INFLUENCE OF HEMP RETTING ON THE HYDRATION OF ORDINARY PORTLAND CEMENT (OPC) AND THE PROPERTIES OF HEMP-OPC CONCRETE

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Abstract

This work shows the influence of hemp retting on the hydration of Ordinary Portland Cement (OPC) and the properties of Hemp-OPC concrete. Hemp is a very efficient thermal insulating material (Lambda = 0.055 W/m.K.). Hemp is also a powerful retarder of OPC hydration. Less than 1 kg of unretted Hemp can block the hydration of 10 kg of OPC (CEM I) for a minimum period of 7 days. The soluble organics of Hemp are the main retarders of hydration. They contain mainly glucose, fructose, maltotetraose and maltotriose. Hemp retting reduces the clarity of Hemp. The yellow degree b* (measured by a DR LANGE colorimeter) decreases from 16.1 to 9.9 with the retting level. Hemp retting also reduces the soluble organic content of Hemp represented by TOC content from 3.76 to 2.4%. We observed a good correlation between the color degree (Yellow degree b*) and the soluble organics content of Hemp. On a composition of Hemp-OPC concrete (Wetting water/Hemp ratio = 3, Efficient water/OPC ratio = 0.35, Hemp/OPC ratio = 0.23) with different retting levels of Hemp (b* = 16.1 to 9.9), the density of dry concrete varies from 480 to 690 kg/m^3; the compressive strength at 7 days increases from 0.1 to 2.4 MPa and the Lambda increases from 0.1 to 0.175 W/m.K. We also observed a good correlation between the properties of concrete and the degree of hemp retting.

Keywords:

Hemp retting, Hemp Concrete, OPC Hydration, Bio-Based Insulating Material

1 INTRODUCTION

France is one of the great hemp producing countries, more than 10,000 ha of culture. For 1 ha of hemp cultivation, we obtain [Niyigena 2016]:

- 6 to 8 tons of dry straw
- 1.5 to 2 tons of long fibers
- 0.8 to 1 ton of seeds
- 4.5 to 6 tons of hemp aggregate.

Thanks to its capillary structure and its hydrophilic properties, hemp has a large capacity for liquid water absorption [Niyigena 2016]. Previous studies have shown that immersed in water hemp can reach a saturation mass of about 5 times their initial dry mass after 48 hours [Nguyen 2010]. The main use of the hemp is in industrial farms as litter.

Hemp is also a good thermal insulating material. Numerous previous studies have demonstrated the good insulating property of hemp concrete. The thermal conductivity of concrete is between 0.1 to 0.2 W/m.K according to the density [Collet-foucault 2004, Dinh 2014, Gourlay 2014]. However, the binders used are based on lime, hydraulic lime or lime-pozzolan association. With these binders, it takes several weeks or months of drying and carbonation to obtain solid concrete.

In this study, we investigate the impact of retting on the properties "Hemp-OPC" concrete with a setting time less than 24h.

2 MATERIALS AND METHODS

2.1 Materials

For this study, samples of hemp with different retting degrees were produced by the cooperatives in France and supplied by FRD (Fibres Recherche et Développement SAS, France). Calcium chloride has been used as accelerator of OPC hydration. The cement used is a CEM I 52.5 R from the factory Le Teil Lafargeholcim.

2.2 Methods

- **Measurement of the water content of hemp**

The water content of hemp is measured by drying 100g of biomass in an oven regulated at 105 °C to ± 2 °C to constant weight. The water content of hemp is calculated according to the following equation:

Water content (%) = (Wet biomass weight - Dry biomass weight)/Wet biomass weight * 100

- **Measurement of the water absorption of hemp**

The water absorption capacity of hemp is determined according to standard NF-1097-6 with a pycnometer. It is expressed as percentage of weight of dry biomass.

- **Measurement of bulk density of hemp**

Bulk density of hemp is determined by weighing biomass in a cube of 15*15*15cm.

Bulk density (kg/cu.m) = "MBiomass / VCube"

Whereas:

MBiomass (kg): total mass of biomass introduced into the cube

VCube (cu.m): volume of cube equal 3.375×10^{-3} cu.m

- **Measurement of the color of hemps**

The colors of the samples were measured by the LANGE AMPP-393 DR spectro-colorimeter according to the following protocol:

To introduce about 100g of hemp in a small translucent plastic bag,

To close the bags by zippers system with lowest air,

To lie the bags on a flat surface, flatten it to obtain a homogeneous layer of hemp,

To measure the color of hemp by the spectro-colorimeter at 10 different places of the bag (to take the average of 10 measurements).

Fig. 1: Spectro-colorimeter DR LANGE AMPP-393.

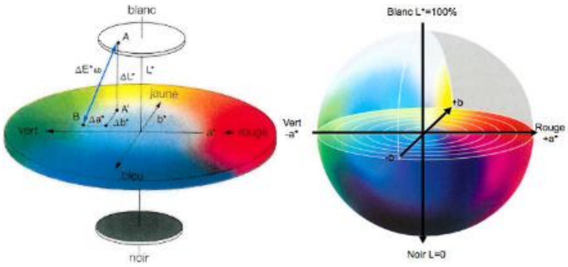

*Fig. 2: Representation L*a*b* and Sphere of Ulbricht.*

Two degree of color, L* and b* were measured:

The degree of white, measured by L* (0 = black, 100 = white)

The degree of yellow, measured by the b*, (-60 = blue, 60 = yellow)

The measurement of a* presents little interest for hemp.

Measuring of organic soluble content of hemp in neutral water and in alkali medium (OPC in water)

The measurement is realized in 3 steps:

Liquid-solid extraction: disperse and stir 10g of the dry hemp in 200 g of demineralized water with or without 2g of CEM I for 2 or 24h at 20 °C

Liquid-solid separation: after 2 or 24h of extraction, the solution is separated from hemp filtration on paper of 1.2 microns of pores size then filtered on a membrane of 0.45 µm of pores size.

The extracted organic matter content of the solution is measured by a TOC-meter (SHIMADZU Serial No. H544355: Total Organic Carbon Analyzer TOC-L with TNM-L Total Nitrogen Measuring Unit).

From the TOC content expressed in ppm, the soluble organic matter content of hemp expressed in % of TOC is calculated according to the following equation:

$$\textbf{TOC (\% Dry Biomass) = TOC (ppm) x } 10^{-6} \textbf{ x } \frac{200\ (g)}{10\ (g)} \textbf{ x 100}$$

Whereas:

Mass of liquid = 200 g

Mass of dry biomass = 10 g

TOC (ppm) = TOC value in ppm of the liquid after extraction,

TOC/BS (% Dry Biomass) = TOC soluble content of hemp.

- **Calorimetric measurement of OPC hydration (TAM AIR)**

For these tests, the hemp was previously milled into flour with a size less than 500µm. Hemp flour and 8g of OPC were weighed and mixed in a glass cell. 4g of distilled water are then introduced and mixed rapidly with cement and hemp. The glass cell is placed in the TAM AIR Micro calorimeter. The hydration is measured at 20°C during 90h.

Fig. 3: TAM Air Thermostat Serial 3116-2 No.278 and glass cell (W/C = 0,5).

- **Concrete manufacturing**

Hemp concrete was prepared using a Rayneri mixer (MALX-85) of 20 liters capacity.

Fig. 4: Mixer Rayneri.

Ingredient of concrete

Hemp containing 11.7% of water:	462.8 g
Prewetting water:	1182.2 g
OPC Le Teil CEM I 52.5 R:	1809 g
$CaCl_2$ of 99%:	18.09 g
Mixing water:	633.2 g

The manufacturing protocol of hemp concrete is as follows:

To mix all the ingredients in the bowl of mixer for 5 min,

To measure the density of fresh concrete

To introduce fresh concrete in several polystyrene cubes of 10*10*10cm

To cure the concrete in cube at 100% Residual Humidity and 20 °C for 24h

To unmold and to measure the Compressive Strength (CS) of concrete at 24h

To dry unmolded concrete at 20 °C, 65% RH for 6 days

To measure CS of concrete at 7 days,

To dry another concrete cube at 60 °C to obtain constant weight and to measure the lambda of concrete by CT-Meter at 20°C.

The compressive strength of hemp wood concrete is measured by a 3R press with a force sensor from 100 to 100,000N. From the breaking force, the breaking stress can be calculated with the following formula: $\sigma = F/S$ whereas σ is the stress in MPa, F the force in N and S the surface in mm^2.

The thermal conductivity of dry concrete is measured by a CT-meter.

3 RESULTS AND DISCUSSION

3.1 Characteristic physical-chemical of hemp

- **Color of hemp in function of retting degree**

Retting is the maceration that is done to textile plants such as flax and hemp, to facilitate the separation of filamentous bark and the stem. Retting is also an enzymatic degradation of hemp straw that causes a change of color. Hemp becomes darker with retting.

Figure 5 : Samples of hemp with different retting degrees.

Retting decreases the degrees of Yellow (b*) from 16.1 to 9.4 and White (L*) from 88 to 68 (Tab. 1).

- **Other characteristics**

Hemp aggregates studied come from industrial manufacturing and in the form of needles. The width varies from 3 to 5 mm. The length is between 8 and 20 mm. The size distribution of hemp aggregates can be measured either by sieving or by image analysis [Niyigena 2016]. But in this study it was not measured.

The bulk density of hemp varies from 114 to 150 kg/cu.m and does not depend on hemp retting or water content of the samples. Bulk density of hemp is considerate for formulation of concrete.

The water content of hemp varies from 10 and 16.3%. There is no clear correlation between the water content and the degree of retting of hemp. Hemp aggregates absorb quickly and a lot of water. Hemp aggregates can absorb during 2 and 24h respectively 4 to 5 times their initial weight of water. These results confirm the high porosity of hemp.

- **Soluble organic content of hemp**

Internal works of Lafargeholcim has demonstrated that the retarding properties of biomasses aggregates depend on the nature of the plants and the soluble organic content of biomasses. It is therefore important to know the soluble organic content of hemp.

In this study, the soluble organic content of hemp was measured by extraction by water in the presence of OPC to keep the pH at 13. The duration of extractions is 2 and 24h. These are delicate operations. The soluble organic content is expressed as TOC content (% of dry hemp).

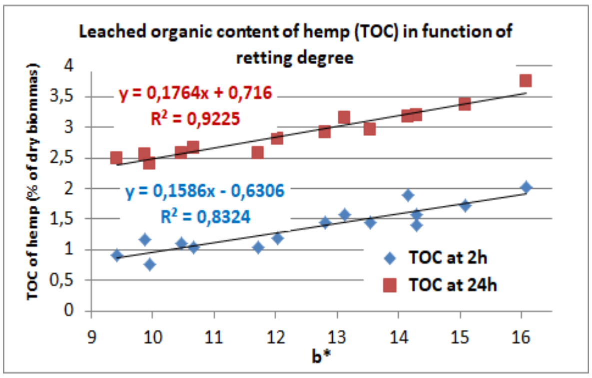

Fig. 6: Soluble organic matter content (TOC) according to the degree of Yellow of hemp.

Fig. 6 and 7 show that the degrees of Yellow (b*), White (L*) and the soluble organic content (TOC) of hemp decrease with retting. The soluble organic content of hemp increases with the duration of extraction.

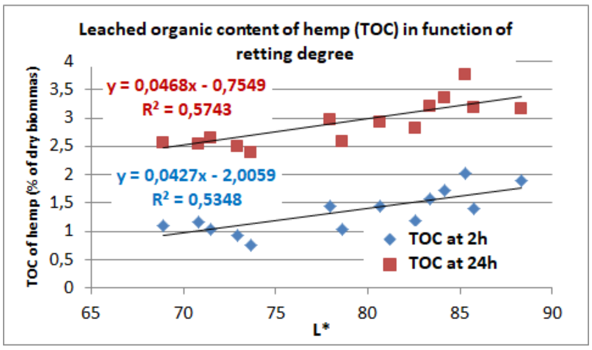

Fig. 7: Soluble organic matter content (TOC) according to the degree of White of hemp.

The reduction of soluble organic content of hemp plant by retting has been studied and demonstrated in the work of ABOT, Sharma et al [ABOT 2010, SHARMA 1986].

Fig. 6 shows a very linear correlation between the soluble organic content and the degree of Yellow of hemp. Furthermore, the measurement of the degree of Yellow (b*) by the Spectro-colorimeter DR LANGE AMPP-393 is very simple, fast and without destruction of the samples. It is possible to use this measure to characterize the degree of retting and also to predict the soluble organic content of hemp.

3.2 Influence of hemp on OPC hydration heat measured by TAM AIR Microcalorimetry

For this study, a low retted hemp sample was used. Its main characteristics are presented in the table 2. We observed that the content of soluble organic matter increases significantly in basically medium and high pH (pH = 13) comparison to the neutral medium (pH = 7). This phenomenon is due to the partial hydrolysis of the polysaccharides of hemp in alkaline medium. Consequence, the content of soluble organic matter increases. This phenomenon was observed by David Sedan during his thesis [Sedan 2007].

- **Influence of the hemp on hydration of OPC**

Results show that the flour of hemp is a very powerful retarder of OPC hydration. Indeed with only 5% of hemp, hydration is delayed by about 15h (Fig. 8). The cumulative heat of hydration decreases (Fig. 9).

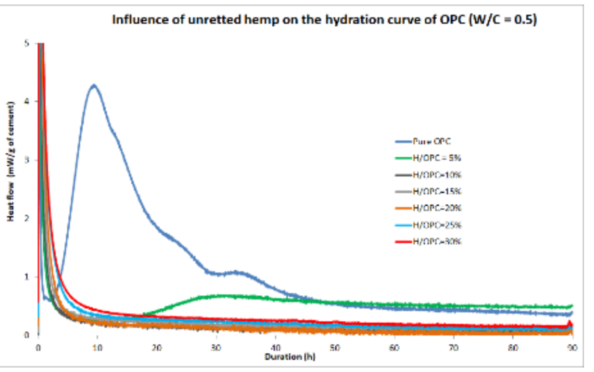

Fig. 8: Curves of heat flow of OPC hydration in the presence of hemp flour.

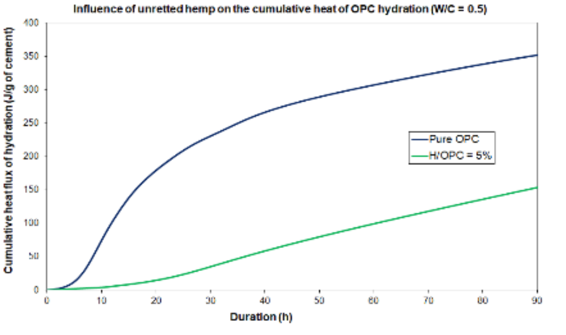

Fig. 9: Curves of cumulated heat of OPC hydration in the presence of hemp flour.

In presence of 5% of hemp flour, the thermal efficiency of hydration is very low even after 90h (only 44%). From 10% of hemp flour, the hydration of OPC is completely blocked for at least 90h (Tab. 3).

- **Influence of soluble organic matters of hemp on hydration of OPC**

The soluble organic matters of hemp were prepared by extraction by demineralized water. These matters have a yellow-brown color and foaming properties. Chromatographic analyzes have shown that these matters contain not only polysaccharide monomers (fructose, maltose, maltotetraose, maltitol and maltotriose) but also unidentified monomers of lignin or tannins.

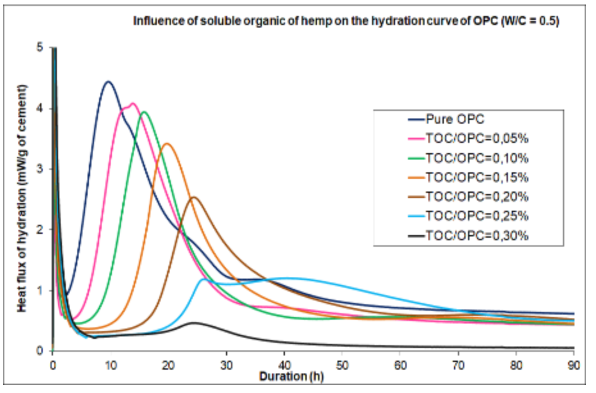

Fig. 10: Curves of heat flow of OPC hydration in the presence of soluble organic matters of hemp.

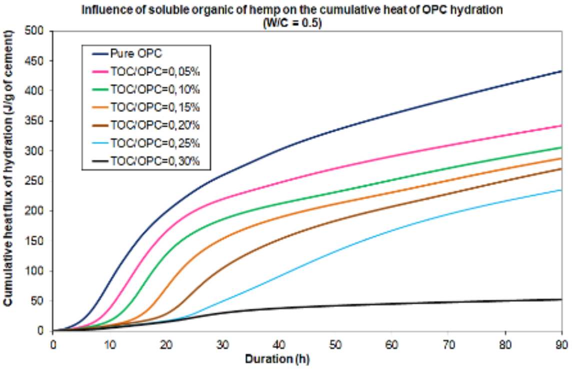

Fig. 11: Curves of cumulated heat of OPC hydration in the presence of soluble organic matters of hemp.

The soluble organic matters of hemp are also retarders of OPC hydration. With very low dosage of TOC (eq. 0.05% of OPC), the hydration delays and the cumulative heat of hydration decreases (Fig. 10, 11 and Tab. 4). These phenomena increase with TOC dosage.

We suppose that hemp can delay the hydration of OPC by several mechanisms:

- The adsorption of the soluble organic molecules on the surface of OPC particles.
- The metallic cations (Ca^{2+}, Fe^{3+}, Al^{3+}...) are chelated by organic molecules.
- These cations adsorb on surface of hemp as observed by D. Sedan [SEDAN 2007].

3.3 Influence of retting of hemp on the properties of "Hemp-OPC" concrete

- **Density of concrete**

The mixing forms a lot of foam in the fresh concrete. Less hemp is retted; more it brings air in fresh concrete. Indeed, the density of fresh and hardened concrete increase with the retting of hemp.

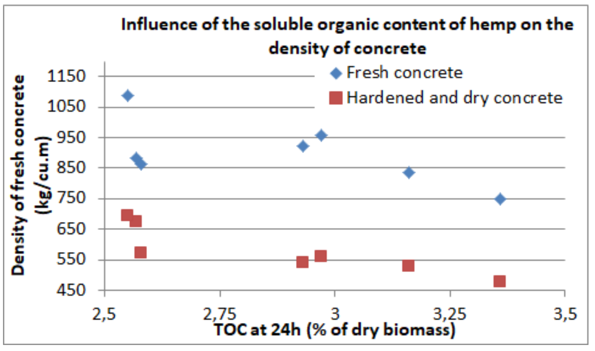

Fig. 12: Density of concrete in function of soluble organic matters content of hemp.

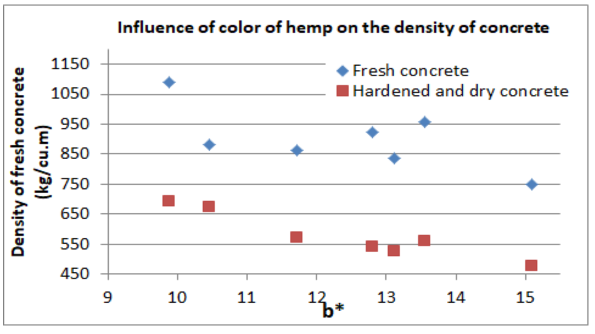

Fig. 13 : Density of concrete in function of the degree of Yellow of hemp.

Fig. 12 and 13 clearly show that higher the TOC content and the degree of Yellow (b*), lower the density of fresh and hardened concrete. The air training is due to the foaming property of the soluble organic matters of hemp.

- **Compressive Strength of concrete**

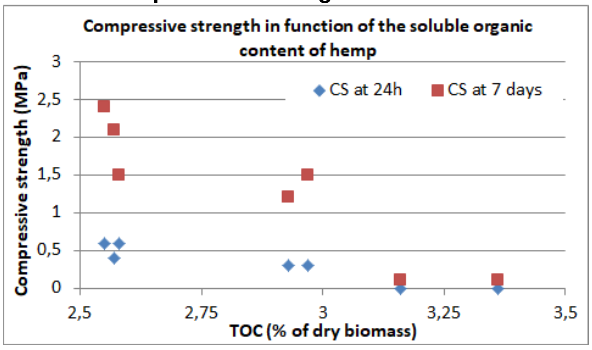

Fig. 14: Compressive Strength of concrete in function of TOC content of hemp.

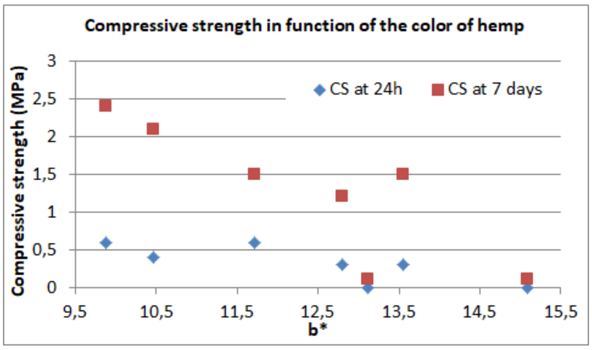

Fig. 15: Compressive Strength of concrete in function of degree of Yellow b of hemp.*

Results show that the compressive strength of concrete decreases considerably with TOC content (Fig. 14). We observe same tendency with the degree of Yellow b* (Fig. 15).For the hemp samples without or with low retting, the concrete does not harden after several days. The compressive strength of these concrete is close to 0 MPa.

Retting is therefore essential for the hardening of "Hemp-OPC" concrete.

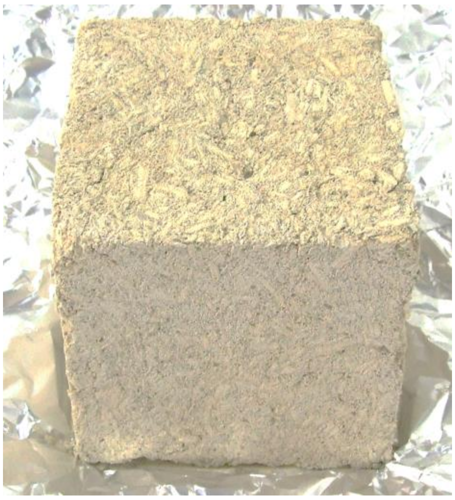

Fig. 16: Hemp-OPC block.

- **Thermal conductivity of concrete**

Fig. 17 shows a good thermal insulating property of “Hemp-OPC” concrete. Thermal conductivity varies from 0.1 to 0.175 W/m.K according to density of dry concrete.

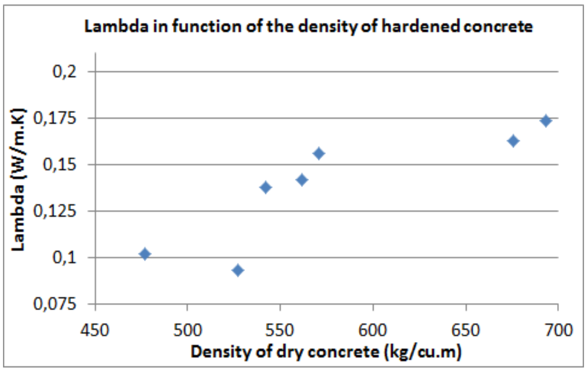

Fig. 17: Thermal conductivity in function of density of dry concrete.

We also observe a very good correlation between the thermal conductivity and the compressive strength of hemp concrete (Fig. 18).

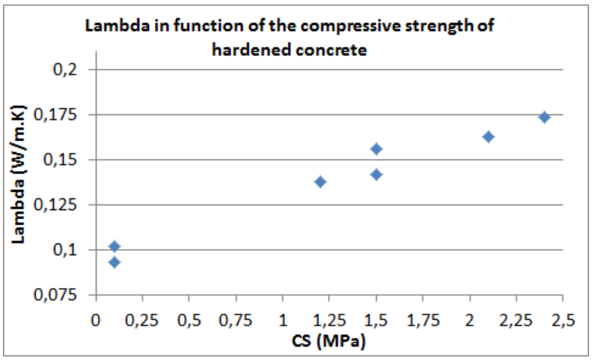

Fig. 18: Thermal conductivity in function of the compressive strength of concrete.

4 CONCLUSIONS AND SUMMARY

This study has shown that hemp and their soluble organic matters are powerful retarders of OPC hydration.

Retting decreases the soluble organic matters content of hemp. Hemp is getting darker with retting.

The results of this study showed a very correlation between the content of soluble organic matters and the degree of Yellow b* of hemp. The degree of Yellow b* is measured by the DR LANGE AMPP-393 Spectro-colorimeter. So we can use this Spectro-colorimeter to predict the retting degree of hemp.

Retting is therefore essential to obtain the hardening of “Hemp-OPC” concrete. The thermal conductivity of these concretes is low, from 0.1 to 0.175 W/m.K according to the density of dry concrete.

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Tab. 1: Physical characteristic of hemp aggregates.

Degree of Yellow b*	Degree of White L*	Water content (%)	Bulk density (kg/m3)	Abs. at 2h (%dry hemp)	Abs. at 24h (%dry hemp)
9,42	72,9	16,32	114	319	404
9,88	70,82	11,89	118	330	400
9,96	73,64	12,36	136	267	349
10,46	68,91	10,87	150	300	370
10,66	71,49	11,35	137	259	336
11,72	78,62	13,19	121	300	386
12,04	82,57	10,07	134	321	409
12,8	80,64	11,97	118	342	450
13,12	74,43	16,18	118	331	420
13,55	77,98	12,82	130	258	336
14,15	88,34	10,95	143	255	330
14,29	83,37	10,39	121	362	464
14,3	85,72	10,95	129	334	422
15,09	84,18	12,2	142	405	482
16,08	85,29	13,27	131	333	429

Tab. 2: Main characteristics of hemp used for measurements of OPC hydration.

Characteristics	Value
Degree of Yellow b* measured by AMPP-393	14.3
Degree of White L* measured by AMPP-393	85.72
Water content (%)	10.95
Absorption at 2h (%)	334
Absorption at 24h (%)	422
Leached organic in water (pH = 7) at 2h “COT/Dry Hemp” (%)	0.88
Leached organic in water (pH=7) at 24h “COT/Dry Hemp” (%)	0.93
Leached organic in OPC medium (pH=13) at 2h “COT/Dry Hemp” (%)	1.4
Leached organic in OPC medium (pH=13) at 24h “COT/Dry Hemp” (%)	3.19

Tab. 3: Main characteristics of hemp used for measurements of OPC hydration.

	Cumulative heat of hydration (J/g of cement)			**Thermal yield of hydration (%)**		
	At 24h	At 50h	At 90h	At 24h	At 50h	At 90h
OPC pure (CEM I 52.5R)	204	289	352	100	100	100
H/C=5%	22	80	154	11	28	44
H/C=10%	0	0	0	0	0	0
H/C=15%	0	0	0	0	0	0
H/C=20%	0	0	0	0	0	0
H/C=25%	0	0	0	0	0	0
COT/C=0,30%	0	0	0	0	0	0

Tab. 4: Cumulative heat and the thermal efficiency of OPC hydration in the presence of soluble organic matters of hemp.

	Cumulative heat of hydration (J/g of cement)			**Thermal yield of hydration (%)**		
	At 24h	At 50h	At 24h	At 50h	At 24h	At 50h
OPC CEM I	227	335	433	100	100	100
COT/C=0,05%	195	271	342	96	94	97
COT/C=0,10%	159	232	301	78	80	86
COT/C=0,15%	115	212	288	56	73	82
COT/C=0,20%	58	184	270	28	64	77
COT/C=0,25%	26	133	235	13	46	67
COT/C=0,30%	21	42	53	10	15	15