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► **To cite this version:**

Ana Laura Berger Cokely, Sandrine Marceau, Grégory Mouille, Sofiane Amziane, Fabienne Farcas. Influence of bioresource variability on the hydration of mineral binders. 5th International Conference on Bio-based Building Materials, Jun 2023, Vienne, Austria. 8 p. hal-04345082

HAL Id: hal-04345082

<https://hal.science/hal-04345082v1>

Submitted on 14 Dec 2023

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Influence of bioresource variability on the hydration of mineral binders

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Abstract. Plant-based concretes are increasingly used as building materials thanks to their insulating properties and their reduced environmental impact. However, existing studies show that it is still impossible to predict their mechanical performances from their initial formulation. This article presents the first results of a project which aims to control the mechanical performance of plant-based concretes and to define compatibility indicators between mineral binders and plant particles. In this study, the impact of six plant species on the hydration kinetics of Portland cement and pozzolanic cement is evaluated by isothermal calorimetry. The addition of plants leads to shifts in the heat flux curves, which are very variable according to the nature of the vegetal and of the binder. These results are generally attributed to certain components of the plants, such as sugars and phenols which have a retarding effect on the setting of cements.

Keywords: biosourced, insulation, plant variability, mineral binder.

1 Context and Problematic

The use of vegetal concretes is increasing in the building sector thanks to their thermal and acoustic insulation properties, mainly due to the intrinsic porosity of the material, which improve the energy efficiency of buildings. Moreover, the fact that they can contain a wide range of local plant resources reduces the environmental impact of these construction materials and therefore the environmental impact of the building industry [1–3].

However, the use of biosourced concretes is still limited by the lack of knowledge and the high variability of their performances which makes it impossible to predict their mechanical performance from their formulation [4, 5]. For example, **Fig. 1** shows the performance dispersion of hemp concretes with the same formulation but containing hemp particles of different origins. In particular, the mechanical performance varies up to ninety percent.

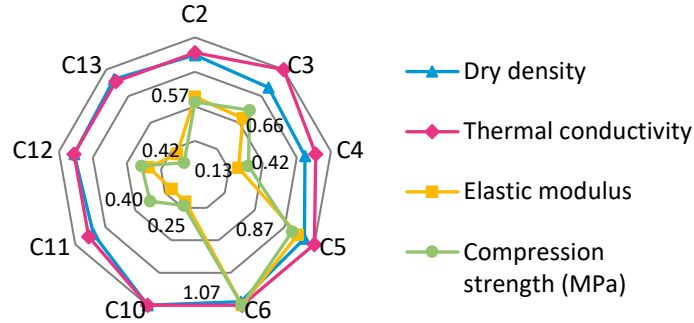


Fig. 1. Performance variability of nine formulations of hemp concretes depending containing hemp shiv from different origins (adapted from [5])

The role of variability in plant resource properties (by species, genotype, location or growing conditions) is not yet well understood, and there are no criteria for selecting plants that are compatible with binders [2, 6–8].

Thus, to overcome the lack of knowledge on this type of material, the BIO-UP project, funded by the Agence Nationale de la Recherche (ANR), aims to define rules for the formulation of plant-based concretes and to obtain controlled properties while taking into account their environmental impact. To this end, the properties of the materials will be characterized at all scales of analysis: from the chemical characterization of the mineral and vegetal components and their interactions, to the characteristics of interfacial transition zones around the plant particles, and the thermal and mechanical properties of vegetal concretes.

One of the axes of this project concerns the chemical interactions between plants and mineral components of materials. First, the influence of several plants on the hydration mechanisms of mineral binders with different chemical compositions is analyzed. The first results concerning Portland cement (CEM I) and pozzolanic cement (CEM IV) are presented in this article. Second, the variability of the biochemical properties of plants will be evaluated and the link between this variability and the hydration mechanisms of binders will be studied. Finally, selection criteria for binder-plant couples and/or treatments to limit these interactions will be proposed.

In the following article, a state of the art on cement hydration and the impact of the presence of plants is presented. Then, the first results concerning the influence of the presence of six different plants on the hydration of CEM I and CEM IV will be detailed, before presenting the perspectives of this work.

2 Influence of the Presence of Plants on the Setting of Cements

2.1 Portland and pozzolanic cement hydration

Portland cement or CEM I is composed of a minimum of 95% clinker (non-hydrated calcium silicates and aluminates) and secondary constituents, notably gypsum as a source of sulphate to regulate setting [9]. During the hydration of Portland cement, the

calcium silicates C3S¹ and C2S lead to the formation of hydrated calcium silicate (C-S-H) and portlandite (CH), which are responsible for the long-term mechanical strength of the material and the alkaline pH of the paste, respectively. The secondary products of hydration are the sulfoaluminous phases AF (AFt and AFm), formed specifically from the hydration of calcium aluminates C3A and C4AF [9].

The hydration kinetics of Portland cement are well known. Since C3A reacts very quickly with water, gypsum is added in commercial cements to delay the setting and maintain the workability of the paste [9].

A lot of other cements are based on Portland cement. CEM IV is a pozzolanic cement in which between 11 and 55% of the Portland cement has been replaced by pozzolanic additions. Pozzolanic additions are silico-aluminous materials that can be natural from volcanic rocks, industrial by-products (siliceous fly ash and silica fume) or produced from the calcination of special clays (metakaolin).

The addition of pozzolan changes the cement hydration kinetics. There are not only the hydraulic reactions, that comes from the Portland cement clinker compounds, but also the pozzolanic reaction, that also forms cementitious products. The silicates from the pozzolanic addition reacts with the portlandite (CH), that were already formed by the hydration of clinker's silicate phases, to form more C-S-H later.

Thus, the pozzolanic reaction induce the consumption of portlandite for the additional formation of C-S-H, responsible for the strength of the paste. Therefore, CEM IV have an improved resistance in compression, a reduced porosity and a reduced pH compared to CEM I [10].

2.2 Influence of plants on the Hydration of Cements

Many studies exist on plant-mineral interactions and use very different approaches. A delay in the setting of binders is commonly observed when plants are added, but also a great variability in mechanical properties of vegetal concretes. These phenomena are generally related to the compounds extracted from the plants, in particular the soluble metabolites such as sugars and phenols [2, 4, 7, 11–13].

A study by monitoring hydration by isothermal calorimetry with inorganic and organic admixtures showed that organic molecules have a retarding effect in the setting of cements, in particular, carboxylic acids and phenolic compounds. Phenolic compounds, which contain adjacent hydroxyl groups, are powerful retarders [14]. One of the possible explanations is the capacity of complexation of the calcium ions of the cement by these molecules thanks to the hydroxyl functions which are in ionized form in basic environments. Thus, carboxylic acids are able to trap ions that are necessary for the formation of cement hydrates, such as calcium (**Fig. 2**) and silica. This phenomenon can slow down or even inhibit the setting and hardening of cement.

Despite the advances made by these studies, it is still not possible to predict the performance of plant-based concretes and to take into account the variability of plant properties.

¹ Cement notation: H=H₂O, C=CaO, A=Al₂O₃, S=SiO₂, F=Fe₂O₃

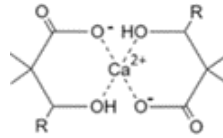


Fig. 2. Bidentate complex with ions Ca^{2+} adapted from [15]

3 Materials and Methods

In order to evaluate the influence of the variability of the biophysical-chemical properties of plants, six different species cultivated in metropolitan France were selected for this study and are shown in **Erreur ! Source du renvoi introuvable.**: rice husk, bamboo, hemp shive, rapeseed, miscanthus and reed.



Fig. 3. Photographs of plant aggregates

The effect of the addition of plants on the hydration of Portland and pozzolanic cements is evaluated by isothermal calorimetry measurements at 25°C . Thus, the heat flux released by the exothermic hydration reaction and the cumulative amount of heat are measured over time to observe the effect of the presence of these plants.

The measurements are performed on cement pastes containing powders from the grinding of plants with a plant to cement ratio of 2% and a water to cement ratio of 0.5.

4 Results and Discussion

The heat flow curves obtained by isothermal calorimetry are shown in **Fig. 4** for mixes containing CEM I, with the gray curve corresponding to the unmodified paste.

From the graphs in **Fig. 4** and according to the literature [16–18], a strong heat release is visible when the samples are introduced into the calorimeter, which masks the beginning of the reaction, i.e. the rapid dissolution and release of calcium, silicate, aluminate, sulfate and alkali ions into the mixture. Then, the flux is minimal, which corresponds to the induction period. In the third stage, the heat flux increases due to the precipitation of portlandite and C-S-H, formed by the hydration of silicates, especially C3S.

The maximum of the main hydration peak is reached about 9 hours after mixing for CEM I paste. Afterwards, the heat flux decreases, due to the deceleration of the reactions because of the hydrate layer which thickens with time on the surface of the anhydrous cement grains and limits the diffusion of water.

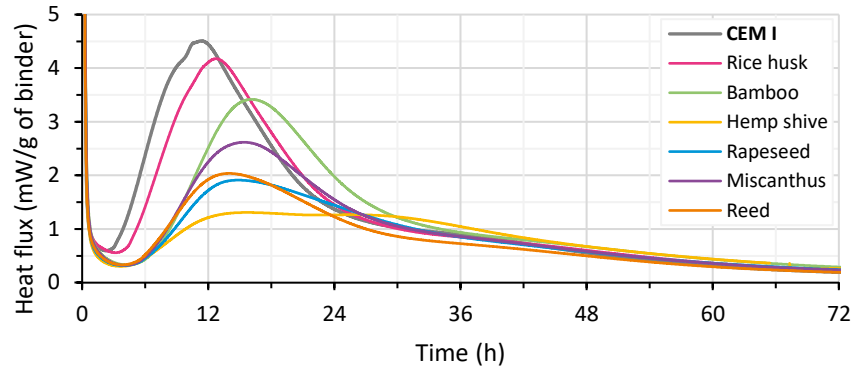


Fig. 4. Heat flux of CEM I pastes

We note a great difference between the curve corresponding to CEM I and the curves obtained for cement pastes containing vegetal powders, which illustrates the modification of the hydration kinetics. A shift of the peaks is observed along the two axes: the addition of plants in CEM I causes a shift of the maximum of the heat flux peaks towards longer times as well as the decrease of the maximum value and the widening of the exothermic peak. In the case of hemp shives, two overlaid peaks are visible, which seems to correspond to the heats of reaction of two types of hydrates, silicates and aluminates, while a shoulder is visible for the other plants.

The setting delays of the cement pastes containing vegetal powders compared to CEM I can be assessed by the position of the maximum value of heat. It varies from a little more than one hour for rice husk to almost five hours for bamboo and hemp shive.

The heat flow curves obtained for the CEM IV pastes are shown in **Fig. 5**, with the gray curve corresponding to the paste without the plant addition.

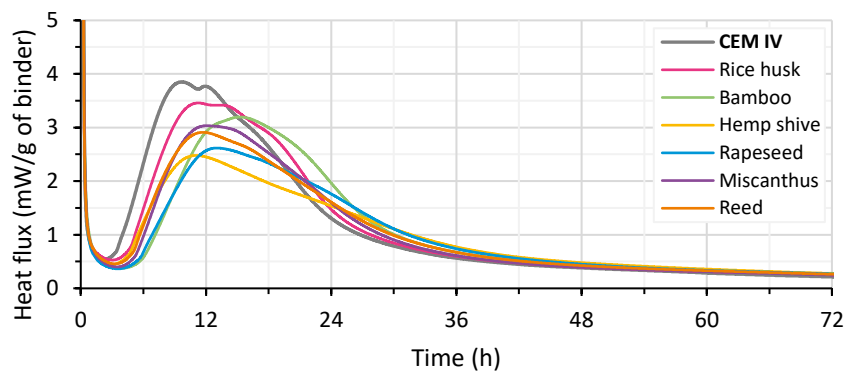


Fig. 5. Heat flux of CEM IV pastes

For mixtures containing CEM IV, the addition of plants has a smaller impact than for CEM I: the shift to longer times is lower and the maximum value of the exothermic peak decreases less. In addition, there is a shift towards longer times of the second peak visible for CEM IV alone, and thus an overall widening of the exothermic peak.

Furthermore, integration of the heat flux curves with respect to time allows the quantification of the cumulative heat during hydration of the cement paste. The results obtained for CEM I and CEM IV are presented in **Fig. 6**. The curve with the highest values is for the cements without additions. The presence of vegetal powders reduces the rate of hydration during the first 5 days. It can therefore be deduced that they also reduce the quantity of hydrates formed.

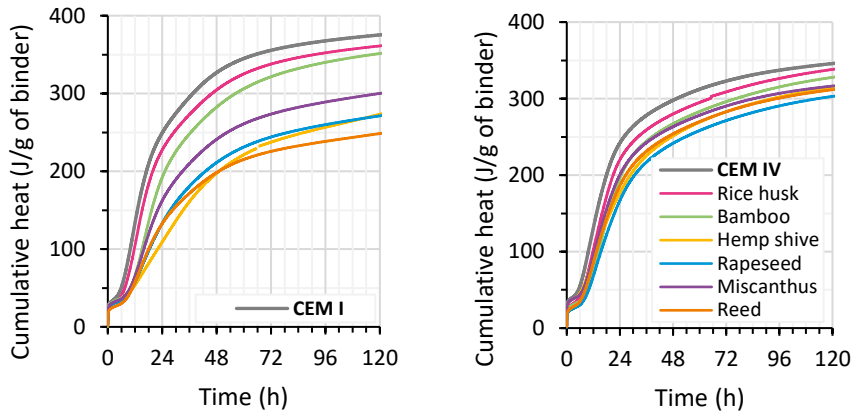


Fig. 6. Cumulative heat of CEM I and CEM IV pastes

After five days (120 h), the cumulative heat of the CEM I hydration reaches at least 90% of that of cement alone for rice husk and bamboo, whereas it is lower for the other plants, down close to 65% for reed. An explanation for the reduced impact of rice husk could be its high content of mineral compounds. Indeed, the particles contain between 12% and 20% silica depending on the supplier. This specificity could lead to a better chemical compatibility of rice husk with mineral binders. In the case of bamboo, the difference of the position of the main peak maximum, that can represent the setting delay, is the highest. However, after five days, the cumulative heat of hydration is more than 90% of that of the cement. This result shows that not only the setting delay should be considered, but also the global hydration phase of the binder.

Moreover, for the cumulative heat, the difference in the influence of the plants' addition on the two cements is more pronounced than for heat flows. For CEM IV, the addition of plants also reduces the rate of hydration, but in a smaller proportion, so that all curves are closer to the reference curve compared to the CEM I graph.

5 Conclusions and Perspectives

The results presented in this paper illustrated the influence of adding plants of different species to Portland and pozzolanic cement pastes by isothermal calorimetry measurements. In general, the curves of the cement's pastes containing the plants are time-shifted in comparison with the reference, which shows a delay in the setting of the cement. Moreover, the curves are also flattened and widened.

Rice husk is the plant that modifies the hydration kinetics the least, followed by the bamboo, while other plants, such as hemp or reed, have a more pronounced effect. The characterization of the bio-physical-chemical properties of the plant aggregates will allow to better understand these results.

However, the same plants added in CEM I and CEM IV have different influences on the hydration kinetics of these cements. This shows that the chemical composition of the cement is also very important. Therefore, in the future works, a more detailed investigation of the hydrates' formation for both cements, also in presence of the plants, is planned with XRD and TGA for example. More mineral binders with different physicochemical composition will also be studied, as well as plants of different geographical origin, year of production and genotype.

Thanks to the evaluation of the mechanisms and kinetics of hydration of the binders according to the composition of the plant aggregates, it will be possible to define an indicator of mineral-plant compatibility which will make it possible to guarantee the performances of the plant concretes produced and to widen the formulation of these materials to all types of plants and mineral binders in order to be able to also optimize their environmental impact.

6 Acknowledgment

This work was carried out within the framework of the ANR BIO-UP project supported by the Agence Nationale de Recherche (ANR-21-CE22-0009).

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