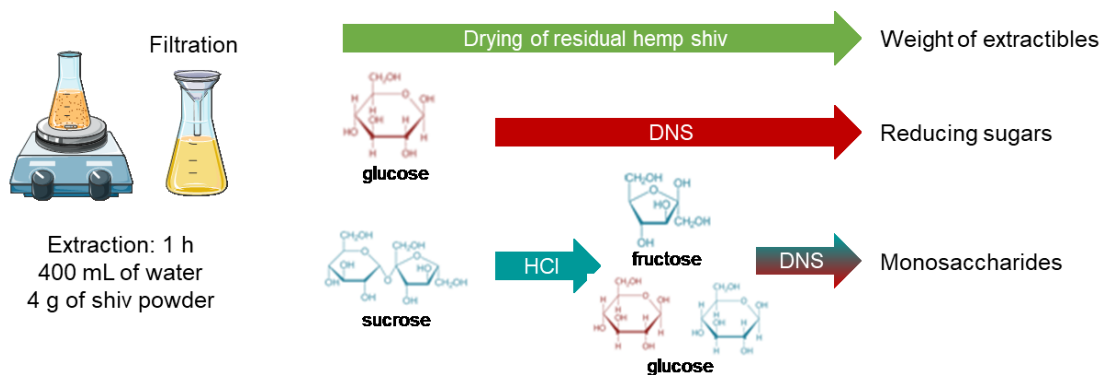


Figure 9. Analyses of solutions containing extractives compounds from shiv: weight of extractive, amount of reducing sugars, total amount of monosaccharides

3.3.1. Extractive molecule content

The level of extractives is calculated by finding the difference in mass of powder of dry hemp material before and after immersion. To do this, the extraction solution is filtered using a cellulose filter paper, with 8-12 μ m pores; then the residue is dried at 105°C until it reaches a constant mass, and then weighed. The levels of extractives measured in the three different extraction conditions (water at 20°C, water at 100°C and basic solution at 20°C) are shown in Figure 10. Whatever the type of shiv used, the level of extractives in water is greater at 100°C than at 20°C, and higher still with extraction in a basic solution. By comparing the different hemp shives to one another, we find small differences in water at 20°C, whereas more significant differences are observed in water at 100°C and in the basic environment. In any case, the highest quantity of extractives is measured on HS1; the hemp shiv containing least extractives is HS3.

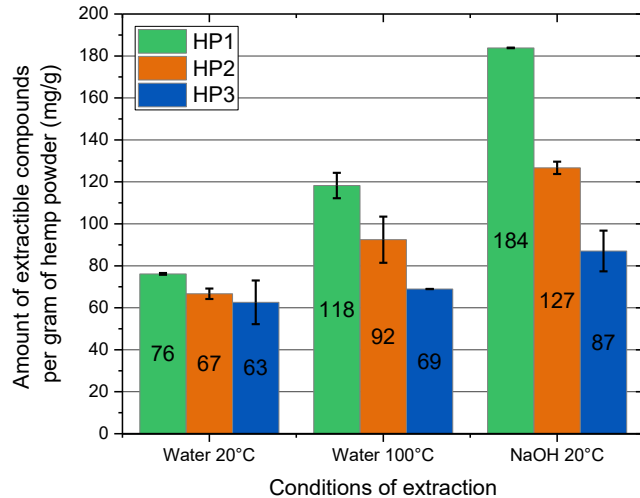


Figure 10. Content of extractive molecules for HP1, HP2 and HP3 after 1 hour in water at 20°C, water at 100°C and in soda solution at 20°C

The values obtained after extraction in water at 20°C are compared with the values obtained by Diquélou [3], for which the extraction is carried out in water over a period of 24 hours. For the three types of hemp shiv analysed in his study, one of which causes poor mechanical properties in mortars using the extraction solution as mixing water, the content of extractive molecules is between 32 and 44 mg/g of hemp. These levels are almost twice as low as those found after extraction in water for 1 hour in our study. Aside from the differences between the types of shiv, this can be attributed to a much lower W/HS ratio (10) and the use of aggregates. At 100°C, the amounts of extractives are in the range of those obtained by Bourdot et al. [41].

3.3.2. Dosages of saccharides

As saccharides have been identified, in the earlier literature, as the main culprits delaying cement hydration, the quantity of sugars extracted in the different solutions was evaluated. The levels of reducing sugars extracted, determined by UV spectrometry after reaction with DNS, are illustrated in Figure 11. For the same type of hemp shiv, the quantity of extracted reducing sugars increases with temperature and with the basicity of the solution. These results obey the same trend as do the values of the total quantities of extractives. By comparing the levels of reducing sugars in the different types of hemp, we observe that HP1 filtrate contains significantly more reducing sugars than those of HP2 and HP3, whatever extraction solution is used.

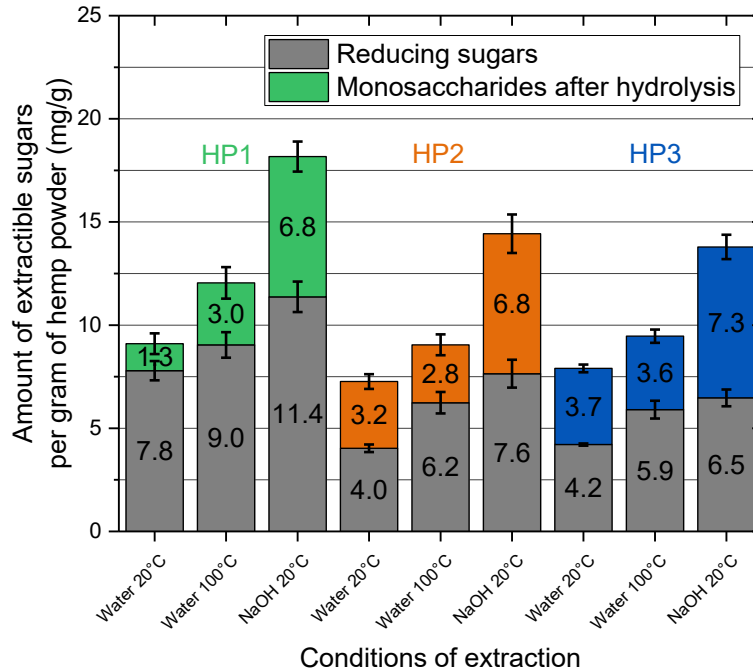


Figure 11. Content of reducing sugars and of monosaccharides after hydrolysis per gram of shiv in extractive solution after 1 hours in water at 20°C, water at 100°C and in soda solution at 20°C

The ANOVA test has been used to assess if the differences of extractive contents are significantly different depending on the extraction conditions and the type of hemp shiv. The results are presented in Table 5 for the influence of temperature and extraction solution for a single type of shiv. Table 6 contains similar results about the differences between the different hemp shiv. If the value of the p factor is lower than 0.05, the differences are statistically significant.

First, the comparison of the extraction conditions for HP1, HP2 and HP3 (Table 5) shows that the differences observed are always significant as all p values are lower than 0.05. This conclusion is true both for reducing sugars and for monosaccharides. The higher value of p is 0.04 for the comparison of reducing sugars after extraction of HP3 in water at 100°C and in NaOH solution.

Table 5. ANOVA results for reducing sugars (1) and monosaccharides after hydrolysis (2) content determination: influence of extraction solution

| | HP1 | | | HP2 | | | HP3 | | |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| | Water 20°C | Water 20°C | Water 100°C | Water 20°C | Water 20°C | Water 100°C | Water 20°C | Water 20°C | Water 100°C |
| | Water 100°C | NaOH 20°C | NaOH 20°C | Water 100°C | NaOH 20°C | NaOH 20°C | Water 100°C | NaOH 20°C | NaOH 20°C |
| (1) | 2.7×10^{-3} | 1.5×10^{-6} | 1.4×10^{-4} | 1.9×10^{-6} | 1.7×10^{-7} | 2.3×10^{-3} | 2.5×10^{-6} | 9.1×10^{-8} | 4.0×10^{-2} |
| (2) | 1.3×10^{-5} | 2×10^{-10} | 5.8×10^{-8} | 3.5×10^{-5} | 7.7×10^{-9} | 2.1×10^{-7} | 1.2×10^{-6} | 4×10^{-10} | 2.1×10^{-8} |

Moreover, for extractions in water at 20°C, the differences measured for the three types of shiv are all significant. In water at 100°C and in NaOH solution, the differences obtained for HP2 and HP3 are not significant as the values of p are higher than 0.12.

Indeed, we can conclude that the leachates obtained from HP1 contain significantly higher amounts of reducing sugars and monosaccharides than HP2 and HP3 extractives, whatever the extraction conditions. After extraction in water at 20°C, the differences between HP2 and HP3 are less striking, but HP2 extractives contain significantly more sugars and monosaccharides in water at 20°C. The amount of reducing sugars in HP2 in the NaOH solution is also significantly higher than in HP3. On the other hand, after extraction in water at 100°C, equivalent quantities of reducing sugars and monosaccharides are dosed for both these types of shiv, because the calculated values of p are respectively 0.25 and 0.12.

Table 6. ANOVA results for reducing sugars (1) and monosaccharides after hydrolysis (2) content determination: influence of the nature of hemp shiv

| | Water 20°C | | | Water 100°C | | | NaOH 20°C | | |
|-----|----------------------|----------------------|----------------------|----------------------|----------------------|------|----------------------|----------------------|----------------------|
| | HP1 | HP1 | HP2 | HP1 | HP1 | HP2 | HP1 | HP1 | HP2 |
| | HP2 | HP3 | HP3 | HP2 | HP3 | HP3 | HP2 | HP3 | HP3 |
| (1) | 4.9×10^{-9} | 4.2×10^{-9} | 3.8×10^{-2} | 6.9×10^{-6} | 1.3×10^{-6} | 0.25 | 3.6×10^{-6} | 5.8×10^{-8} | 4.5×10^{-3} |
| (2) | 2.7×10^{-5} | 2.8×10^{-4} | 3.1×10^{-3} | 1.1×10^{-5} | 1.8×10^{-5} | 0.12 | 1.6×10^{-5} | 4.5×10^{-7} | 0.19 |

Whilst reducing sugars slow the reactions of hydration of the binders, Kochova *et al.* [23] showed that oligosaccharides, such as sucrose, have an even more significant delaying effect on the hydration. In order to compare the influence of the compounds extracted from the three types of shiv, it is important to know the total quantity of sugars extracted. To use UV spectrometry dosage after reduction of the DNS, the oligosaccharides and polysaccharides must be transformed into reducing monosaccharides. For that purpose, acid hydrolysis is carried out. The difference between the content of reducing sugars initially extracted and that obtained after total hydrolysis can be used to estimate the quantity of non-reducing sugars present in the solution. The results are presented in Figure 11.

For all types of shiv and all extraction solutions, the total quantity of monosaccharides is higher than the quantity of reducing sugars initially dosed. The hydrolysis demonstrates the presence of oligosaccharides in the hemp shiv extraction solutions.

Regardless of the extraction conditions, HP1 is the shiv which is richest in monosaccharides, both initially and in total. During extraction at 20°C in water, the low quantity of reducing sugars formed after acid hydrolysis demonstrates a predominance of reducing sugars extracted in relation to the oligosaccharides. However, in the same conditions, HP2 and HP3 contain more non-reducing sugars than HP1. In the case of extractions in water at 100°C and in a basic solution, the same quantity of monosaccharides stemming from the hydrolysis of oligosaccharides or polysaccharides is dosed whatever the type of hemp shiv.

Based on the ANOVA results reported in Table 5 and Table 6, we can conclude that, whatever the extraction conditions, HP1 has a significantly higher total sugar content than HP2 and HP3, notably for reducing sugars.

By comparing our results by immersion of the hemp powders in water at 20°C to those obtained by Diquélou [3], we dosed larger quantities of monosaccharides (respectively between 7 and 9 mg/g of hemp and between 5 and 7 mg/g of hemp with W/HS=10 and 24 hours immersion). The immersion duration of 24 hours enabled the microorganisms to consume the sugars in solution.

3.4. Influence of saccharides on the cement hydration

To account for the differences in cement hydration delays observed as a function of the type of hemp shiv added, we hypothesised that the delays were due to the quantity of extractives present in the shives, and that the compounds which had the greatest impact were the sugars extracted from the hemp. To verify these hypotheses, isothermal calorimetry tests were conducted on a cement paste, to which we added quantities of standard sugars identical to those measured in the soda solutions in section 3.3. Indeed, these extraction conditions are as close as possible to those obtained in the presence of cement.

The effect of reducing sugars is simulated by glucose (Figure 11), and the effect of non-reducing polysaccharides dosed after hydrolysis is simulated by sucrose, whose significant delaying capacity has been observed in previous studies [9]. Although not all the non-reducing sugars extracted from the hemp material were sucrose, by adding it to the cement, we are able to maximise the visible effect of sugars on the setting. The sucrose molecule is made up of a molecule of glucose and a molecule of fructose, so after hydrolysis, the dosage of two monosaccharides into the hydrolysed solution is equivalent to a molecule of sucrose in the extractives solution. In reference to the mass concentrations of sugars dosed into the hemp extract solutions (Figure 11), for a cement paste made up with a HP/C of 0.02, 0.6mg of glucose and 0.2mg of sucrose are added to the mixing water to simulate the effect of the sugars extracted from HP1, while 0.03mg of glucose and 0.2mg of sucrose are added to simulate the sugars extracted from HP3. The isothermal calorimetry results obtained for the different cement pastes are presented in Figure 12.

Compared with the hydration of the cement CEM I alone, the hydration of the cement pastes containing the standard sugars is delayed by 3 hours when we add the solution equivalent to HP1, and by 2 hours when we add the solution equivalent to HP3. The delays in hydration observed here confirm the influence of the quantity of sugars on the setting of the binder, because the higher the quantity of sugars, the greater is the delay.

If we compare the hydration delays obtained for these cement pastes with added standard sugars to the delays measured on the cement pastes containing hemp powders, we can see that, in spite of the addition of quantities of sugars equivalent to those extracted from the vegetal powders and the use of sucrose, which significantly delays setting, the hydration of the cements containing glucose and sucrose is quicker than that

of the cements containing hemp powders. For HP3, the hydration peaks are at 11.5 hours in the presence of standard sugars and 14.5 hours in the presence of hemp powder HP3, as compared to 9 hours for pure cement paste. Thus, we can say that sugars are responsible for around half the delay in setting which is observed in the presence of powder. It is notable that the particularly significant hydration delay with cement paste containing HP1, in comparison to equivalent cement paste with a 10-hour difference between the maxima of the two hydration peaks. The shifts in setting time observed between the cement pastes containing standard sugars and the cement pastes containing aggregate powders show that the sugars are not the only compounds extracted from the vegetal materials which are responsible for the delays in setting. Other molecules present in the hemp also influence the hydration of the cement.

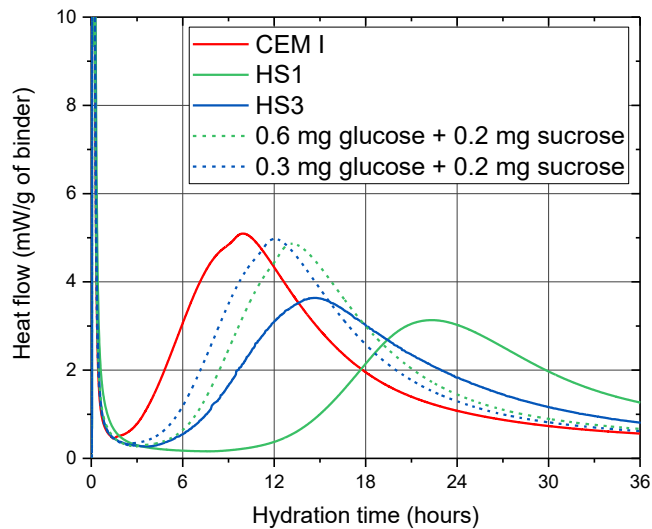


Figure 12. Heat flow for pastes of CEM I, CEM I with HP1 and HP3 (HP/C=0.02) and with equivalent in sugars solutions with glucose and sucrose

3.5. Other extractive compounds

For the three types of hemp shiv studied, regardless of the extraction solution, we observe that the total quantity of sugars extracted varies between 7 and 18 mg/g of hemp shiv (Figure 11).

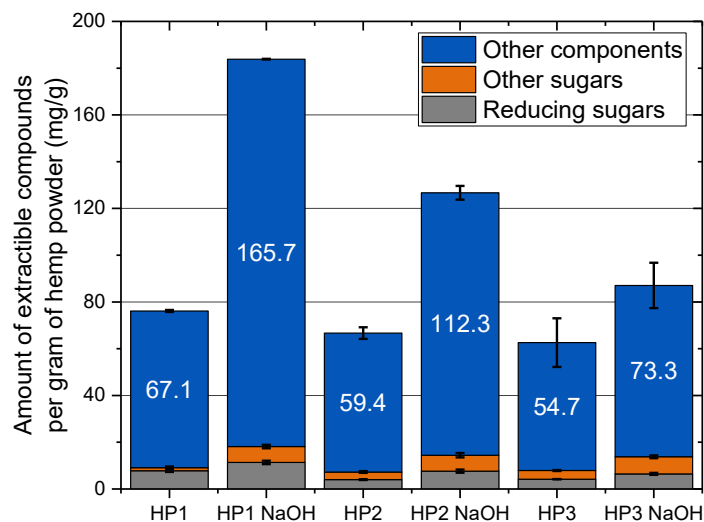


Figure 13. Composition of extractibles

Comparing it with the total quantity of extractives presented in Figure 10, this quantity of sugars corresponds to around 10% of the total extractives (Figure 13). A loss on ignition at 500°C for two hours on these extractives shows that they contain around 15% ash. Therefore, a large proportion of the compounds remain unidentified as in other studies [3]. These components can include some carbohydrates, like starches, lipids (oils, waxes...), proteins, hydrocarbons like terpenes or phenolic compounds.

In addition, when we look at the extraction solutions for the different hemp shives, e.g. in water at 20°C (Figure 14), the solution of HS1 extractives shows a more intense colouration than the extraction solutions for HS2 and HS3. The sugars cannot be responsible for this colouration, because they do not contain electron doublets which are sufficiently delocalised to absorb in the domain of visible light.

The colour of the three extractive solutions was determined by spectrophotometry, and the chromatic parameters are presented in Table 7. All the chromatic parameters of the three solutions are constant, except the value of b^* , which increases for the solution of HP1 extractives, confirmed by the stronger yellow colour observed for this solution.

Table 7. Chromatic characterisation of extractive solutions

| Solution | L* | a* | b* |
|----------|------------|--------------|-------------|
| HP1 | 32.0 ± 0.1 | -0.43 ± 0.01 | 3.20 ± 0.02 |
| HP2 | 32.4 ± 0.1 | -0.37 ± 0.01 | 1.90 ± 0.02 |
| HP3 | 32.4 ± 0.1 | -0.34 ± 0.01 | 1.64 ± 0.02 |

By analysing the same solutions by UV-visible spectrometry (Figure 14), we observe that the spectra of the extraction solutions from all three hemp shives have the same shape. Only the absorbance of the extraction solution is higher for HS1 across the whole range of the spectrum. We can conclude from this that the compounds extracted from the three samples are of the same nature, and the concentration of extracted compounds in the HS1 immersion solution is higher. The higher absorbance between 400 and 500 nm of the HS1 extraction solution in comparison to HS2 and HS3 leads to the more intense yellow colouring of HS1.

In the spectral zone corresponding to UV light absorption (190-400nm), an absorption band at 280 nm shows the presence of extracted phenolic compounds [3], associated, for example, with lignin, with flavonoids, coumarins or tannins [42–44]. Like sugars, these phenolic compounds can influence the hydration of the cement [3,45]. However, it is not possible, by UV-Visible spectrometry, to identify the exact nature of these compounds.

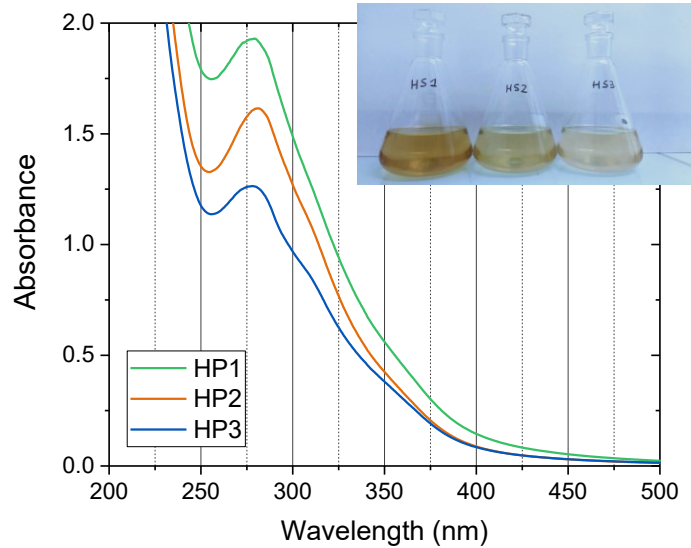


Figure 14. Pictures of extractive solutions in water at 20°C for HS1, HS2 and HS3, and UV-Visible spectra for the extractive solutions in water at 20°C

4. CONCLUSION

Certain concretes made up with vegetal particles and mineral binders exhibit unsatisfactory mechanical strength, due to incomplete hydration of the hydraulic binder. This phenomenon can be put down to interactions between the free compounds present in the plant material and the binders, either delaying or totally preventing the mixture from setting. The objective of the current study is fix a methodology to extract and analyse the vegetal components which are responsible for these altered setting behaviours.

First, three types of hemp shiv were used to characterise their influence on the cement hydration, by isothermal calorimetry. These analyses showed that when we increase the quantity of hemp powder added (HP1/C = 0.01, 0.05 and 0.1), the peak for hydration of the C₃S in the binder shifts towards later times. When the cement paste contains a HP1/C of 0.1, the peak is no longer visible, and only the hydration of the aluminates is observed over short time periods. By comparing the influence of the three types of hemp shiv, it is possible to demonstrate that HS1 is indeed the product which most delays the setting.

To draw the link between the delay in setting and the extractive compounds from the hemp shives, an extraction protocol was developed by fixing temperature and pH of the solution, extraction time and solution-

to-shiv ratio. Using this method, it has been shown that HS1 contains more extractives (than the other two shives. In addition, the extractives from this shiv contain the largest quantity of sugars.

In reference to the quantities of sugars measured in the extraction solutions from the different shives, and formulating new cement pastes containing the same cement/sugar ratio using standard sugars, new measurements by isothermal calorimetry were taken to study the setting of the cement. In this case, we also observe a shift in setting time toward longer times, as happens in cement pastes containing vegetal powders. This shift is also more marked for the paste containing the same quantity of sugars as HS1. However, this shift is lesser than that which is measured with the hemp powders, which shows that sugars are not the only compounds which are responsible for the delays in setting. Indeed, they represent around 10% of the total mass of extractives. Analysis of the solutions by UV-visible spectroscopy showed that these phenolic compounds are also present. These compounds, such as lignin derivatives, can also impact the setting of binders.

Thus, the prospects for these studies are to more finely characterise the chemical composition of the vegetal materials, and in particular, their extractive compounds, to identify those which play a part in the setting of cements. This will help define criteria to select vegetal materials that are compatible with the hydraulic binders in order to be able to guarantee the performances of plant-based concretes used in construction.

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