BULETINUL INSTITUTULUI POLITEHNIC DIN IAȘI
Publicat de
Universitatea Tehnică „Gheorghe Asachi” din Iași
Tomul LIV (LVIII), Fasc. #, ####
Secția
CONSTRUCȚII. ARHITECTURĂ

MINERALIZATION OF BIO-BASED MATERIALS: EFFECTS ON CEMENT-BASED MIX PROPERTIES

BY

L. COURARD[*], A. DARIMONT, A. LOUIS and F. MICHEL

University of Liège, ArGEnCo Department, GeMMe Building Materials (Belgium)

Abstract. The lightweight concrete with bio-based products knows an interesting development in the construction field, especially as thermal insulation panels for walls in buildings. Before identifying and quantifying the basic physical characteristics of concrete made from wood, miscanthus, hemp or bamboo (acoustic and thermal properties in particular), it is necessary to optimize the composition of the product. It is clear that the final product is not unique and a compromise has to be found between insulation and mechanical properties. The long term stability as well as the reinforcement may be obtained by means of a mineralization process of the natural product: a preparation with a lime and/or cement-based material is necessary to reinforce the cohesion of the bio-based product. Optical and SEM analysis helped to clearly understand the interactions between the bio-based fibrous material and the cementitious materials, the quality of the bond and their effects on the properties of the cement-based concrete products.

Key words: miscanthus, wood, mineralization, adhesion, cement

1. Introduction

Whether global warming or energy requirements, buildings are essential: that means that their construction, use, maintenance or recycling should be questioned and investigated under the aspect of interaction with environment. The agricultural resources are now being in a new focus since they provide an innovative solution to the problem of rapid construction of cheap housing.

Agro-materials are used since man built: woven reeds to reinforce the wall of China (Fig.1), milk casein or beef blood for making binders or paints, straw or horsehair for building walls cob or plaster and, more recently, rice husk ashes used as additives for concrete technology (Gonçalves et al., 2007). Before the use of bricks, the Great Wall was mainly built from earth, stones and wood (Jones, 1996). Due to the large quantity of materials required to construct the Great Wall, the builders always tried to use local sources. In desert, where

[*] Corresponding author: Luc.Courard@ulg.ac.be

suitable earth was not available, sand mixed with debris and willow branch of juniper tamarisks was used as a replacement for bricks and stones.

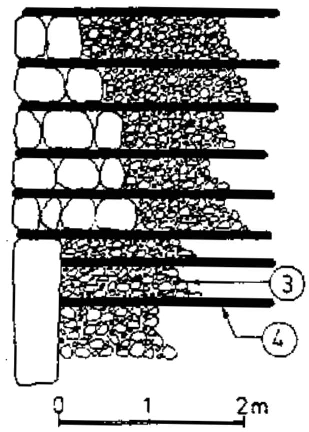

Figure 1- Great Wall of China (clay and gravel (3) reinforced with tamarisk (4) branches) (Jones, 1996).

Wood wastes are also classically used in the manufacture of fiberboard or particleboard. The major challenges associated with the use of plants, are:

- moisture content of the plant and its susceptibility to moisture variations,
- constant properties,
- adhesion to the binder.

Agro-materials used in construction are mainly from cereals (straw), fiber crops (hemp, linen, ...), perennial (poplar, willow, miscanthus, ...) or the timber industry. Constraints in the use of agro-materials are mainly limited range of mechanical and natural variability of their properties. Currently, the hemp industry is the most successful. The hemp concrete (a mixture of boon and lime-based binder) is used to fill the walls in wood framed structures, to produce insulating screeds or coatings, providing good insulation. Hemp is usually grown in head rotation (as well as beet or potatoes).

Compared to the hemp plant (annual), miscanthus (Fig.2) and willow are perennial plants, located for several years (up to 20 years for miscanthus and up to 10 years for coppice willow), which reduces costs of crop establishment. Compared to 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). The modulus of elasticity of Miscanthus giganteus and Miscanthus sinensis vary between 2 and 8 GPa (Kaack et al., 2001).

Figure 2 - Miscanthus malepartus

Figure 3 - Miscanthus chips

The strength and the physical properties of agro-materials are coming from its ultra structure (Figs.3 and 4). The different layers that constitute the cell wall of wood (Grimont, 2008) show the complex interactions between the cellulose material and binder necessary to combine these particles and homogenize the behavior of the finished material. In our case, the inorganic binder, based on hydraulic or pozzolanic products, offers a variable behavior depending on water content but also in sugar or carbohydrates. In addition, the adhesion between the mineral matrix and the plant requires good mechanical interlocking of two materials: the principle of mechanical adhesion (Courard, 2000) is the basis of the effectiveness of the process of mineralization and the production of agro-materials with vegetal. Wettability of the vegetal by the mineral binder remains however the first condition for adhesion (Courard, 2002). The study of these mechanisms, through the measurement of physical (density, absorption of water by capillarity) and mechanical properties (tensile and flexural strength, tensile and shear adhesion), is completed on mineralized plants (Grimont, 2008).

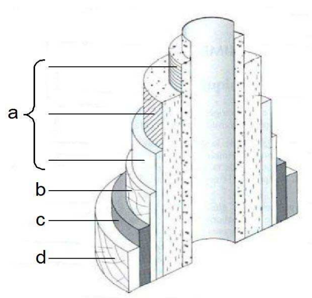

Figure 4 - Structure of wood cell (a: secondary wall, b: primary wall, c: middle lamella, d: external wall (neighboring cell)

2. Mineralization processes

Wood is a highly porous and very durable material but it seems essential to be treated before use as aggregate in concrete. Indeed, without pretreatments of wood particles, the mixtures made with wood chips show great difficulties in obtaining a fixed composition and a stable result. In addition, the stability of the concrete timber can not be achieved because untreated chips react chemically with the environment and whose 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 wood chip and its environment, the mineralization appears to be the good way (Fig.5).

Figure 5 - Miscanthus chips after mineralization

This treatment consists in soaking the wood 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. However, the composition of the "mineralizing" ideal solution is not yet clear defined and mainly depends on the type of vegetal. For example, the external wall around a miscanthus chip (Fig.6) is more impermeable than in a wood chip: that means that the penetration of the mineral solution into the external layer will be less efficient.

The type of mineralization is obviously an important factor to consider: the products on the market are cement, but also lime and byproducts of the steel industry, electricity production (ash) or extractive industries (limestone filler). For applications in building interior, the use of gypsum waste may be also considered. The studies conducted until now (Grimont, 2008 and Rosolen, 2010) promote the use of mixtures of cement and lime. The various stages will allow playing on the parameters of composition to meet the physical, chemical and mechanical minimum requirements:

- compatibility between selected species and different mineralizing agents,
- measurement of setting time of different mixtures,
- study the thermal effects of the hydration reaction of the binder on the penetration of fine particles into plant chips, compressive strength at short, medium and long term.

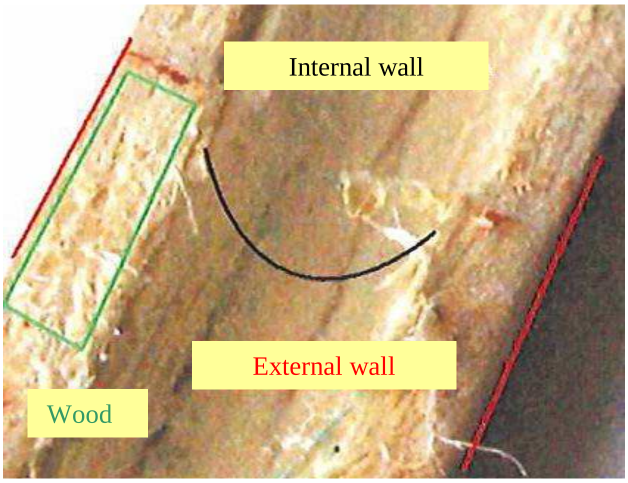

Figure 6 - external wall of a miscanthus chip (Rosolen, 2010)

Investigations were here performed in order to observe the quality of the bond between cement based envelopes and vegetal. ESEM and optical microscope allowed having a view, at different scales, of the interpenetration of the slurry inside the different layers of vegetal.

3. Microscopic investigations

Four types of chips are here presented: epicea, red cedar, miscanthus and bamboo. The three first are coming from local origin while bamboo is produced in U.S.A. Samples were prepared in such a way: chips are impregnated with resin and polished. After optical examination, specimens are metallized with Platinum and introduced into the vacuum chamber of the electronical microscope.

First investigations are realized with optical binocular microscope (Figs.6 and 7). Vegetal is covered with a cement-based hardened material whose thickness varies from 0 to 1 mm. This thickness is variable and doesn't seem to depend on the type of the material: it seems however be strongly influenced by fragmentation, granulometry and on the porous structure of exposed faces.

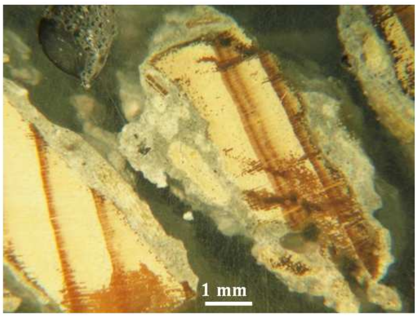

Figure 6a - wood chips after mineralization

Figure 6b - Red wood chips after mineralization

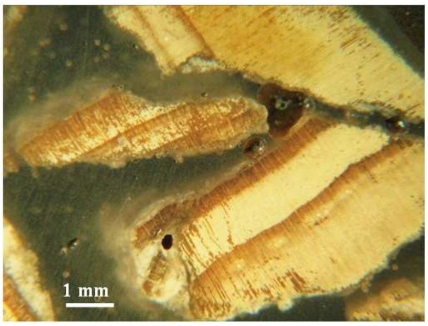

Figure 6c - micanthus after mineralization

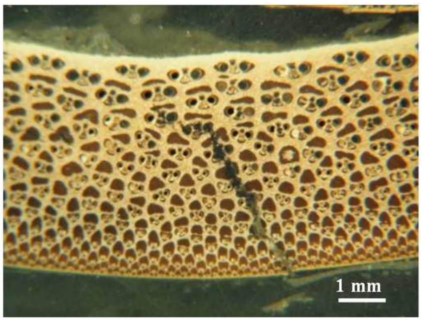

Figure 6d - bamboo after mineralization

The porosity of the external wall in miscanthus chips (Fig.6c) appears less open than for wood. It is mainly due to the fact that miscanthus chips are produced by cutting rods in small pieces. The integrity of the external wall, which is impermeable, may be preserved after cutting.

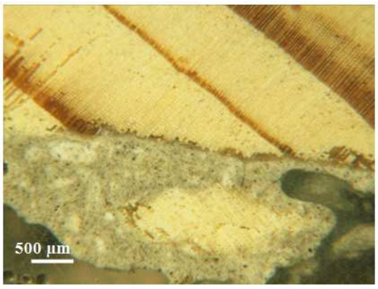

Figure 7a - wood chips after mineralization

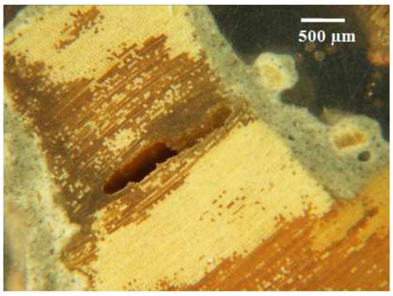

Figure 7b - red wood chips after mineralization

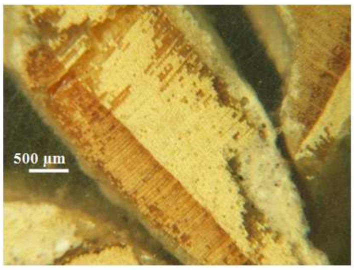

Figure 7c - miscanthus after mineralization

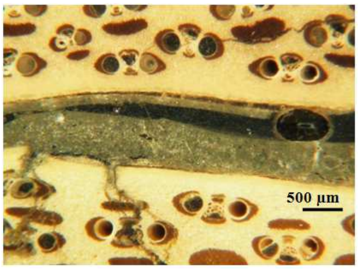

Figure 7d - bamboo after mineralization

Wood chips are very sensitive to variation of humidity. If water content is less than the Fiber Saturation Point (commonly 25-32 %), shrinkage may induce cracks. On Figs. 7d and 8a, we can observe the penetration of the cement slurry inside the microcracks of the wood and the bamboo, respectively. The microcracks could also be induced by preparation procedure, including cutting, crushing and sieving.

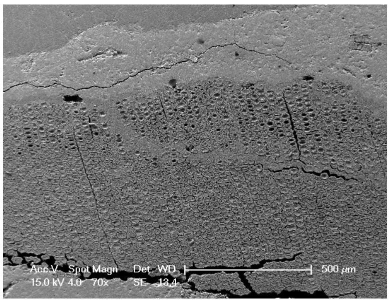

Figure 8a - Wood chips after mineralization

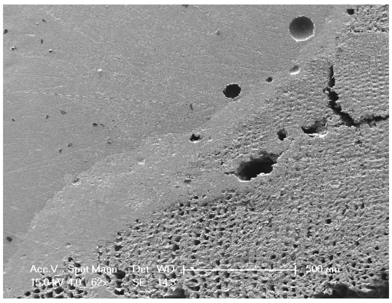

Figure 8b - Red wood chips after mineralization

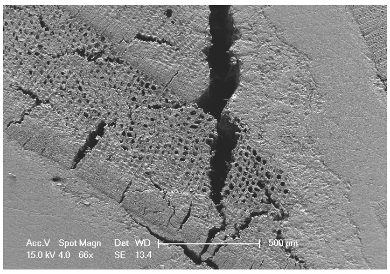

Figure 8c - Miscanthus after mineralization

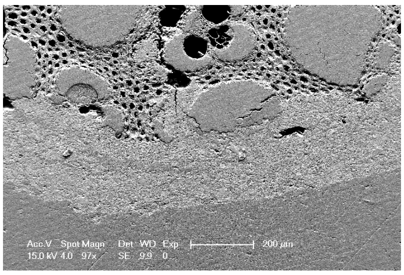

Figure 8d - Bamboo after mineralization

Although a few peripheral cells of the wood chips are met by mixing cement, no penetration of the internal cells was observed (Fig.9). The adhesion of cementitious mineralization is superficial and essentially depends on the porosity of surface of walls. Bamboo (Figs.8d and 9d) is particularly unappropiate as its surface is no permeable to water or cementitous slurry (Fig.8d). Vegetal materials conserve their porous internal structure, which was the objective in order to produce lightweight and thermal insulating aggregates.

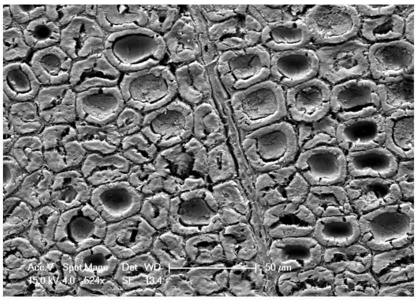

Figure 9a: wood chips after mineralization

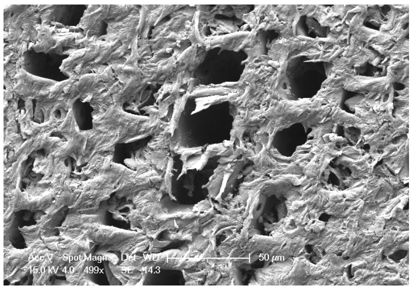

Figure 9b: red wood chips after mineralization

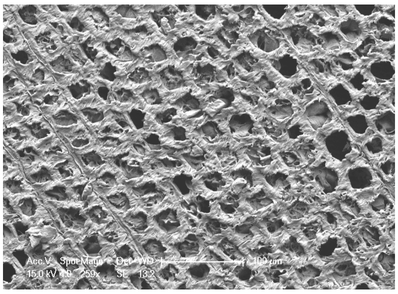

Figure 9c - Micanthus after mineralization

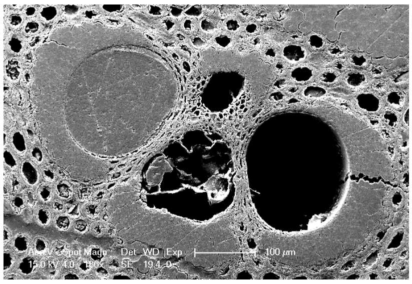

Figure 9d - Bamboo after mineralization

4. Physical characteristics of mineralized vegetals

Physical characteristics of the chips, before and after mineralization, have been determined in order to point out the real effect of the mineralization process: results presented here are relative to wood and miscanthus.

A first important characteristic is apparent density: it gives a good idea of the capacity of water (liquid or vapour) penetration into vegetal aggregates. For porous materials able to adsorb humidity, it is important to define test conditions: density has been evaluated in dry conditions (Table 1) and in equilibrium with specific environment (21°C and 40% R.H.) (Table 2).

Table 1

Apparent density – dry conditions (kg/m³)

Sample	Raw miscanthus	Crushed miscanthus	Wood	Mineralized wood
1	97	93	103	283
2	90	90	109	250
3	91	91	112	255
Mean value	91	91	108	256
Coefficient of variation	1.5	1.5	4.9	6.6

Table 2

Apparent density – 21°C and 40% R.H conditions (kg/m³)

Sample	Raw miscanthus	Crushed miscanthus	Wood	Mineralized wood
1	111	98	113	268
2	113	103	120	277
3	115	103	123	277
Mean value	113	101	118	274
Coefficient of variation	1.8	3	5.1	5

The granulometry is a second important property for understanding the behavior of chips (Fig.10): crushed miscanthus chips are smaller than other chips and consequently offer a higher specific surface for interaction with water and mineralization. Taking into account the granulometry of the chips, it is obvious that the smallest one (like crushed miscanthus) will absorb more water. However, it seems that wood and miscanthus have similar densities. It is also clear that wood chips mineralization induced a significant reduction of water absorption as apparent and bulk densities are not significantly different.

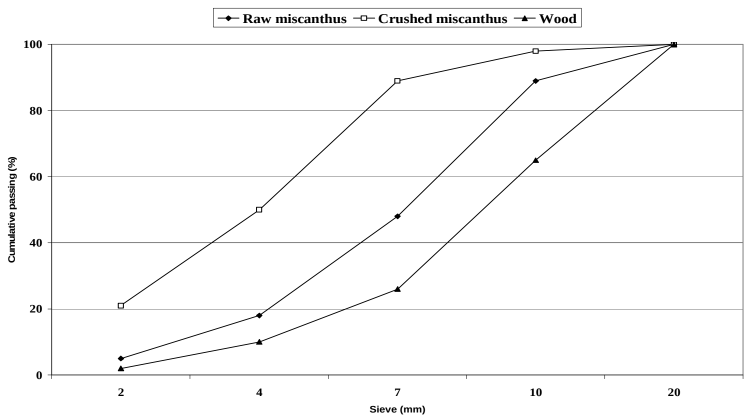

Figure 10 - Sieving curves of chips

Sorption actually encompasses two phenomena: absorption and adsorption. Adsorption is the accumulation of molecules on the surface of the solid, whereas absorption deals with the penetration of liquid into the solid. The adsorption without chemical reaction between molecules of the solid and the liquid is completely reversible and does not alter the structure of the solid. This phenomenon results from electrostatic interactions between molecules and atoms. In the case of wood, rather than forces of Van der Waals or polarization, these are hydrogen bridge links which ensure a strong cohesion between the fibers and microfibrils, composed of cellulose? But it means that wooden based materials are highly hygroscopic.

Water absorption would also give 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 and Justnes, 1995). 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. 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 weight of the specimen with time. However, it was necessary to adapt the test to chips (Fig.11): samples of particles, after being dried in an oven, are placed in nylon tights under water. The tights let the water go through without loosing 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.

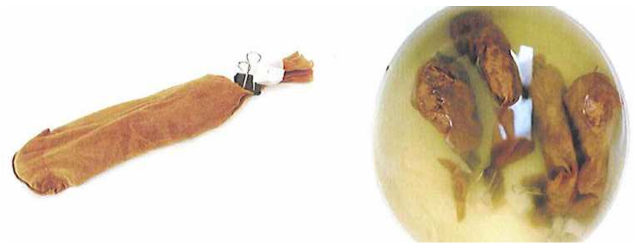

Figure 11 - Nylon tights for water absorption measurements on chips

There is a clear difference in behavior between miscanthus, wood and mineralized wood (Fig.12). The wood absorbs less water than miscanthus, probably due to his higher density. The influence of particle size is also clearly visible: crushed miscanthus reached more quickly the saturation level than raw miscanthus; after this point, the difference in behavior is minimal. The effect of wood chips mineralization is remarkable: there is a drastic reduction in capacity for absorption and saturation is reached in a very short time.

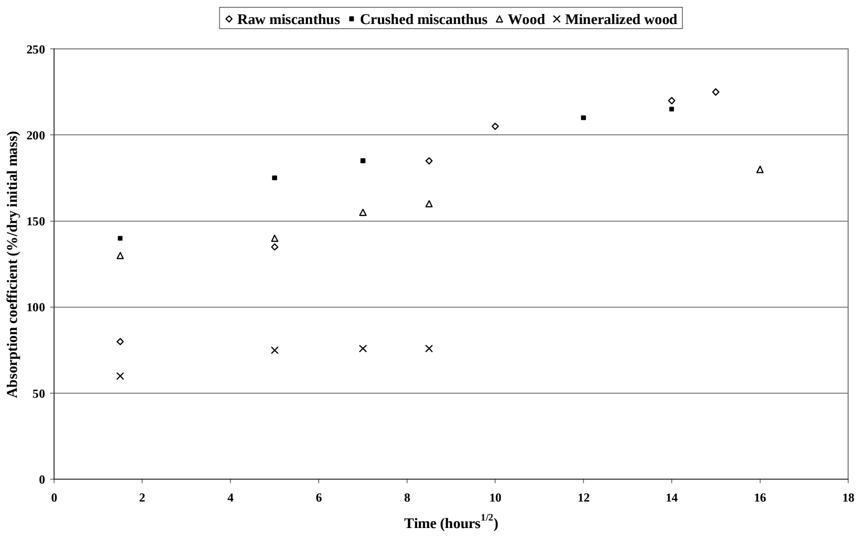

Figure 12 - Absorption of water by vegetal chips (long term)

New test allowed analyzing the water absorption in the early contact of the solid with water (Courard, 2005): this was used to observe the behavior of the chips, prepared in the same conditions – nylon tights – as previously. This was very important to be able to follow 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.

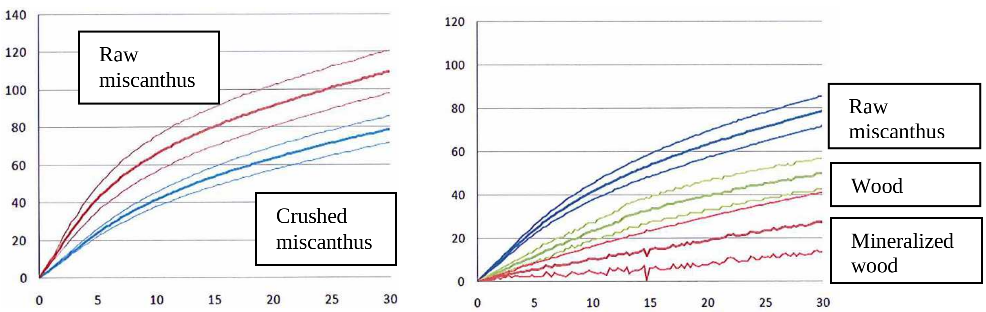

Figure 13 - Coefficient of absorption (%/dry initial mass) vs time (s)

We observe once again (Fig.13) that finest particles offer an absorption rate largely greater than larger particles (raw miscanthus). Wood is absorbing two times less water than miscanthus. Mineralization induces a reduction of absorption rate (Fig.13). 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.

4. Conclusions

The following conclusions can be drawn from this investigation with regards to interface between wood, miscanthus and mineralization layer:

- the density is a simple and efficient measurement in order to study the capacity of the vegetal to absorb water;
- the fineness of the chips influences their capacity to absorb water: the finest the miscanthus, the larger it absorbs;
- the observations under microscope indicates that the quality of the interpenetration is directly influenced by the porosity of the external wall of the vegetal and than mainly by the degree of fragmentation: intact miscanthus rods appear to be less “penetrable” as it offers a more closed surface;
- the mineralization is clearly efficient to reduce the absorption rate.

The surface mineralization of wood or miscanthus is than useful, depending on the preparation of the chips. They can be used for the design of lightweight concretes. Attention must be paid however to the quality of the material and the consistency of supply: if the product changes, the type of mineralization should be adapted to continue to provide an effect on the sorption properties.

5. Acknowledgements

The authors would like to acknowledge the Regional Government of Wallonia (Belgium), which partly financially supported the research (First Entreprise (convention n°5417): *Design of a construction process of prefabricated houses from wooden concrete*), Group Portier (PREFER) Company who provided samples and Raphaël Grimont and William Rosolen, who performed experiments.

Received, Month #, ####

”Gheorghe Asachi” Technical University, Jassy
Department of Transportation Infrastructure and Foundations

REFERENCES

1. Courard, L. (2000) Evaluation of thermodynamic properties of concrete substrates and cement slurries modified with admixtures. L. Courard. Mater. Struct. 35: 149-155.
2. Courard, L. (2002) Parametric Study for the Creation of the Interface between Concrete and Repair Products. Mater. Struct. 33: 65-72.
3. Courard, L. and Degeimbre, R. (2003) A capillary suction test for a better knowledge of adhesion process in repair technology. Can. J. Civil Eng., 30(6): 1101-1110.
4. Courard, L. (2005) Adhesion of repair systems to concrete: influence of interfacial topography and transport phenomena. L. Courard. Mag. Concrete Res., 57(5): 273-282.
5. de Bruijn, P. B., Jeppsson, K.-H, Sandin, K. and Nilsson, Ch. (2009) Mechanical properties of lime–hemp concrete containing shives and fibres. Bio systems engineering 103: 474-479.
6. Elfordy, S., Lucas, F., Tancret, F., Scudeller Y. and Goudet L. (2008) Mechanical and thermal properties of lime and hemp concrete (‘‘hempcrete’’) manufactured by a projection process. Construction and Building Materials 22: 2116–2123
7. Gonçalves, M.R.F., Bergmann, C.P. (2007) Thermal insulators made with rice husk ashes: Production and correlation between properties and microstructure. Construction and Building Materials 21: 2059–2065.
8. Grimont, R. (2008). A study of the mineralization and the adhesion in wooden concrete. Master Thesis. Faculté des Sciences Appliquées, Université de Liège, Belgium: 142p (in French).
9. Jones, C.J.F.P. (1996). Earth Reinforcement and Soil Structures. Thomas Telford, 400p.
10. Justnes, H. (1995) Capillary suction of water by polymer cement mortars. Proceedings of the RILEM Symposium on Properties and Test Methods for Concrete-Polymer Composites, Oostende (ICPIC, Ed. D. Van Gemert): 29-37.
11. Kaack, K., Schwarz K.-U. and Brander, P.E. (2003) Variation in morphology, anatomy and chemistry of stems of Miscanthus genotypes differing in mechanical properties .Industrial Crops and Products 17: 131-142.
12. Kymäläinen, H.-R., Hautala, M., Kuisma, R. and Pasila A. (2001) Capillarity of flax/linseed (Linum sitatissimum L.) and fibre hemp (Cannabis sati_a L.) straw fractions. Industrial Crops and Products 14: 41–50.
13. Philippou, J.L. and Karastergiou S.P. (2001) Lignocellulosic materials from annual plants and agricultural residues as raw materials for composite building materials. Proceedings of the International Conference: FOREST RESEARCH: A Challenge For an Integrated European Approach (ed. K. Radoglou): 817-822.
14. Rossolen, J. (2010) Contribution to the study of bio-based aggregates and application to miscanthus concrete. Master Thesis. Faculté des Sciences Appliquées, Université de Liège, Belgium: 126p (in French).
15. Duran X., Lenihan H., O'Regan B. - A model for assessing the economic viability of construction and demolition waste recycling -the case of Ireland - Resources, Conservation and Recycling 46, 2006, p. 302–320

TITLUL LUCRĂRII ÎN LIMBA ROMÂNĂ

(Rezumat)

Betonul uşor pe bază de bio-produse cunoaste o dezvoltare amplă în domeniul construcțiilor, în special ca panouri termoizolante pentru pereti în clădiri.

Înainte de identificarea şi cuantificarea caracteristicilor fizice de bază din betonul realizat din material lemnos, Miscanthus, cânepă sau bambus (proprietăți acustice şi termice), este necesar să se optimizeze compoziția produsului. Este clar că produsul final

nu este unic si trebuie găsit un compromis între izolație şi proprietățile mecanice. Stabilitatea pe termen lung, precum şi consolidarea poate fi obținută printr-un proces de mineralizare al produsului natural: pregătirea materialului pe bază de var şi / sau ciment este necesar să consolideze coeziunea produsului bazat pe biotehnologie. Analizele optice şi MES (Microscop electronic de scanare) au ajutat să se înțeleagă clar interacțiunile dintre materialul fibros bio □i ciment, calitatea şi efectele lor asupra proprietăților betonului pe bază de ciment.