



HAL
open science

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

► To cite this version:

Nicolas Massoni, Sophie Le Gallet, Lionel Campayo, Robert J. Koch, Scott T. Misture, et al.. Densification of non-radioactive porous siliceous particles loaded with cesium potassium copper hexacyanoferrate by spark plasma sintering. *Journal of the European Ceramic Society*, 2021, 41, pp.1506 - 1513. 10.1016/j.jeurceramsoc.2020.10.024 . hal-03492742

HAL Id: hal-03492742

<https://hal.science/hal-03492742>

Submitted on 15 Dec 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

1 630 kg/m³. 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/m³. [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/m³, metakaolin and sunflower (MS) with a density of
35 510 kg/m³ and finally, metakaolin and maize bark (MM) with a density of 530 kg/m³. 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 kg/m^3 and medium densities around
7 500 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 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 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 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 ³)	470 ±5	440 ±6	600 ±10	550 ±5	590 ±6	410 ±8	150 ±4	160 ±5