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## Densification of non-radioactive porous siliceous particles loaded with cesium potassium copper hexacyanoferrate by spark plasma sintering

Nicolas Massoni, Sophie Le Gallet, Lionel Campayo, Robert J. Koch, Scott T. Misture, Agnès Grandjean, Frédéric Bernard

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1 630 kg/m<sup>3</sup>. The same range of values was measured by [11][12][13] for hemp composites made with  
2 lime and metakaolin and by [14] for maize and sunflower stalk based composites. In all these cases,  
3 the sample densities were ranging between 500 and 600 kg/m<sup>3</sup>. [15] studied the impact on thermal  
4 conductivity of the composition of two corn stalk and magnesium phosphate cement composites.  
5 They noticed that samples with a higher corn stalk content had a lower thermal conductivity. [16]  
6 found this same result on hemp composites, detailing however that the relation between the  
7 amount of hemp shiv and thermal conductivity is not linear. Furthermore, [15] observed that for a  
8 same corn stalk content, large stalks presented a lower thermal conductivity than small ones, which  
9 was explained by a lower density and a higher porosity. Many parameters have an impact on thermal  
10 properties of bio-based composites such as water content, density and the formulation. It has been  
11 highlighted in the past that density has the biggest influence because a larger air volume in the  
12 material results in a low thermal conductivity [10][15][16].

13 In addition to their promising thermal performances, bio-based composites are known to exhibit  
14 good to excellent hygroscopic potential [9][17]. It traduces their ability to be used as a passive  
15 humidity regulation system thanks to their high capacity of adsorption (and desorption) of water  
16 vapor molecules from (to) the surrounding atmosphere. Due to the latent heat of adsorption and  
17 desorption processes, these materials might also have the potential to be used as passive  
18 temperature regulation system [11], even if the real impact of this effect on building energy  
19 consumption still needs to be better assessed.

20 Other important assets of bio-based composites are their high vapor permeancy and their light  
21 weight, which make them suitable to be used to rehabilitate the national heritage, typically built in  
22 stone, adobe, rammed-earth, etc. [14][16][18]. Indeed, they do not constrict vapor exchanges  
23 between walls and their environment and they do not overcharge the existing structure.

24 On the other side, bio-based composites do not have mechanical performances as good as classic  
25 building materials [10][17][19][20]. That is why they are most of the time rather used as filling and/or  
26 insulation materials, for which a high loading capacity is not mandatory. Anyway, it is commonly  
27 agreed that compressive strength and deformation modulus are good indicators of binder-aggregate  
28 compatibility. The several studies led on these parameters lead to the conclusion that there is no  
29 good or bad aggregate or binder, but good or bad combinations of them [21]. For example, [22] show  
30 that a first composite made of corn stalk and ordinary Portland cement threw a 1.5 MPa compressive  
31 strength value, while a second composite made of corn stalk and magnesium phosphate cement  
32 presented a compressive strength more than two times higher (3.83 MPa). Another sound example is  
33 given by [14]. In this study compressive strength at 60 days was measured on composites made of  
34 lime and sunflower (LS) with a density of 540 kg/m<sup>3</sup>, metakaolin and sunflower (MS) with a density of  
35 510 kg/m<sup>3</sup> and finally, metakaolin and maize bark (MM) with a density of 530 kg/m<sup>3</sup>. These  
36 composites developed a mechanical resistance of 0.21 MPa, 0.34 MPa and over 0.35 MPa  
37 respectively.

38 Most of the time, the aggregate used in the formulation of bio-based composites is the hemp shiv. In  
39 France, for example, the soles professional rules that exist for this kind of materials are dedicated to  
40 hemp composite [5]. Nonetheless, it is essential to give alternatives to hemp [8][14][23] so as to have  
41 access to varied resources regarding geographical origin with the goal of reducing transport carbon  
42 print. For that purpose, a large variety of aggregates can be found, such as flax, straw, wood, coconut,  
43 miscanthus, corn or sunflower, etc. [18][19][24][25][26].

1 Based on this observation, this paper focuses on sunflower and maize pith, which, like hemp shiv, are  
2 considered as agricultural by-products. Both sunflower and maize grow in most European countries  
3 and they already have been studied by some authors [14][23][27][28][29][30][31].

4 The binders used are lime based and contain cement and admixtures in certain cases. The goal is to  
5 determine the impact of the use of pith instead of hemp on the performance of the composite. For  
6 that purpose, two ranges of densities (low densities around  $150 \text{ kg/m}^3$  and medium densities around  
7  $500 \text{ kg/m}^3$ ) and three binders are considered. Let us underline that it has already been determined in  
8 a previous paper [32] that the geographical origin of the sunflower and maize piths does not impact  
9 the performance of the composites. Their performance was assessed through their mechanical,  
10 thermal, sorption and vapor transport properties. Thermal conductivity was studied through two  
11 different methods, the hot wire method and a novel device conceived for more accurate  
12 measurement. Finally, the hygrothermal potentials of the composites were evaluated through the  
13 moisture buffering test, and the consistency between results was analyzed using the MBV analytical  
14 expression provided by [33].

15 Since hemp dominates the bio-based construction field and the regulations about vegetal composites  
16 are based on it, the aim of this paper is to determine whether maize and sunflower pith aggregates  
17 can be used at the same level, not to replace hemp but to provide more choice. In addition, the  
18 impact of the aggregate, of the binder and of the interaction of both will be assessed. We will as well  
19 determine whether used binders, which have originally been conceived for hemp shiv, are  
20 appropriate for maize and sunflower pith or not.

## 21 2. Materials

### 22 2.1 Plant aggregates

23 As part of this experimental campaign, three types of plant aggregates were studied: hemp shiv (H),  
24 sunflower pith (S) and maize pith (M) (cf. **Fig 1**). The hemp shiv aggregates were received from an  
25 agriculture cooperative based in the north of France. Loose hemp shiv aggregates had a density of  
26  $100 \text{ kg/m}^3$ , an average width of 4.1 mm and an average length of 7.6 mm. The sunflower pith comes  
27 from an agriculture cooperative based in the south-east of France. Loose density of this sunflower  
28 pith was around  $14 \text{ kg/m}^3$ , an average diameter of the aggregates was around 4.2 mm. The maize  
29 pith comes from an agriculture cooperative based in west France with a more oceanic climate. The  
30 maize pith aggregates had a loose density of  $18 \text{ kg/m}^3$ , an average width of 2.2 mm and an average  
31 length of 9.6 mm. The density of the aggregates has been determined following [34]'s protocol,  
32 whereas the average aggregate dimensions have been calculated through a sifting granulometric  
33 curve for pith and through a 2D image granulometric analysis developed by [35] for hemp shiv.



34 **Fig. 1.** Aggregates used in this study (A) Hemp shiv, (B) Sunflower pith and (C) Maize pith

1 **2.2 Binders**

2 Three different types of binders were used in this study. The first one named C1 is a calcic lime based  
 3 binder. The second one named C2, is a formulated lime which is composed of hydraulic lime,  
 4 calcareous charges, hydrophobic and rheological admixtures. The last one, named HB, is a cement  
 5 and lime mixture with further additives, this formulation was developed by an industrial partner and  
 6 whose exact composition is not available.

7 **2.3 Bio-based composites**

8 The samples were manufactured in the same conditions (50%RH and 23°C) and the main proportion  
 9 of the mixtures of all kinds of formulations used are summarized in **Table 1**. Samples were sprayed in  
 10 cylindrical formworks with a 16 cm diameter and a 32 cm height in a single layer except for C2-H\*,  
 11 which was manufactured in 6 layers of about 5 cm each. Each layer was compacted at 0.05 MPa  
 12 following [5]. It is recalled that H, S and M are the aggregates explained in §2.1, more specifically  
 13 hemp shiv, sunflower pith and maize pith respectively, while C1, C2 and HB are the binders explained  
 14 in §2.2. C2-H\* corresponds to a formulation that was compacted.

15  
16  
17 **Table 1** Summary of the formulation and mass ratio.

Type of binder	C1	C2				HB		
Type of aggregates	H	H	H*	S	H+S	H	S	M
Designation	C1-H	C2-H	C2-H*	C2-S	C2-H+S	HB-H	HB-S	HB-M
Hemp shiv/binder** (-)	0.33	0.33	0.33	0	0.17	0.33	0	0
Pith/binder** (-)	0	0	0	0.10	0.06	0	0.20	0.16
Water/binder** (-)	0.81	0.88	0.88	0.80	1.07	0.88	2.92	2.92
Mass proportion of hemp shiv (-)	0.15	0.15	0.15	0	0.07	0.15	0	0
Mass proportion of pith (-)	0	0	0	0.05	0.03	0	0.05	0.04

18 \* corresponds to a formulation which has been densified using a tamper tool.

19 \*\* correspond to mass ratio between constituents

20 A pycnometer was used in order to determine the physical properties such as the skeletal porosity,  
 21 dry and skeletal densities of the different formulations according to the standard NF EN 1097-7 2008.  
 22 Results are shown in the **Table 2**.

23 **Table 2** Summary of the physical characteristics.

Formula tion	C1-H	C2-H	C2-H*	C2-S	C2-H+S	HB-H	HB-S	HB-M
Porosity	0.76±0.0	0.79±0.0	0.70±0.0	0.77±0.0	0.70±0.0	0.78±0.0	0.94±0.0	0.92±0.0
	2	1	2	1	2	2	1	1
Dry density (kg/m <sup>3</sup> )	470 ±5	440 ±6	600 ±10	550 ±5	590 ±6	410 ±8	150 ±4	160 ±5