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Carbonated concrete blocks for CO_2 captation

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Abstract. The CO_2 captation process called carbonation, improves specific properties of the concrete during the conversion of carbon dioxide CO_2 into calcium carbonate $CaCO_3$. Current environmental concerns motivate the study of carbonation in order to maximize the absorption of carbon dioxide. Moreover, lightweight concrete with bio-based products knows an interesting development in the construction field, especially as thermal insulation panels for walls in buildings. Concrete blocks produced with miscanthus mineralized aggregates offer interesting mechanical properties and minimal environmental impact.

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Słowa kluczowe: ca.

Concrete products are sustainable building materials. Their compositions are based on natural, abundant and locally available raw materials. The concrete block manufacturing requires low cement content and almost no energy during the curing phase – there is no baking – which greatly limits CO_2 emissions.

At a time when the cement industry is largely responsible for the production of CO_2 in the construction sector, it is useful to make this production a reverse phenomenon: that's CO_2 capture. The CO^2 absorption process, called carbonation, improves specific properties of the concrete during the conversion of carbon dioxide CO_2 into calcium carbonate $CaCO_3$. Current environmental concerns motivate the study of carbonation in order to maximize the absorption of carbon dioxide.

Finally, the use of bio-sourced aggregates such as miscanthus vegetal will decrease again the environmental impact of concrete blocks manufacture and increase insulating properties.

Principles and advantages of carbonation

Carbonation is a chemical reaction between the cement paste and hardened carbon dioxide [Courard et al., 2003 (a)]. This reaction can occur in a mature concrete between the hydrated products (CSH and Ca $(OH)_2$) and CO_2 ~~(Eqs. (1) and (2))~~. The carbonation can also take place in the presence of moisture between the hydraulic components of clinker (C_3S and C_2S) and CO_2 ~~(Eqs. (3) and (4))~~. The proposal made here is to induce early carbonation by infusing CO_2 immediately after release. ~~Products of the reaction are a mixture of hydrates and hybrid carbonates (Eqs. (3) and (4))~~. In the case of concrete building blocks, the carbonated products are improving concrete performances in terms of strength, durability and dimensional stability, thanks to the lower content or disappearance of $Ca(OH)_2$.

~~$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (1)~~

~~$3CaO \cdot 2SiO_2 \cdot 3H_2O + 3CO_2 \rightarrow 3CaCO_3 + 2SiO_2 \cdot 3H_2O$ (2)~~

~~$2(3CaO \cdot SiO_2) + 3CO_2 + 3H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3CaCO_3$ (3)~~

~~$2(2CaO \cdot SiO_2) + CO_2 + 3H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + CaCO_3$ (4)~~

During Seventies, mechanisms of carbonation were studied in relation with reactivity and strength of calcium silicate activated by CO_2 [Young et al., 1974]. This technique was introduced for the production of panels cement fibre based, in order to reduce the manufacturing time; the first plant operating on this principle was built in Hungary in 1985, but was closed for reasons of cost of CO_2.

A feasibility study of CO_2 sequestration through a technique of accelerated cure was conducted at McGill University (Montreal, Canada) between 2004 and 2006 [Shao et al., 2006]. The possibilities of fixing CO_2 in cement matrices were explored and performances in the short and long term implications were verified: it showed some interesting opportunities offered by this technique, based on specific accelerated carbonation process.

Currently, concrete blocks are produced on a wet cure (water vapor) based process. It is estimated that for 1 m³ of concrete blocks manufacturing, wet cure at atmospheric pressure consumes 0,59 GJ while curing in autoclave consumes 0,71GJ [Shao et al., 2006]. If a CO_2 injection process is put in place, for the same volume of concrete, the energy for recovery and compression of CO_2 is estimated to be 0,02 – 0,10 GJ/ m³, for a minimum value of CO_2 capture into cement of 10 and 50%, respectively. That means that the total energy, excluding CO_2 transport necessary to carbonation, is significantly lower than that required for a traditional wet cure.

The building blocks of concrete are particularly suited to carbonation, because of their mass production, their high porosity and the need to practice a wet cure. The reaction between the cement paste at early age and carbon dioxide thus constitutes a form of CO_2 sequestration. If we consider a hollow block 39 x 19 x 19 cm and 18 kg, which contains about 10% by mass of cement, we can consider that it is able to fix at least 0,18 kg of CO_2 [Shao et al., 2006]. If the cement is replaced by

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slag, the capture rate will remain about the same [Monkman et al., 2006]. Furthermore, if the aggregate (86% by mass) are also used to fix CO_2, the fixed amount considerably increases. Carbonated steel slag could set another 6% by mass. Therefore, if one considers that each aggregate is able to fix about 5% of its mass in CO_2, a total sequestration of 0,77 kg may be attempted, for aggregates and a block. A block of concrete construction would be potentially able to fix 0,95 kg of CO_2.

This concept could lead to term, if based on the adequate choice of materials for the „aggregate" part, to a situation of „zero-emission". This will be the case if bio-sourced or recycled aggregates can be used [Courard et al., 2012]. Moreover, the accelerated carbonation blocks should lead to improved mechanical performances, lower porosity and a reduced risk of efflorescence: the denser microstructure of concrete, which improves the durability of the product and, therefore, the duration of life. Finally, the developed industrial process does not change the potential for recycling at end of life, particularly in the manufacture of new blocks.

Materials

Miscanthus original aggregates. Compared to the hemp plant (annual) [Elfordy et al., 2008], miscanthus is a perennial plant, located for several years (up to 20 years), which reduces costs of crop establishment: energy consumption is evaluated around 9,223 GJ/ha (for hemp: 13,298 GJ/ha).

In comparison with wood, miscanthus has a high content of parenchyma, surrounded by a tough fibrous structure. It therefore combines a high rigidity with a low density [Philippou et al., 2001].

Without woodchip pretreatments, the mixtures offer unstable results [Rossole[illegible]., 2010]. In addition, the stability of the concrete cannot be achieved because untreated chips react chemically with the environment and dimensions considerably vary with changes in humidity. In order to increase the durability of the composite and to reduce vapor or liquid transfers between the chips and their environment, the mineralization appears to be the best solution (Fig. 1). This treatment consists in soaking the chips with a mineral solution; a mixing procedure of about 3 min allows an impregnation of the chips. Currently, the components used for mineralization are mainly calcium chloride, silica fume and derivatives of lime and cement.

Fig. 1. Miscanthus maepertus chips
Rys. 1.

Physical characteristics of the chips, before and after mineralization, have been determined in order to point out the real effect of the mineralization process. A first important characteristic is apparent density: it gives a good idea of the capacity of water (liquid or vapour) penetration into vegetal aggregates but also thermal insulation properties. For porous materials able to adsorb humidity, it is important to define test conditions: density has been evaluated in dry conditions and in equilibrium with specific environment (21°C and 40% R. H.) (Table 1).

Water absorption also gives indication on the effect of mineralization. Most commonly tests used to analyze water transfer at the interface is the capillary suction test [Courard et al., 2003]. The capillary suction test is described by several standards: they differ essentially by the water level above the bottom surface of concrete specimen and the time when measurement is taken. Mass change is usually registered after 5, 15, 30 and 45 minutes, as well as after 2, 6 and 24 hours (Fig. 2). Mass is measured on samples wiped off with a damp tissue. From the capillary suction test, it is possible to calculate the coefficient of water absorption, which is related to the evolution of the mass of the specimen with time [Courard et al., 2003]. However, it was necessary to adapt the test to chips: samples of particles, after being dried into an oven, are placed in nylon tights under water. The tights let the water go through without losing particles. The measurement of mass variation is not performed on one sample but on a pool, containing several chips to start. The measure may be slightly influenced by the size of the chips.

Table 1. Apparent density (kg/m³)
Tabela 1.

Sample	Dry conditions		21°C and 40% R.H conditions		
	Raw miscanthus	Crushed miscanthus	Raw miscanthus	Crushed miscanthus	Mineralized miscanthus
1	97	93	111	98	370
2	90	90	113	103	371
3	91	91	115	103	386
Average value	93	91	113	101	376

There is a clear difference in behavior between raw and mineralized miscanthus. New test procedure [Courard, 2005] allowed following what really happens in the first minutes of contact between chips and water, because it exactly corresponds to the time of mixing for mineralization process: finest particles offer an absorption rate largely greater than larger particles (Fig. 2).

Mineralization induces a reduction of absorption rate [Courard et al., 2012]. However, there is a larger dispersion of the results, probably due to an incomplete process: more time should be needed to have a complete mineralization.

Concrete blocks preparation. Concrete blocks are produced with CEM I 52.5 N with the proportions given in Table 2.

Mixing procedure for concrete blocks is described hereafter and is inspired by the work realized by Delhez [Courard et al., 2010]:

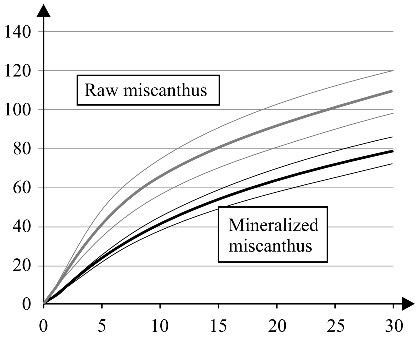

Fig. 2. Coefficient of absorption (%/dry initial mass) vs time (s) for raw materials
Rys. 2.

Table 2. Mix proportions for miscanthus concrete blocks
Tabela 2.

Components	Quantity (%)	Quantity (g/block)
Mineralized miscanthus aggregates	40,54	1335
~~Ciment~~ CEM I 52.5 N	24,32	803
Water	35,14	1150

- introduce aggregates and sand into the mixer and mixing for 120 seconds;
- wait 60 seconds;
- add cement and mix for 2 minutes;
- add water and mix for 2 minutes;

The steps of vibration as are follows (Fig. 3a):

- ■ place the mold on the vibrating table (50 Hz);
- ■ cast half of the fresh concrete in the cubic metal mold;
- ■ put a mass (± 8 kg) in the mold on the fresh concrete;
- ■ set the vibrating table on for a period of 30 seconds;
- ■ remove the mass;
- ■ cast the other half of the fresh concrete in mold;
- ■ place the mass of 8 pounds in the mold of the fresh concrete;
- ■ set the vibrating table on for 30 seconds;
- ■ remove the samples (Fig. 3b);

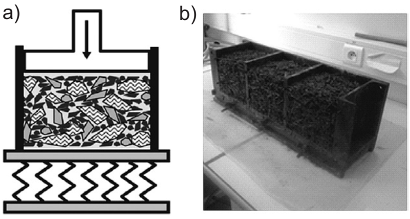

Fig. 3. Preparation of the samples (a) vibration and loading principles, (b) demoulding of the concrete blocks
Rys. 3.

A CO_2 injection technique procedure was set up: an air-conditioned room called *incubator*, with controlled humidity and temperature and specific CO_2 injection system connected to the incubator have been used. The following three parameters can be taken into account by the latter: the temperature, the relative humidity and the percentage of injected CO_2. The temperature is controlled using a thermostatically controlled bath while relative humidity is achieved by means of a saline type $Ca(NO_3)_2 \cdot 4H_2O$. Incubators available in the lab allowed to work with rate of 20% and commercial CO_2 [Parmentier et al., 2013].

Results and discussions

Carbonation of miscanthus aggregates. After mineralization process which includes cement, silica fume, $CaCl_2$ and superplasticizer, miscanthus aggregates are stored into incubator for 7 hours and mass increase is registered for 1, 3 and 7 hours, respectively. Aggregates are disposed in such a way that CO_2 is able to diffuse from all the faces. Quantification of CO_2 gain in mass (Table 3) is based on Monkman equation [Courard et al., under press].

Table 3. Quantification of CO_2 absorption by miscanthus aggregates
Tabela 3.

Variables	Sample 1	Sample 2	Sample 3	Total
Initial mass (g)	[illegible]	422,34	325,37	1111,23
Final mass (g)	363,20	421,95	325.06	1110,21
Water loss mass (g)	6,34	7,37	5,68	19,40
Dry binder mass (g)	118,80	138,02	106,33	363,15
Mass gain (%)	5,07	5,06	5,05	5,06

Miscanthus carbonated aggregates are more resistant to wear than those who were not carbonated [Courard et al., under press]: carbonated chips have a Micro-Deval coefficient of about 7,23, while those who were not carbonated get a coefficient approaching 12,69. We can say that the CO_2 capture on plant fibers miscanthus type is positive from mechanical point of view and should positively influence the compressive strength of blocks.

Concrete blocks were stored in two types of curing conditions during 7 hours:

- wet climatic room (100% R.H.);
- incubator with 20% CO_2.

Compressive strength of blocks (Table 4) is 5 times higher when stored in CO_2 incubator, even if it is quite low. But the objective is to obtain insulation materials and not structural elements. The average compressive strength of these blocks (Table 5) is almost 7 times as large as the blocks stored in a humid chamber. It is also four times greater than that of concrete blocks made from non-carbonated mineralized miscanthus.

Table 4. Compressive strength of concrete blocks after 7 hours
Tabela 4.

Test	Compressive strength (N/mm²)		CO_2 mass gain (%)
	Wet Curing	CO_2 Curing	
miscanthus aggregates			
1	[illegible]	0,0522	1,49
2	0,0091	0,0689	1,14
3	0,0091	0,0546	1,36
Average	0,0091	0,0586	1,33
carbonated miscanthus aggregates			
1	0,0275	0,202	1,43
2	0,0285	0,209	1,23
3	0,0314	0,205	1,37
Average	0,0290	0,205	1,34

Conclusions

On the basis of the experimental results, the following conclusions can be drawn:

- ■ capture of CO_2 in concrete blocks proves to be a good alternative for the environment and, more specifically, in the fight against global warming through limiting greenhouse gas emissions;
- ■ use of bio sourced materials like miscanthus requires a mineralization process in order to guarantee a minimum rigidity and to reduce water absorption capacity;
- ■ carbonation of bio sourced aggregates before concrete blocks production can increase concrete blocks performances;
- ■ the strength of concrete blocks is increased by using CO_2 injection, with regard to classic humid curing.

Optimization of CO_2 injection process is however needed, taking into account carbon dioxide concentration and humidity, in order to increase strength performances of concrete blocks.

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