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The influence of wood aqueous extractives on the hydration kinetics of plaster

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Abstract

The influence of wood aqueous extractives on the hydration of plaster is discussed in this paper. Two species were chosen: poplar and forest pine, and the effect of a thermal treatment, which acts as a dimensional stabiliser for wood, was considered. Calorimetric measurements prove that delays of the setting must be expected, especially for the retified poplar. Conductimetric experiments show that wood extractives seem to act as a retardant of the nucleation phase of the hydration reaction. The chemical analysis of the extracts reveals the presence of acetic acid and phenolic molecules, but other experiments prove that their action is not sufficient to explain the retarding effect. Special attention should be given to the influence of polyphenolic substances known as tannins.

Keywords:

Hydration; Kinetics; Plaster; Retardants; Wood extractives

I. Introduction

The reinforcement of mineral binders (cement, concrete or plaster) has been a matter of major concern for several decades. Since then, efforts have been made to replace the usual mineral reinforcing agents (glass or asbestos fibres) by organic agents such as sisal, Kraft pulp, or cellulose fibres [7] and [8].

The use of 'raw' ground wood was also investigated [5] and [6]. Authors concluded that wood may release organic substances (called 'extractives') which could delay the setting of cement [11], [12], [13] and [14]. In some other cases, it was even impossible for the cement to set. But few studies considered the case of plaster–wood composites.

The hydration mechanism of calcium sulphate hemihydrate (commonly known as 'plaster') [10] remains incompletely explained. Therefore the influence of various substances was merely observed, [1] and [2] and few explanations can be found in the literature.

The pH of the hydrating liquid is known to have an influence on the kinetics [4], but Singh *et al.* [11] showed that it depends on the nature of the considered substance (in this case, various acids).

This paper describes our attempt to observe the influence of wood aqueous extractives on the hydration kinetics of plaster, to determine the reaction stage whose kinetics are modified by the extractives and to relate this to the molecular structure of the involved substances.

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The delays in the hydration kinetics of plaster were observed by means of isothermal calorimetry. Isothermal conductimetry and a technique coupling gaseous phase chromatography and mass spectrometry allowed us to investigate on the nature of the retardants and their mode of influence.

II. Experimental Procedures

II.1. Samples preparation

Wood is a three-dimensional polymeric composite made of cellulose, lignin and hemicelluloses, with a small amount of extractives and ashes. The Centre SPIN developed a thermal treatment under neutral atmosphere called retification. A mild pyrolysis of wood mainly cracks hemicelluloses and begins to modify lignin. By-products of hemicelluloses pyrolysis condense and polymerize on lignin chains, hence the notion of reticulation (creation of chemical bonds between polymeric chains) which gave its name to "retification" (an abbreviation between reticulation and torrefaction). These reactions create a new "pseudo-lignin" which is more hydrophobic and rigid than the initial one. An infrared spectroscopy study has indeed revealed a modification of chemical bonds in treated wood: the number of oxygen containing groups (mainly hydroxyl groups) decreased while the number of C=C double bonds increased. Cellulose crystallinity does not seem to be affected [3].
Experiments are carried out in a batch pilot-scale reactor (300 l). It's basically a forced convection kiln with electric heating up to 240 °C. Retification consists in a progressive heating of wood boards up to pyrolysis temperature, followed by a rapid cooling (via an air driven double shell) to ambient temperature. The resulting retified wood is more resistant to biological attacks (fungi, insects), less hydrophilic and less subject to shrinkage or swelling when placed in a wet atmosphere.
Such a material may prove to be a valuable reinforcing agent for a mineral binder, therefore the influence of its extractives was also observed.
Two wood species were chosen: maritime pine (*Pinus pinaster*) and poplar (*Populus*). One half of each was treated by the process described above, then the materials were ground with a lab grinder.
Wood extracts were prepared with various water / wood ratios in order to observe the influence of concentration. Ten grams of ground wood were dipped in ultrapure water for 1 h under magnetic stirring.
The mixture was then filtered on a Büchner funnel, and the resulting aqueous extract was refrigerated until the experiments took place. A common plaster from Lafarge Company of commercial grade was chosen. Table 1 shows chemical composition of plaster. This plaster was obtained from gypsum dehydration in oven at 126 °C for 70 min. Table 1 shows mineralogical composition of gypsum extraction.

II.2. Calorimetry

We used a Setaram C60 Calvet calorimeter with an electrical accessory allowing us to stir the mixture between plaster and wood extracts.
The aqueous extracts / plaster ratio was equal to 1 and we chose to stir the mixture for 2 min after putting them in contact. The sample temperature was maintained at 25 °C during the experiment.

II.3. Conductimetry

Isothermal conditions were provided by a double-shell flask and a circulation of water maintained at 25 °C. A liquid / plaster ratio of 20 was chosen and the mixture was continuously stirred by a magnetic stirrer during all the experiment. The data were acquired through a Tacussel CD78 conductimeter.

II.4. Coupled GPC/MS analysis

We used a Shimadzu GC-17A gas chromatograph coupled with a QP-5000 mass spectrometer which acts as a detector and analyses the compounds at their exit.

A polar column (length: 30 m, diameter: 250 µm) was used with an injector set at a split of 1/4 and a temperature of 240 °C.
The data were acquired and processed by a commercial software with mass spectra libraries, which allowed the elucidation of the molecular structures of the extracts.

III. Results and discussions

III.1. Isothermal calorimetry

Figure 1 shows examples of typical measurements obtained for the hydration of calcium sulphate hemihydrate by plotting the heat flow per unit mass of solid versus time. The first exothermic phenomenon is the dissolution of plaster in the liquid immediately after contact and stirring. The heat flow then decreases to zero during a certain time when no reaction is observed. Gypsum nucleation is suspected to take place at this stage of reaction.
The bell-shape curve represents the hydration reaction itself: the ascending branch corresponds to simultaneous gypsum crystal growth and plaster dissolution, the peak time corresponds to total depletion of plaster, whereas further crystal growth occurs during the last part of the curve.
The results show clearly that the forest pine extracts have a delaying effect on the hydration of hemihydrate (see Figure 1).
The peak time increases with the wood / water ratio, which means that the retarding influence depends on the concentration of extracts. Few differences between treated pine and natural pine can be observed.
The results obtained for poplar show noticeable differences between the influence of natural wood and treated wood extracts (see Figure 2).
The natural poplar extracts induce a slight delay of the kinetics and no noticeable dependence on the concentration while the retified poplar extracts have the most intense retarding effect of all our samples.
The discrepancies between these species are summarised in Figure 3 where the peak times are plotted against the wood / water ratio of the extracts. It is obvious that only poplar shows a different behaviour when heat treated.

III.2. Conductimetry

Typical curves obtained by this method are shown on Figure 3. The dissolution of plaster first induces the presence of calcium and sulphate ions in solution, therefore a sharp increase of the conductance.
Then a plateau stage occurs, which corresponds to the apparently non-reactional phase observed in calorimetric measurements; no change in the solution conductance means that no plaster is further dissolved, and no ion is consumed in any crystal growth mechanism. Once again, nucleation is suspected to occur in this phase.
The conductance then decreases as the ions are consumed by gypsum crystal growth while more plaster is dissolved until depletion (at the inflection point of the sigmoid curve).
The final value of the conductance corresponds to the solubility of plaster (around 2 g/l).
Figure 3 confirms the calorimetric observations; the treated poplar extracts have the most intense retarding effect on the kinetics. Furthermore, the curves show that the nucleation kinetics seem to be slowed down by the extracts (of both natural and retified wood), as the plateau phase is longer and the slope of the curve in the early stages of crystal growth decreases.
The final conductance increases, which may lead to the conclusion that the solubility of gypsum is also increased; but other measurements showed that the initial conductances of the wood extracts have non-null values. Wood extracts have an acid pH (between 4 and 6) therefore they contain ions which raise the conductance of the solution. The pH of the system does not have a direct influence on hydration, but it defines the efficiency of a given retardant [11].

These experiments show that natural poplar releases organic compounds which act as retardants for the hydration of plaster, and that the thermal treatment produces higher quantities of those compounds or other molecules whose effects are more intense.
This points out the interest of the chemical analysis of the aqueous extracts.

III.3. GPC/MS analyses

Figure 4 shows the GP chromatogram of the natural poplar extract for a wood / water ratio of 1 / 9. Only one relevant peak is observed, it corresponds to the acetic acid (identified by mass spectrometry).
Figure 5 puts the stress on the fact that the retification treatment drastically modifies the chemical composition of the extractives. Peak 1 corresponds to acetic acid, but in a higher concentration than in the natural poplar extracts (the figures are not at the same scale).Peak 2 represents propanoic acid, peak 3 phenol, and peaks 4–10 represent various phenolic molecules (among them, vanillin) produced by the cracking of lignins during the treatment.

III.4. The influences of separated extracts

The increase of the concentration of acetic acid in the extracts due to the treatment could account for an increased retarding effect. Aqueous solutions of acetic acid, phenol and phenolic compounds were then prepared, and their influence on the hydration kinetics was observed by conductimetry.
Figure 6 shows that the presence of acetic acid has an influence on the plateau and final values of the solution conductance, but has no influence on the plateau duration and the crystal growth initial slope.
This leads to the conclusion that other agents induce the observed delays.
Figure 7 shows the influence of aqueous solutions of phenol. The plateau conductance and the germination rate seem to be slightly decreased. But once again, no such delays as those induced by the treated poplar extracts are observed.
Figure 8 shows the influence of a mixture of phenolic molecules, each in a concentration of 1 g/l:

- vanillin
- guaiacylaceton
- syringaldehyde
- 4-hydroxy 3, 5 dimethoxy benzaldhyde

corresponding to peaks 6–9 in Figure 5.These experiments show that all the considered phenolic substances (including phenol itself) have the same influence on the kinetics.
This leads to the conclusion that the influences of the separated extracts do not account for the overall influence of the treated poplar aqueous extracts.
A synergy between acetic acid and phenolic substances may still occur. Therefore, aqueous solutions of a mixture of the previously considered substances were prepared and tested. Figure 9 shows that a slight synergetic effect between the studied substances can be observed, as there are noticeable delays of the kinetics.
However the influence of such a mixture, referred to as 'synthetic extract', is not similar to the one observed with the extracts themselves.
This leads to conclude that other substances, that were not detected by our GPC experimental procedure, are involved in the kinetic delays. Special attention should be given in further studies to polyphenolic molecules, also known as tannins, which are able to create complex ions with calcium [9].

IV. Conclusions

1. A noticeable influence of the poplar and forest pine aqueous extracts on the hydration kinetics of calcium sulphate hemihydrate was observed by calorimetry. All of them

induced delays of the reaction, however poplar extracts have an unexpected behaviour, depending on the wood being thermally treated or not, retified poplar extracts having the most intense effect.

2. Conductimetry studies showed that the extractives seem to delay the nucleation of gypsum in the system, leading to an overall delay of the reaction.
3. The aqueous extracts of treated poplar were the most efficient retardants.
4. The chemical analysis of the extracts showed the presence of acetic acid in various quantities, and enlightens the presence of the thermal treatment by-products, namely phenol and phenolic molecules in the treated poplar extracts (along with an increase of the acetic acid concentration).
5. A comparative study of the influence of these by-products led to the conclusion that neither acetic acid nor the phenolic compounds are the principal retarding agents.

Only a slight synergy between these compounds was observed, which means that the true retardants were not detected by our GPC protocol. The presence of trace elements such as tannins may account for the kinetic delays that were observed.

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Figures

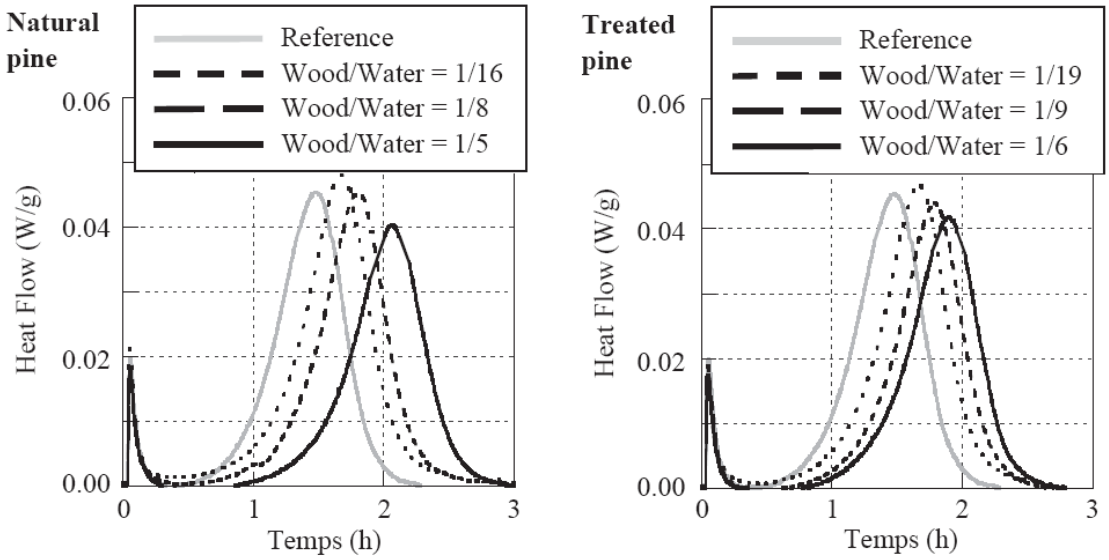


Figure 1: The influence of the forest pine / water ratio on the hydration kinetics of plaster.

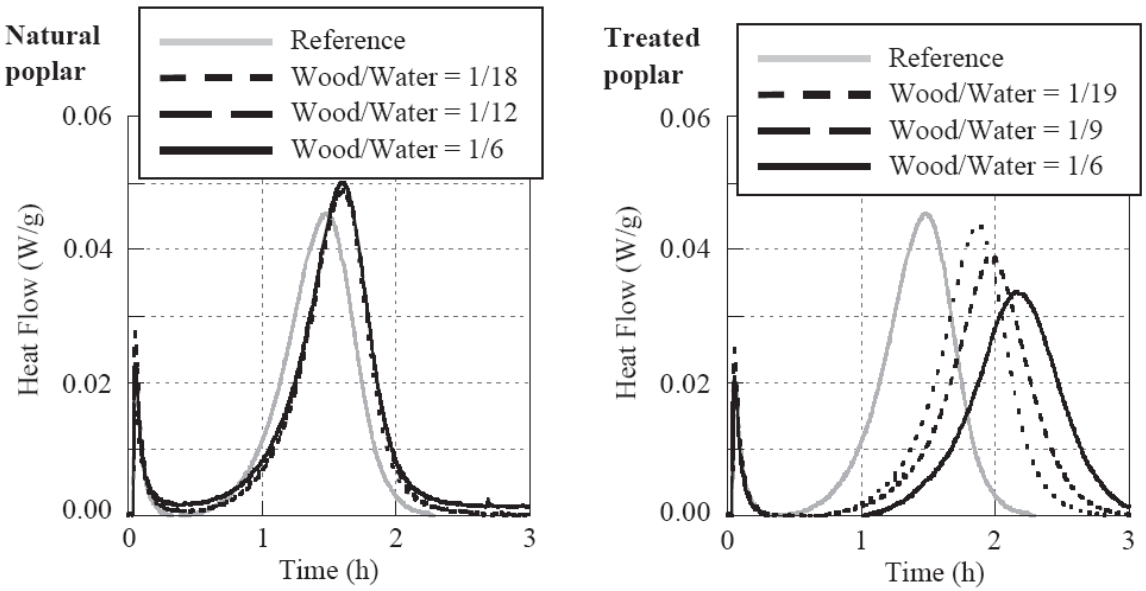


Figure 2: The influence of the poplar / water ratio on the hydration kinetics of plaster.

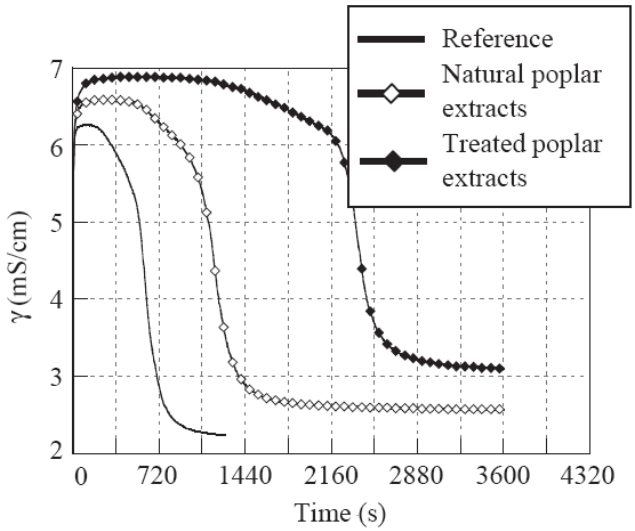


Figure 3: The influence of the poplar extracts on the hydration kinetics of plaster—conductimetric analysis.

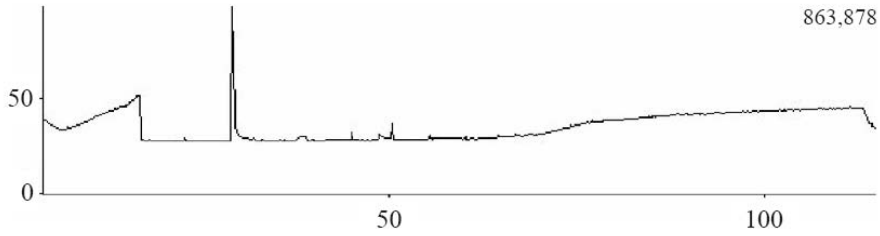
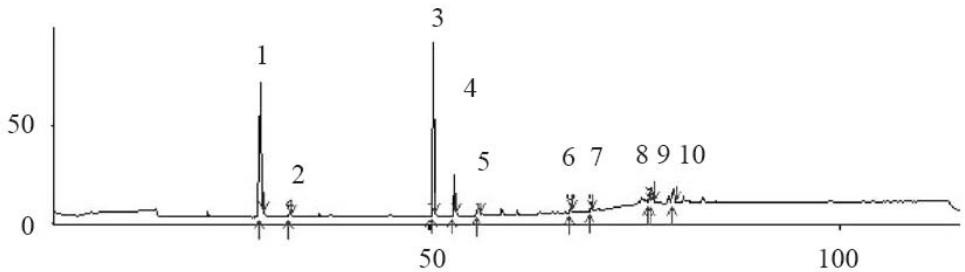


Figure 4: Gaseous phase chromatogram of the natural poplar aqueous extracts.



Peak number	Retention time (min)	Compound name
1	29	Acetic acid
2	33	Propanoic acid
3	50	Phenol
4	53	Pentanal
5	56	Allyl butyrate
6	67	Vanillin
7	69	Guaiacylaceton
8	76	Syringylaldehyde
9	77	4-hydroxy 3,5 dimethoxybenzaldehyde
10	79	Syringyl acetone

Figure 5: Gaseous phase chromatogram of the treated poplar aqueous extracts.

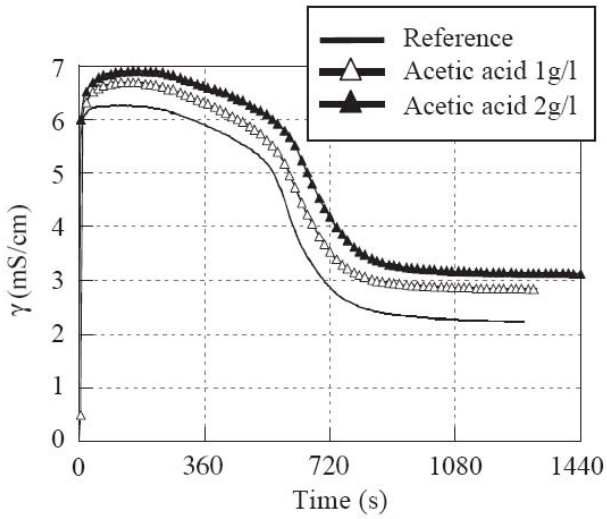


Figure 6: The influence of acetic acid aqueous solutions on the hydration kinetics of plaster.

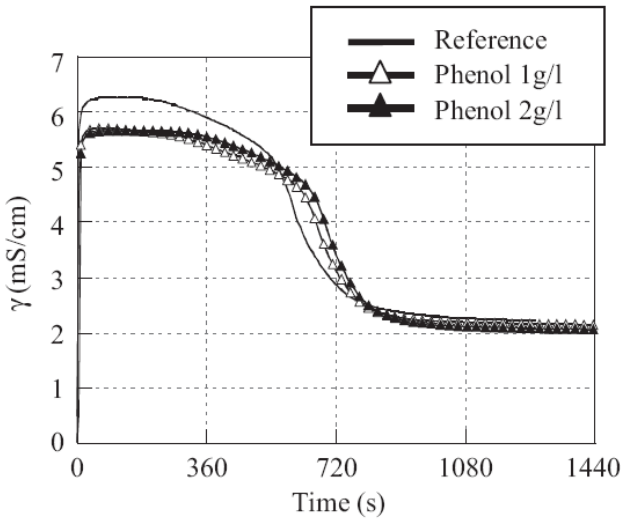


Figure 7: The influence of aqueous solutions of phenol.

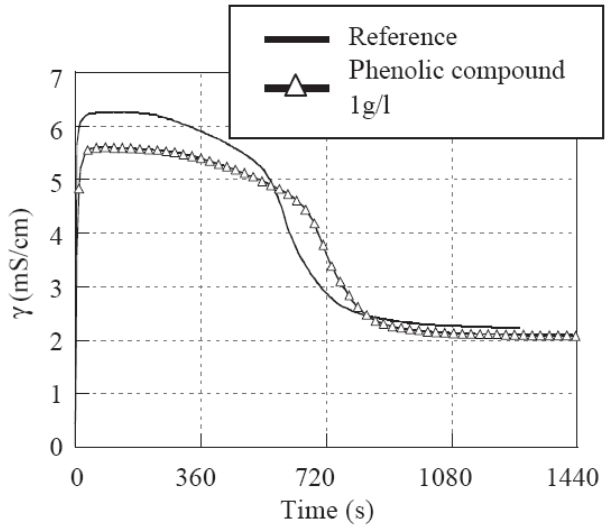


Figure 8: The influence of aqueous solutions of phenolic substances.

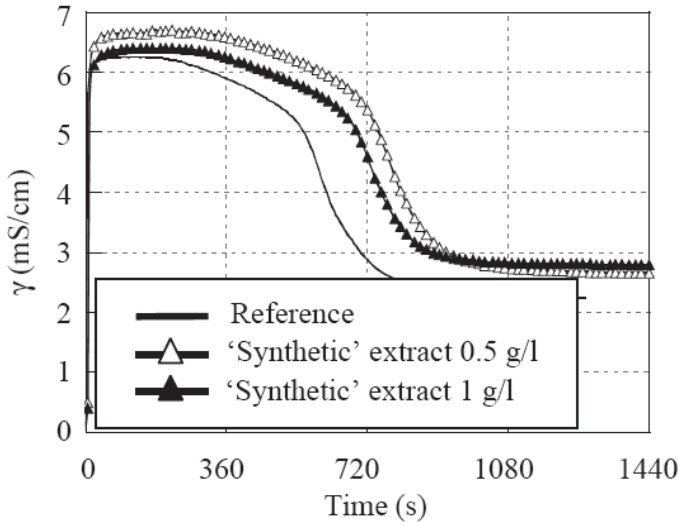


Figure 9: The influence of aqueous solutions of a mixture of the most common molecules detected.

Tables

Table 1: Chemical composition of gypsum and plaster

Component	Weight (%)
Gypsum	
$CaSO_4, 2H_2O$	89.70
$CaSO_4$	0.65
$SrSO_4$	0.85
$CaMg(CO_3)_2$	6.60
$Ca(Fe, Mg)(CO_3)_2$	0.45
SiO_2	1.75
Plaster	
$CaSO_4$	11.30
$CaSO_4, 2H_2O$	0
$CaSO_4, 1/2H_2O$ Purity	88.23