



INVESTIGATION OF MECHANICAL PERFORMANCES OF INSULATING BUILDING MATERIALS BASED ON RICE HUSK AND HEMP HURD

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Abstract

The purpose of this paper is to investigate the mechanical properties and the lime-based binder hardening of green concretes made of rice husk or hemp hurd. Concrete specimens were subjected to different curing conditions. Under natural conditions, they were cured during 10 months in a climate-controlled room (20°C – 50%RH) and exposed outdoors. The work also focused on an accelerated carbonation curing (CO₂ curing) aiming to improve the short term compressive strength (1-2 months) of the concrete materials. Under natural conditions, the results indicated that the lime binder was almost strengthened in the same way for both concretes with a similar rate of carbonation. However, the rice husk concrete was characterized by a ceiling effect of the mechanical performances over time which was attributed to the lower bonding strength between rice husks and lime. Concerning specimens exposed outdoors, the strength gain over time was more significant owing to more favorable humidity conditions for carbonation. The accelerated carbonation curing led to an increase of the mechanical properties of the concretes in the short term. The compressive strength after the CO₂ curing was approximately equivalent to those obtained after 10 months of outdoor exposure under natural carbonation.

Keywords:

Rice husk, Hemp hurd, Lime, Mechanical testing, Outdoor exposure, Accelerated Carbonation

1 INTRODUCTION

The development of eco-friendly concrete materials using plant aggregates has increased significantly for the last years. In this field, Lime and Hemp Concrete (LHC) is an example worth following.

The diversification of renewable and easily available lignocellulosic resources helps to popularize bio-based concretes. This work follows our previous research about the use of whole rice husk as plant aggregate to develop an insulating lightweight concrete like LHC for building envelopes [Chabannes 2014]. The recovery of this crop residue without any burning or grinding to design such a material was almost unexplored.

Mechanical performances obtained after 2 months of setting showed that our material using rice husk was suitable for infill walls. However, it cannot be used as a load bearing material as its compressive strength is only slightly more than 0.30 MPa.

The materials studied in this work are made up of rice husk or hemp hurd with a lime-based binder (aerial lime and hydraulic lime). Arnaud and Gourlay [Arnaud 2012] have reported the evolution of LHC compressive strength with time using a lime-pozzolan binder. The latest was increased from 0.35 MPa to 0.85 MPa

between 21 days and 24 months of setting and was largely attributed to slow carbonation.

The main weakness of lignocellulosic concretes using lime is that they take up a very long time to cure when they are cast in-situ. Therefore, the improvement of the mechanical performances of the lime binder at early ages is certainly a path that needs exploring.

An attractive possibility is to accelerate carbonation in a CO₂ rich atmosphere. It has been studied on lime mortars and compared to natural carbonation [Cultrone 2005, Lawrence 2006]. The extent and the quality of carbonation depend upon several parameters. CO₂ reactivity is linked to the nature of the binder phases and CO₂ diffusivity is linked to the pore network and exposure conditions in particular relative humidity (RH) [Cizer 2012]. Using accelerated carbonation appears very promising with particularly porous lignocellulosic concretes designed with an important part of Ca(OH)₂.

The first objective is to monitor the compressive strength of rice husk and hemp concretes until 10 months in 2 kinds of curing conditions. Specimens are cured in standard conditions (20°C – 50%RH) or cured outdoors. The time evolution of the chemical nature of the binder phases is characterized with the purpose to follow and compare LHC with LRC (Lime and Rice husk Concrete) in terms of quality of the lime binder.

The second objective is to characterize specimens after an Accelerated Carbonation Curing (ACC). This is carried out in the prospect of moving towards a load-bearing material for single-storey houses using precast bricks as structural elements.

2 MATERIALS AND METHODS

2.1 Raw materials

Two different crop residues were used to design bio-based building materials: as received whole rice husks coming from a nearby rice field and a commercial hemp hurd.

The binder used in this study (Tab. 1) was a 50/50 wt.% combination of natural hydraulic lime NHL3.5 and hydrated lime CL90 (EN459-1 Standard).

Tab. 1: Main Mineralogical components of lime binders

wt.%	Ca(OH) ₂	C ₂ S	Unburnt CaCO ₃
CL90	90-95	-	5
NHL3.5	30	30	25

2.2 Concrete design

Rice husk concrete (LRC) and Hemp concrete (LHC) were manufactured according to a manual compaction process in cylindrical $\Phi 11 \times 22$ cm³ moulds with a steel device.

Mix proportions are reported in Tab 2. Specimens were designed with a binder on aggregates mass ratio B/A = 2. The mixing water (W_m) was taken in such a way that W_m/B was 0.5 and the prewetting water (W_p) was determined using water absorption tests of the aggregates [Chabannes 2014]. Because of the different true density of rice husk which is nearly twice as high as that of a hemp particle and the different behavior of aggregates towards water, the target density of LRC was higher than those of LHC for a same B/A mass ratio (Tab. 2). As a consequence, the binder content was higher for LRC (as the amount of aggregates).

2.3 Curing conditions

Curing under natural conditions

Specimens were demoulded after 24h and stored in 2 different kinds of curing conditions for duration of between 1 and 10 months:

- Inside Standard Conditions (ISC) in a climate-controlled room at 20°C and 50%RH;
- Outdoor exposure (O) under shelter with an acquisition system of temperature and RH.

The profile of temperature and RH is reported in Fig. 1. Important variations in RH throughout the period can be drawn from the profile. A more accurate analysis of the values shows that RH mostly ranged between 45% and 75% during the outdoor exposure curing.

Initial conditioning before Accelerated Carbonation Curing (ACC)

The diffusion of CO₂ within concrete and the chemical reaction kinetics are influenced by the RH in the

environment but also by the degree of saturation of the pore spaces. The water content of the concrete just before the start of the ACC process is an important factor as well as the RH in the gaseous mixture during the carbonation test. For ordinary concrete, a preconditioning of the specimens is required in order to desaturate the pores on the surface and facilitate the diffusion of CO₂. An oven-drying at 40°C during 14 days is regularly used [Turcry 2014]. Taking into account the high level of porosity of plant-based concretes, this preconditioning appears very severe. Therefore, it has been decided to store specimens during 40 days in the climate-controlled room at 20°C and 50%RH before the beginning of the CO₂-curing. If the water saturation degree is too low after drying, carbonation may have trouble to start. After 40 days of preconditioning, the relative humidity in the core of concrete specimens was measured using an hygrometric probe and was 60 ± 5%. This rate was considered as well suited for the beginning of ACC.

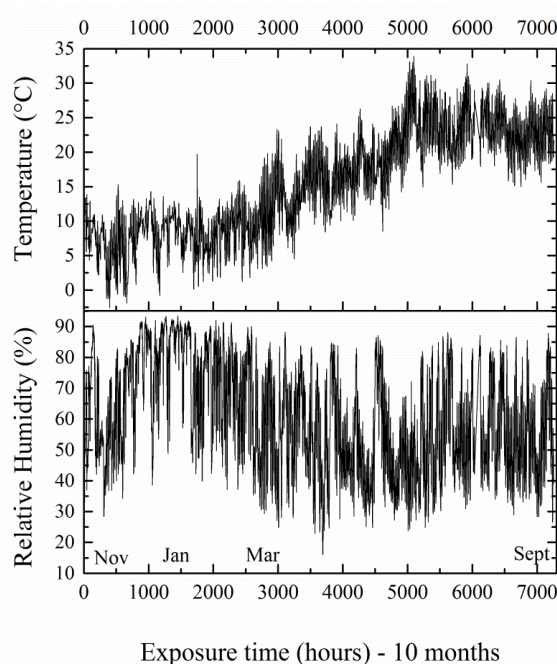


Fig. 1: Data acquisition of temperature and RH under natural conditions up to 10 months

ACC process

After 40 days, LRC/LHC specimens were introduced in two different glass enclosures fed by CO₂ during one month (Fig. 2). The RH in the enclosure was fixed at 65 ± 5 % with a saturated salt solution of ammonium nitrate (NH₄NO₃) which is considered as the optimal RH to favor carbonation [Turcry 2014]. The CO₂ curing system was placed in the room at 20 ± 2 °C. The CO₂ feeding was not continuous but the gas was injected regularly at given intervals of time with the regulator on the CO₂ tank. The CO₂ curing process was conducted in the following manner:

Tab. 2: Mix proportions

Concrete	B/A	W/B	Binder	Aggregates	W _p	W _m	Fresh density
LRC	2	1	395	195	195	195	980
LHC	2	1.5	285	145	285	145	860

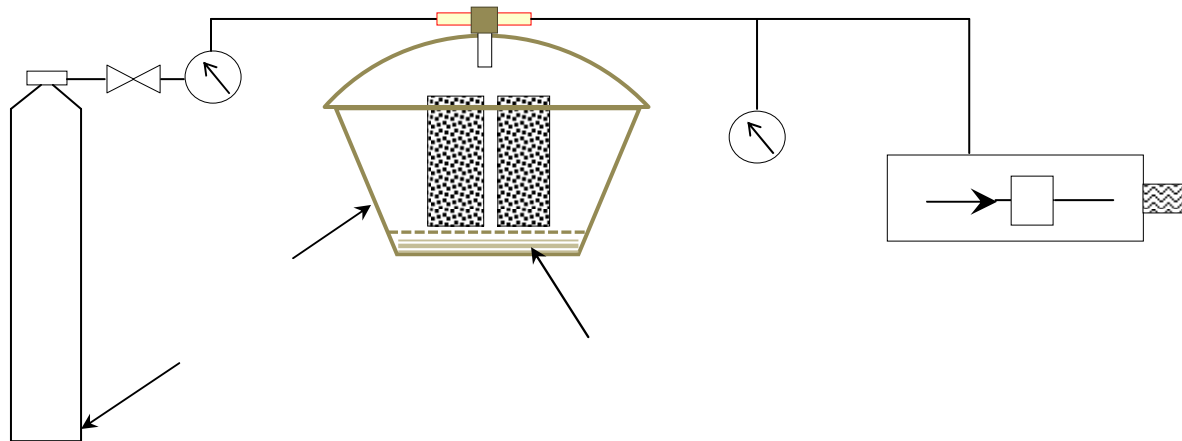


Fig. 2: CO₂ curing system

- A partial vacuum was created in the enclosure with a vacuum pump in order to have an absolute pressure $P_{\text{vacuum}} = 0.50 \pm 0.05$ bar.
- CO₂ was injected until the absolute pressure reached atmospheric one (about 1 bar).

This ensures to have an enclosure with [CO₂] = 50%v/v just after the CO₂ injection in standard temperature conditions and atmospheric pressure. At given intervals of time defined by the feedback, the pressure read on the manometer between the tank and the glass enclosure allows the assessment of the CO₂ consumption. If the pressure is 0.50 bar, this means that CO₂ has been entirely consumed by the carbonation reaction and a new CO₂ feeding is required. Both enclosures (LRC and LHC) were refilled 42 times by CO₂ and the mass of CO₂ consumed in the enclosure (m_{CO_2}) was calculated after each refilling as follows (Eq. 1):

$$m_{\text{CO}_2} = M_W(\text{CO}_2) \times \frac{\% \text{vol} \times V_{\text{acc}}}{V_m} \quad (1)$$

With:

$M_W(\text{CO}_2)$: molar mass of CO₂;

%vol: volume fraction of CO₂ consumed after each refilling deduced by pressure measurements;

V_{acc} : theoretical accessible volume in the enclosure taking into account the total porosity of the concretes (60% for LRC and 80% for LHC);

$V_m = 24 \text{ L}\cdot\text{mol}^{-1}$: molar volume in standard conditions. The degree of progress in the carbonation process was evaluated considering that the full potential of CO₂ consumption is equivalent to the quantity of Ca(OH)₂ present in the binder (with molar ratio). The carbonation of C-S-H is regarded as negligible in a lime binder contrary to cement-based systems. From mineralogical compositions of lime binders presented in Tab. 1, it can be deduced that a 50/50 wt.% of CL90 and NHL3.5 contains about 60% of Ca(OH)₂.

Results were compared to the rate of carbonation obtained by the weight gain after ACC. Indeed, carbonation results in an increase of mass as molar mass of CaCO₃ is 35.1% higher than Ca(OH)₂. This method may cause errors associated with the production of water during carbonation as 1 mole of H₂O is released for each mole of CO₂ consumed by lime. In this study, it has been decided to store specimens 8 additional days after ACC in the room at 20°C and 50%RH. Specimens were weighed after

hydric stabilization and the weight is compared with those just before ACC after 40 days in the same environment. The weight gain of specimens in relation to the Ca(OH)₂ content is thus calculated according to Eq. 2:

$$W_G / \text{Ca(OH)}_2 (\%) = \frac{\Delta M}{m[\text{Ca(OH)}_2]} \times 100 \quad (2)$$

Where ΔM is the weight gain of specimens after 30 days of ACC and 8 days at 20°C and 50%RH for hydric stabilization and $m[\text{Ca(OH)}_2]$ is the mass of Ca(OH)₂ used for the concrete manufacturing.

The rate of carbonation ROC is therefore calculated as follows (Eq. 3):

$$\text{ROC} (\%) = \frac{W_G / \text{Ca(OH)}_2 (\%)}{35.1} \times 100 \quad (3)$$

It is defined as the rate of progress in the carbonation of Ca(OH)₂.

2.4 Testing programs

Compressive strength measurements

Mechanical properties in compression were investigated after 1 – 2 – 4 – 10 months of setting and hardening with a curing under natural conditions (ISC and O) and after ACC (40 days of initial conditioning and 1 month of CO₂-curing). This was done with an electromechanical testing machine (MTS Criterion). Displacement control tests were conducted with a loading rate of 5mm/min. Cycles of loading/disloading were applied for 1%, 2% and 3% strain. The disloading was performed until the stress reaches 50% of its initial value.

Carbonation depth by phenolphthalein spray

A color indicator solution was prepared mixing 1 % of phenolphthalein powder weight by weight in a solution composed of 70% ethanol and 30% distilled water. The solution was sprayed on the specimen section after the compressive strength test. The phenolphthalein half-way stage occurs for a pH \approx 9. For a pH under 9, the region appears unstained whereas beyond 9, it is stained in pink.

Characterization of the binder structure by TGA

Mineralogical investigation of the binding matrix was performed using a STA 409 Cell, Netzsch, thermogravimetric analyzer (TGA). After compressive strength tests at 1 – 4 – 10 months, powdered matrix samples were collected in the bulk of the specimens

(LRC-B and LHC-B) and on the surface (LRC-S and LHC-S). These samples were passed through a sieve (80 μm mesh size) before being analyzed by TGA. Thermal degradation was conducted up to 950°C at 10°C.min⁻¹ under air atmosphere with about 150 mg samples.

TGA was used to quantify the binder phases (hydration products, hydrated lime and CaCO₃). This technique is more accurate to characterize partially carbonated regions non-detectable by the phenolphthalein spray test. The weight loss occurring between 100°C and 400°C is considered to be due to the loss of water from C-S-H hydrates. The loss of water between 400°C and 500°C corresponds to the dehydroxylation of Ca(OH)₂. The amount of CaCO₃ was calculated from the loss of carbon dioxide (LCO₂) occurring between 600°C and 900°C according to the following equation (Eq.4):

$$CaCO_3(\%) = LCO_2(\%) \times \frac{M_w(CaCO_3)}{M_w(CO_2)} \quad (4)$$

With M_w (CaCO₃) and M_w (CO₂) the molar masses of CaCO₃ and CO₂.

3 RESULTS AND DISCUSSION

3.1 CO₂ consumption and weight gain during ACC

The mass of CO₂ consumed in each enclosure until 42 intakes was estimated for each gas refilling. Given the fact that the binder content is higher for LRC, the CO₂ consumption has been normalized according to the amount of Ca(OH)₂ in specimens and it is reported in Fig 3.

Table 4: Calculation of the ROC by the weight gain

Concrete	LRC	LHC
Bulk density after initial curing (kg.m ⁻³)	638 ± 8	462 ± 3
Bulk density after ACC (kg.m ⁻³)	702 ± 13	509 ± 5
% increase in the bulk density	10	10.2
W _G / Ca(OH) ₂ (%)	27.4	27.2
ROC (%)	78.1	77.5

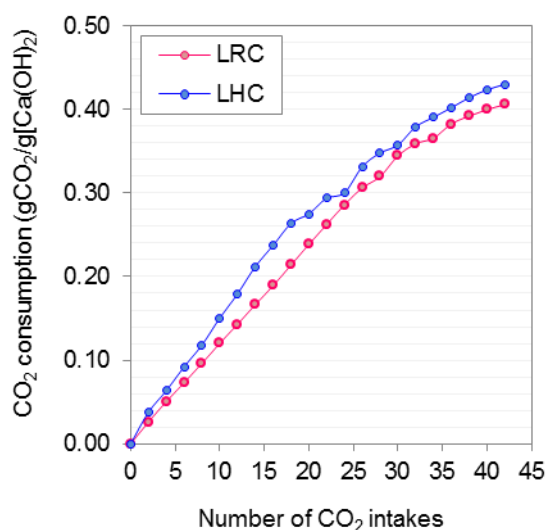


Fig. 3: CO₂ consumption Considering the mass of CO₂ consumed at the end of the test and comparing it with the theoretical maximum consumption, it appears an approximate rate of carbonation of 70% in both cases (Tab. 3). Indeed, taking into account the quantity of Ca(OH)₂ in each concrete, the rate of CO₂ consumption is about 0.4 gCO₂/g[Ca(OH)₂] for LRC and LHC.

Tab. 3: Rate of carbonation by the CO₂ consumption

Concrete	ROC (%)
LRC	68.3
LHC	72.4

These results are compared with those obtained by the specimen weight gain in Tab. 4. The increase of the bulk density is 10% for LRC and LHC. It corresponds to approximately 27% in relation to the Ca(OH)₂

content. Through this approach, a ROC of about 78% is obtained in both cases. This percentage is very close to those estimated with the CO₂ consumption. It can be mentioned that the water released by the carbonation process could be partially used for hydration. This can cause a minor error in the percentage estimation by the weight gain.

3.2 Mechanical characteristics in compression

Under natural conditions

The compressive strength of the specimens for increasing ages is reported in Fig. 4.

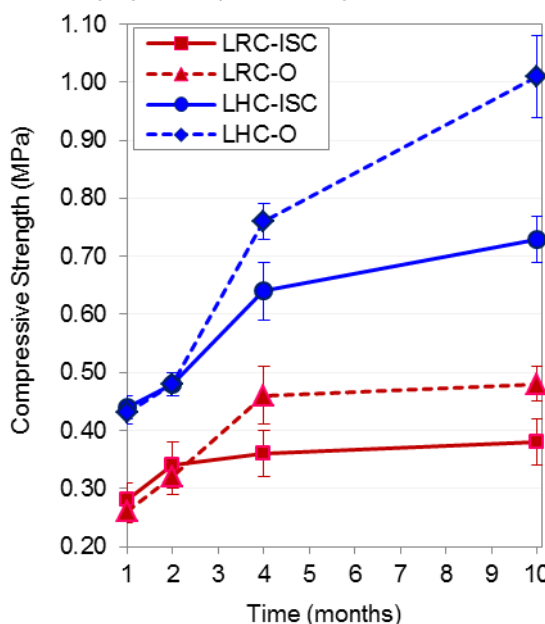


Fig. 4: Compressive strength of LHC and LRC for increasing ages and different curing conditions

The first observation concerns the lower compressive strength of LRC regardless of curing conditions and

age. By following the strength evolution of these concretes until 10 months, it appears a ceiling effect for LRC. The strength seems to be limited between 4 months and 10 months whereas it continues to increase significantly for LHC. As a consequence, the strength gain over time for LHC is much greater, for which the compressive strength after 10 months in ISC reaches 0.73 ± 0.03 MPa whereas those of LRC is only 0.38 ± 0.04 MPa.

Another important result is the difference between indoor and outdoor curing beyond 2 months. The strength gain is higher for specimens exposed outdoors whether for LRC or LHC. This highlights a sharp improvement of the carbonation process in the conditions which occurred during the outdoor exposure (mostly %RH). Indeed, as previously exposed (Fig.1), RH mostly ranged between 45% and 75% during the outdoor exposure curing and carbonation kinetics is known to be maximal between 50 and 70%. When the RH is higher than 70%, pores tend to saturate with water making the diffusion of CO_2 through the concrete very slow. On the other hand, when it is lower than 50%, pores tend to become dry and the dissolution of $Ca(OH)_2$ and CO_2 necessary for the carbonation reaction has trouble to take place. For outdoor curing conditions, the compressive strength of LHC increases from 0.43 ± 0.02 MPa after 1 month to 1.01 ± 0.08 MPa after 10 months (2.3 times higher). However, the

compressive strength of specimens exposed outdoors is not improved before 2 months. The higher %RH outdoors has a great chance to delay the beginning of carbonation by hindering CO_2 diffusion in the saturated pores at early ages.

The hydration of C_2S is known to be slower than that of C_3S . According to some authors, a large amount of C_2S can be hydrated only after 28 days in hydraulic lime-based mortars [Arizzi 2015]. In this way, the contribution of hydration can be considered in the strength over time.

The higher mechanical strength for specimens cured outdoors is necessarily linked to the evolution of the lime-based binder structure. However, the differences between LRC and LHC can also be explained by the bonding strength between plant aggregates and lime. Subsequently, the evolution of the chemical nature of the binder phases over time for both concretes will be investigated in order to compare the quality of the lime binder in each concrete.

The evolution of elastic moduli for increasing ages calculated on load cycles (1% strain: $E_1 - 2\%$: $E_2 - 3\%$: E_3) for both concretes is represented in Fig. 5. The trends are similar with a more pronounced ceiling effect for LRC compared to LHC. Moreover, moduli are higher for specimens exposed outdoors and for LHC as it is the case of the compressive strength.

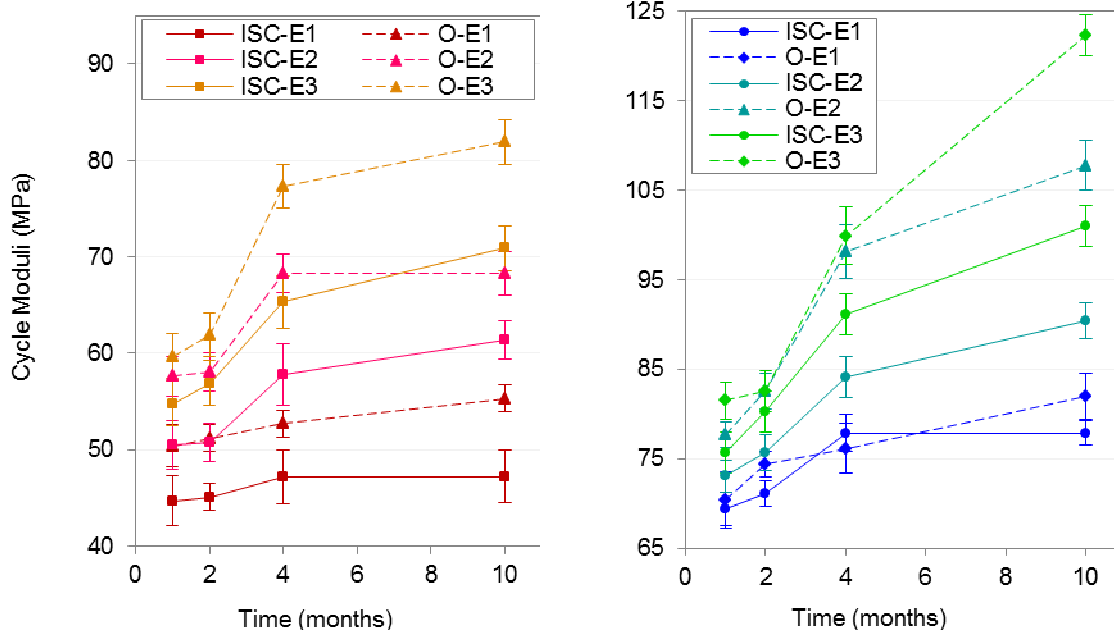


Fig. 5: Elastic moduli calculated on load cycles for increasing ages (a) LRC - (b) LHC

The age and the curing conditions of the concretes can improve their hardening and thus their mechanical performances (compressive strength and stiffness). However, it should be underlined that the rate of strain at failure is not reduced with increasing ages and is about 6.5%. Even after 10 months, LRC and LHC have a strongly ductile behavior, particularly with the use of an important quantity of aerial lime in this study. Add to that, the lower mechanical performances of LRC despite a higher bulk density (Tab. 5). It makes sense to follow the bulk density over time for specimens cured in ISC to have an indication of the carbonation process. The percentage increase in the bulk density up to 10 months is about 5%. However, for specimens

exposed outdoors, it is erroneous to refer to the weight gain to follow carbonation since these concretes are hygroscopic materials for which the density is unstable due to moisture uptake and release.

Table 5: Bulk density of specimens for increasing ages expressed in $kg.m^{-3}$

Concrete	1 month	4 months	10 months
LRC-ISC	625 ± 2	642 ± 2	654 ± 3
LRC-O	666 ± 4	665 ± 6	687 ± 5
LHC-ISC	454 ± 5	467 ± 3	476 ± 2
LHC-O	489 ± 4	494 ± 4	503 ± 3

After ACC

The compressive strength measured after the initial curing (40 days) and ACC during 1 month is reported in Fig 6. It is compared to that of the concrete specimens cured 2 months and 10 months under natural conditions.

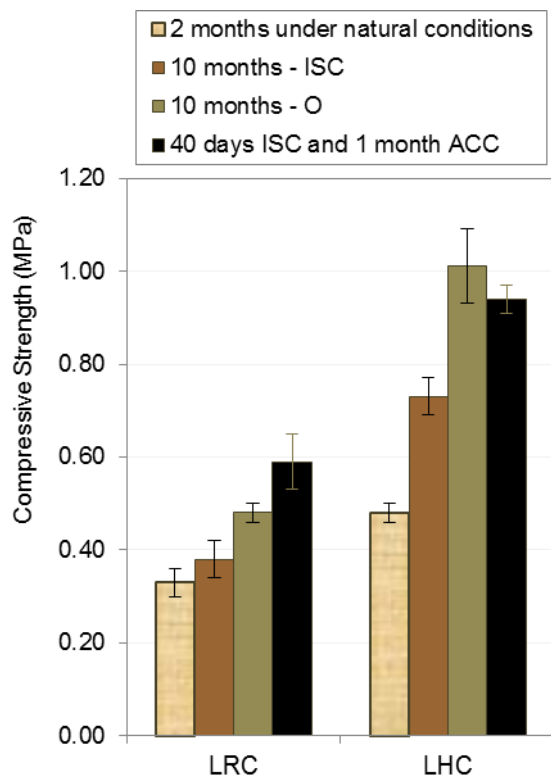


Fig. 6: Compressive strength of LRC and LHC specimens after ACC compared to natural conditions

The results show that the compressive strength after ACC is equivalent to those obtained after 10 months of outdoor exposure. Indeed, the compressive strength of LHC almost reaches 1 MPa obtained after 10 months outdoors and LRC exhibits a compressive strength of 0.59 ± 0.06 MPa which is even higher than those reached after 10 months outdoors. Furthermore, the compressive strength after ACC was doubled if compared to those measured after 2 months under natural conditions (i.e. natural carbonation).

The trend is the same for the cycle moduli. These ones are higher than those obtained after 10 months of outdoor exposure for LRC and range from 60 MPa to 105 MPa depending on the cycle whereas the cycle moduli of LHC after ACC are almost identical, ranging from 80 to 125 MPa.

3.3 Characterization and monitoring of the lime-based binder

Phenolphthalein test

Carbonation profiles obtained by the phenolphthalein spraying test after 10 months under natural conditions (ISC-10m and O-10m) and after ACC are reported in Fig 7. For specimens stored in ISC, the section of the specimens is almost entirely stained in pink with no differences between LRC and LHC. This does not mean in any way that lime is uncarbonated. As it was explained by Lawrence et al. [Lawrence 2006], a stained area indicates a transitional state between the start and the finish of the carbonation process. If the pH is not enough low (higher than 9), the area remains

stained. However, a carbonation front is visible for specimens exposed outdoors. The carbonation depth according to the colorless region (considered as almost totally carbonated) is about 0.8 cm for LRC and 1.5 cm for LHC. This confirms that carbonation has been promoted in outdoor conditions.

After ACC, the carbonation front is approximately the same than those obtained after 10 months of outdoor exposure. However, the core of LRC specimens appears more carbonated than those of LHC as the bulk area is stained in pale pink.

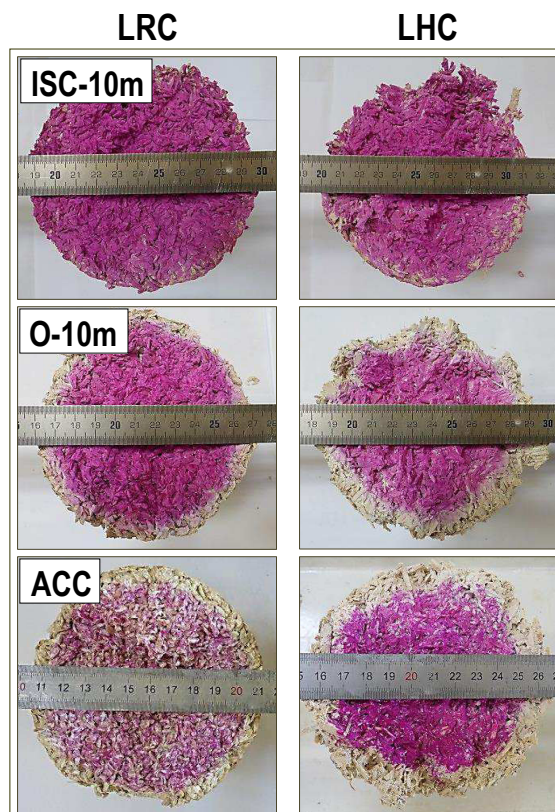


Fig. 7: Cross sectional view of specimens a few seconds after spraying with phenolphthalein

TGA investigations

Carbonation

The time evolution of the percentage of CaCO_3 in bulk samples (collected in the core of the specimens) was performed with the weight loss curves obtained by TGA and Eq. 4. The results obtained under natural conditions up to 10 months are first reported in Fig 8.

Considering that lime powder initially contains 15% of CaCO_3 , the core appears very slightly carbonated after 1 month. Up to 4 months, the evolution of the CaCO_3 content is similar regardless the curing conditions. However, at 10 months, the CaCO_3 content is higher for specimens cured outdoors. The higher rate of carbonation for specimens exposed outdoors is only noticeable in the long term by TGA since the binder is collected in the core. Once again, it can be concluded that the outdoor exposure has promoted carbonation because of the better RH conditions which enhanced the dissolution of CO_2 in the pores.

The investigations on surface samples collected on specimens cured indoors and outdoors have revealed that the surface of specimens is almost entirely carbonated as of 1 month with about 73% of CaCO_3 .

An important result of TGA is the same evolution of the

CaCO₃ content over time for LRC and LHC. Under natural conditions, the phenolphthalein test and the analysis of the CaCO₃ content in the bulk and on the surface of the specimens by TGA show that the higher compressive strength of LHC is not due to a better carbonation.

The CaCO₃ content in the core of specimens after ACC is secondly reported in Fig. 8. It is 72.7% for LRC and 62.5% for LHC. According to the mineralogical composition of the lime-based binder and molar mass of the chemical phases, the amount of CaCO₃ on the surface and in the bulk of LRC and LHC specimens leads to a rate of carbonation (ROC) of about 81%.

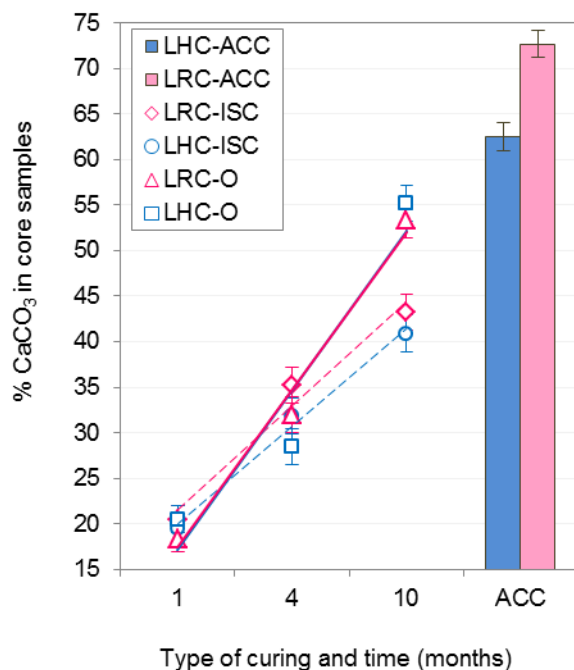


Fig. 8: %CaCO₃ in bulk samples up to 10 months under natural conditions and after ACC by TGA

TGA coupled with the phenolphthalein test has shown that the final rate of carbonation at the end of ACC is approximately the same for both concretes but that CO₂ reactivity-diffusivity mechanisms differ from each other. According to the rate of carbonation in the bulk of specimens after ACC, it can be deduced that LRC is more favorable to CO₂ diffusivity in the core than LHC. On the contrary, the local reactivity of CO₂ is better for LHC for which the unstained region is slightly bigger. This can be explained on the one hand by the lower amount of lime to carbonate in LHC (see the binder content in Tab. 2) and on the other hand by a barrier effect in LHC since the diffusivity of CO₂ throughout the totally carbonated area appears to have been hindered.

Hydration

The weight loss occurring between 100°C and 400°C is mainly due to the loss of water from C-S-H. Results for this range of temperature are reported in Fig. 9 and give a valuable indication of the hydration rate.

Firstly, it must be mentioned that the loss of water in bulk samples is the same for LRC and LHC regardless the age of the concrete and the storage conditions.

The hydration rate has increased between 30 days and 10 months to the same extent for LRC and LHC (B-30d and B-10m). Furthermore, the C-S-H content is higher on surface samples than in the bulk as of 30 days (S-

30d-10m). It has been previously demonstrated that the carbonation rate has considerably increased in core samples from 30 days to 10 months and the surface is more carbonated than the core as of 30 days. As a consequence, a synergy effect between carbonation and hydration is assumed. The hydration rate is higher when the carbonation process is more advanced.

After ACC, the loss of water in core samples (B-ACC) is slightly higher than those of core samples collected after 10 months of outdoor exposure. This is well correlated with the rate of carbonation in core samples.

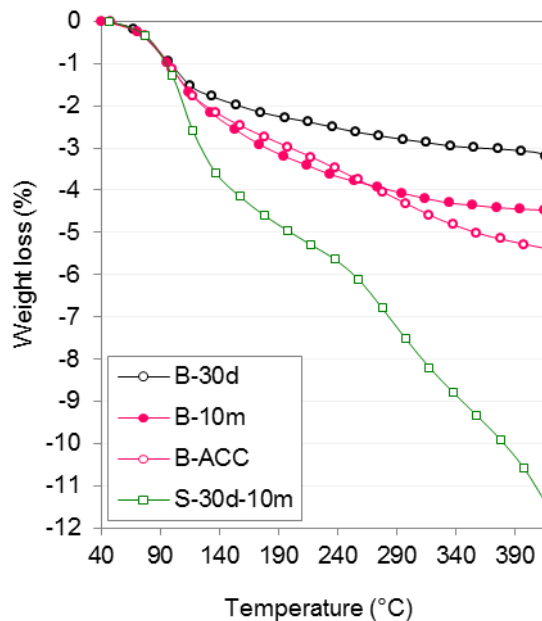


Fig. 9: TGA curves of lime samples between 40°C and 400°C (B: Bulk – S: Surface)

The correlation between carbonation and hydration is represented in Fig 10. The loss of water between 100°C and 400°C and the CO₂ weight loss are reported for bulk samples collected in specimens under natural conditions from 1 to 10 months and after ACC. The surface samples are not considered in the graph because the weight loss between 250°C and 400°C is suspected to be partially attributed to the decomposition of cellulosic compounds. Although precautions were taken to get rid of the smallest plant particles, microparticles may have been collected on the rigid skin by scraping the aggregates.

Besides that, the evolution of the C-S-H content correlates fairly well with the carbonation rate with a regression coefficient which is about 0.9. This linear correlation shows that C₂S hydration is promoted by Ca(OH)₂ carbonation. This can be explained by the water locally provided by the carbonation reaction which could benefit to C₂S hydration. This means that the initial mixing water is not effective to perform C₂S hydration at early ages. According to Cizer et al. [Cizer 2010], the hydration of hydraulic lime can proceed gradually up to 2 years with a competition effect between carbonation and hydration. Carbonation can prevail over C₂S hydration at early age (1 month) for the following reasons:

- The relatively dry curing conditions (50%RH in ISC - under 80%RH outdoors) which favor carbonation but slow down hydration of C₂S;

- The significant amount of $\text{Ca}(\text{OH})_2$ agglomerates which prevent free mixing water access to unhydrated C_2S by trapping them.

In the longer term, when carbonation of hydrated lime is sufficiently advanced, C_2S hydration seems to be promoted by the water locally released as if hydration could only take place after a given rate of carbonation. Based on this assumption and considering that the linear correlation is linked to the stoichiometry of the carbonation reaction, the slope of the linear correlation ($= 7.8$) leads to a molar ratio $n(\text{H}_2\text{O})/n(\text{CO}_2) = 0.3$. According to this approach, about 30% of the water released by carbonation would be used for C_2S hydration at the most.

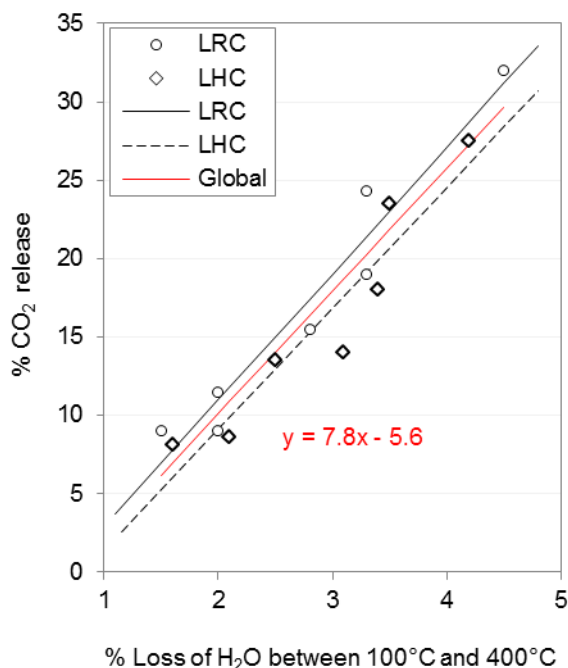


Fig. 10: Correlation between $\% \text{CO}_2$ release by decarbonation of CaCO_3 and loss of water from C-S-H

4 CONCLUSION

The main findings of this paper are the following:

- The monitoring of the mechanical properties of both concretes under natural conditions has shown that the strength gain of LHC over time is twice as high as those of LRC which is characterized by a ceiling effect. Compressive strength and elastic moduli of LHC were already higher than those of LRC as of 30 days. The rate of carbonation and hydration in LRC can be considered as very close to those of LHC. The binder was thus strengthened in the same way. The lower mechanical performances of LRC are thus necessarily attributed to the bonding strength between rice husks and lime. A number of works underlined interface as the weakest part of hemp concretes. They mainly focus on fluid movements between hemp aggregates and binder (lignocellulosic extracts, migration of water). The bio-based concretes studied in the paper have the particularity of being very different in terms of intrinsic properties of the plant aggregates. A large difference between their stiffness can lead to a different bonding strength with the matrix and create elastic compatibility problems. The poor bonding strength can also be justified by the different roughness and chemical

composition of the external surface of the aggregates.

- The outdoor exposure has enhanced carbonation in specimens, especially those of LHC for which the compressive strength reached 1.01 ± 0.08 MPa after 10 months. This was attributed to the favorable RH conditions for CO_2 diffusion and dissolution.
- The effect of an accelerated carbonation curing system (ACC) performed during one month was investigated. It led to an increase of the mechanical properties of both concretes which were approximately equivalent to those obtained after 10 months of outdoor exposure. The compressive strength of LRC and LHC after ACC was doubled if compared to those measured after 2 months under natural carbonation. The rate of carbonation was estimated between about 70% and 80% depending on the method used.
- A correlation between carbonation of hydrated lime and C_2S hydration of the lime-based binder was proposed in this paper. C_2S hydration was probably promoted by the water locally released by carbonation. This shows that C_2S hydration in this system containing a big amount of $\text{Ca}(\text{OH})_2$ is difficult and very long. The contribution of hydration has therefore to be considered in the strength gain over time.

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6 REFERENCES

- [Chabannes 2014] M. Chabannes et al. Use of raw rice husk as natural aggregate in a lightweight insulating concrete: An innovative application. *Construction and Building Materials*, 2014, 70, 428-438.
- [Arnaud 2012] L. Arnaud, E. Gourlay. Experimental study of parameters influencing mechanical properties of hemp concretes. *Construction and Building Materials*, 2012, 28, 50-56.
- [Cultrone 2005] G. Cultrone et al. Forced and natural carbonation of lime-based mortars with and without additives: Mineralogical and textural changes. *Cement and Concrete Research*, 2005, 35, 2278-2289.
- [Lawrence 2006] R.M.H. Lawrence et al. Determination of carbonation profiles in non-hydraulic lime mortars using thermogravimetric analysis. *Thermochemica Acta*, 2006, 444, 179-189.
- [Cizer 2012] Ö. Cizer et al. Real-time investigation of reaction rate and mineral phase modifications of lime carbonation. *Construction and Building Materials*, 2012, 35, 741-751.
- [Turcry 2014] P. Turcry et al. Analysis of an accelerated carbonation test with severe preconditioning. *Cement and Concrete Research*, 2014, 57, 70-78.
- [Arizzi 2015] A. Arizzi et al. A chemical morphological and mineralogical study on the interaction between hemp hurds and lime particles: Implications for mortar manufacturing. *Construction and Building Materials*, 2015, 75, 375-384.
- [Cizer 2010] Ö. Cizer et al. Competition between carbonation and hydration on the hardening of $\text{Ca}(\text{OH})_2$ and C-S binders. *Adv Mater Res*, 2010, 133-134.