Effects of two types of waste wood species on the hydration characteristic of Portland cement

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Effects of Two Types of Waste Wood Species on the Hydration Characteristic of Portland Cement

Zhiqiang Dong,1 Youming Yu2*,4, Pingan Song3*,4, Lingfei Ma2,4 and Fengzhu Lu3,4

Abstract

Despite much work on wood-cement composites, effects of wood species on the hydration of cements remain unclear until now. Thus, we herein investigated systematically effects of two typical wood species wastes on the hydration of Portland cement in this work. It was found that adding the poplar flour prominently affects the formation of the calcium silicate hydrate gel (C-S-H gel) delaying the hydration process, while the Chinese fir flour hardly retards the process due to different components. Compared with the neat cement, addition of both wood flours makes it easier to generate the ettringite. Besides, another important hydration product, calcium hydroxide Ca(OH)₂, requires much longer time to form in the presence of both wood flours during hydration relative to the neat cement, e.g. nearly double time for the poplar-filled cement system. The findings provide useful information for extending the potential application of wood flours waste in cement composites.

1. Introduction

Recently, people have increasingly paid more attention to the sustainability in their production processes and made greater efforts to reduce the carbon footprint on our biosphere. Therefore, it has become a research focus that utilizing as many green materials as possible by adopting the environmental friendly processing methods. The concept that utilizing the waste from other industrial activities as the raw material has already be a significant consensus (Soroushian et al. 2004; Qi et al. 2006). Nowadays, wood wastes are widely used for manufacturing wood-cement composites (Torkaman et al. 2014; Ashori et al. 2012). However, there are still some problems extremely restricting the development of wood cement composites, such as high variation in the compatibility of wood species mixed with cement components and the inhibitory effect of some wood species on cement hydration (Matsushita et al. 2003). It is widely accepted that wood materials do not react with cement (Hachmi et al. 1990) and different wood species hold different components and contents, thus resulting in significantly different effects in inhibiting the formation of hydration products (Fan et al. 2012). Moreover, the complex chemical and physical interactions between wood and cement components also have a significant influence on the property of the wood-cement composites (Nazerian et al. 2011). Therefore, it is rather necessary to clarify how wood species affect the hydration of the cement system.

In order to determine the hydration behavior, some researchers attempted to analyze the effect of wood species on the hydration characteristic of cement via measuring the cement hydration heat and the hydration rate (Wei et al. 2000; Ashori et al. 2011). Semple et al. (2002) found that inhibitory effects could be diverse when the cement was mixed with different wood species. However, there are still some problems extremely restricting the development of wood cement composites, such as high variation in the compatibility of wood species mixed with cement components and the inhibitory effect of some wood species on cement hydration (Matsushita et al. 2003). It is widely accepted that wood materials do not react with cement (Hachmi et al. 1990) and different wood species hold different components and contents, thus resulting in significantly different effects in inhibiting the formation of hydration products (Fan et al. 2012). Moreover, the complex chemical and physical interactions between wood and cement components also have a significant influence on the property of the wood-cement composites (Nazerian et al. 2011). Therefore, it is rather necessary to clarify how wood species affect the hydration of the cement system.

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This work aims to systematically investigate the effect of wood species on hydration characteristics of Portland cement by determining the changes of microstructure and morphology as well as the evolution chemical compositions during the hydration process of...
the wood-cement system. Herein, we chose the wastes of two typical wood flours (Chinese fir, poplar) in China as fillers, with the hope of providing useful information for extending their potential application in cement composites.

2. Materials and methods

2.1 Materials

The wood waste of poplar and Chinese fir were collected from Lin’an lumber market of Zhejiang province (China). The chemical composition of these two wood waste are shown in Table 1. In addition, among the pentosane there are many sugar and sugar acid. These organic molecules can dissolve in alkaline solution. To obtain the content of total soluble sugar, we extracted these two wood wastes using 1% aqueous solution of NaOH at 50°C for 2 hours. The total soluble sugar (sugar and sugar acid) content were determined by anthrone spectrophotometric methods under room temperature. The content of total soluble sugar are shown in Table 2. The Portland cement used in this study was purchased from Shanggan cement plant of Lin’an, with its chemical compositions and mineral compositions listed in Table 3.

2.2 Sample fabrication

After being cut into thin rod-like matches, the air-dried wood waste was then ground into small powders using a plants crusher and screened with sieves and only the wood powders with a size range of 20-40 mesh were collected. As collected wood flours were subsequently further dried in an oven at a constant temperature of 103 ± 2 °C until the mass remained constant followed by storing in a dry dish for use.

Before the determination, about 200 g cement and 15 g wood flours were mixed uniformly in a beaker, and then blended with 90.5 g distilled water for 2 min. After that, the mixtures were aged for 30 min, 2h, 4h, 8h, 12h, 1d, 3d, 7d, 15d under the ambient condition of 20 ±1°C. In each stage, the central part of samples was added into the mortar containing ethanol, grounded and then soaked for 2-3 hours until the hydration process was completely stopped. After removing alcohol with a drainer, dried samples were stored in the sealed vials for further use. In addition, the neat cement sample was also fabricated under the same condition as a reference.

2.3 Characterization

The microstructure of the wood-cement composites and pure cement were observed on a scanning electronic microscope (SEM, Shimadzu SS-550) at an accelerating voltage of 15kV. The infrared spectra were recorded in a wavenumber range of 400-4000cm-1 using a Fourier transforms infrared (FTIR) spectroscopy (IR-Prestige-21, Shimadzu). Samples were ground with potassium bromide (KBr) and then compressed into small pellets.

For X-ray diffraction (XRD) analysis, only the specimens that passed the 80 mesh sieve were used. The XRD test was performed on a XRD-6000 (Shimadzu) analyzer with the Cu radiation (40kv and 30mA). The scanning 20 ranged from 10 ° to 70 ° at a step of 2°/min.

For the simultaneous thermal analysis (STA 409 C, NETZSCH Company, German), The specimens that passed the 80 mesh sieve were measured by heating from room temperature to 900 °C at a heating rate of 10 °C min-1 under nitrogen atmosphere.

3. Results and discussion

3.1 Cement hydration mechanism

It is well known that the Portland cement mainly contains four kinds of mineral components, namely tricalcium silicate (3CaO·SiO2 or C3S), β-dicalcium silicate (β-2CaO·SiO2 or β-C2S), tricalcium aluminate (3CaO·Al2O3 or C3A) and tetracalcium aluminoferrite (4CaO·Al2O3·Fe2O3 or C4AF). Previous studies have shown that C3S generally reacted rapidly with water. Upon contacting water, the calcium silicate hydrate gel (xCaO·SiO2·yH2O or C-S-H) and crystalline calcium hydroxide [Ca(OH)2 or CH] formed immediately (Pereira et al. 2006). However, the C-S-H may reside on the surface of the unhydrated cement particles, thus restricting the hydration reaction. Besides, the reaction between β- C2S and water is normally slow, mainly due to its more compact crystal structure than C3S. Moreover, a large number of studies have showed that the

<table>
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<tr>
<th>Chemical composition</th>
<th>Chinese fir</th>
<th>poplar</th>
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<tbody>
<tr>
<td>hot water extractives /%</td>
<td>3.43</td>
<td>2.25</td>
</tr>
<tr>
<td>benzene-alcohol extractives /%</td>
<td>2.53</td>
<td>1.94</td>
</tr>
<tr>
<td>Acid-insoluble lignin /%</td>
<td>32.87</td>
<td>17.04</td>
</tr>
<tr>
<td>Pentosane /%</td>
<td>10.16</td>
<td>22.71</td>
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<tr>
<td>Cellulose /%</td>
<td>48.31</td>
<td>47.64</td>
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<table>
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<th>Table 2 Content of total soluble sugar.</th>
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<td>total soluble sugar /%</td>
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<tr>
<th>Chemical compositions (%)</th>
<th>Mineral compositions (%)</th>
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<tr>
<td>SiO2: 22.4</td>
<td>Al2O3: 5.02</td>
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C₃A can also react with water speedily accompanied with a large amount of heat release to create crystalline C₃A·6H₂O.

### 3.2 X-ray diffraction analysis

Figure 1a shows the XRD results for neat cement after hydration 30min, 2h, 4h, 8h, 12h, 1d, 3d, 7d, 15d. The diffraction peaks the hydration product, CH located at 2θ of 18.0º and 47.2º, can be detected until 2h of hydration reaction (Fan et al. 2012). After 4h the CH peaks become increasingly obvious. With hydration, the content of CH in hydration products continues increase while the calcium silicate (β-C₂S and C₃S, with the diffraction angle 28º<2θ<35º) significantly reduces. In comparison, the CH diffraction peak of the mixture filled with the Chinese fir flour appeared until the sample was aged for 8h. The change trends of contents both CH and calcium silicate are similar to those of neat cement but at a slower rate, as shown in Fig. 1b. This indicates that the presence of Chinese fir powder delays the hydration process of cement to some extent. Figure 1c presents that gypsum (the peak located at a 2θ of 11.0º) was still present after 12h of hydration reaction (Pereira et al. 2006). As for gypsum in poplar-cement system, it can hardly be detected even after 30 min of hydration reaction in the neat cement and Chinese fir-cement system, suggesting that the gypsum in the system has been consumed at the initial hydration stage. In addition, though the peak of CH can be found, its intensity is very weak after hydration for 12h. Meanwhile, the characteristic peak of the calcium silicate was still slightly intenser than that in the neat cement and Chinese fir-cement system. Until 1d later, the content of CH increases with hydration, and the change tendency of the calcium silicate is similar to that of other samples, demonstrating that the hydration of C₃S and β-C₂S in the cement-poplar system was remarkably inhibited relative to these in the cement-Chinese fir system and neat cement system.

Many studies have already confirmed that the soluble sugar and sugar acid can cause prominent inhibition during the cement hydration stage (Monosi et al. 1983; Previte et al. 1971; Ma et al. 2015). At the initial stage of hydration, the complex formation between Ca²⁺ and organic molecules (e.g., sugar) will lead to a lower level of Ca²⁺ in solution (Miletone. 1979), so that an inhibition can be observed in the wood-cement mixture. Also, such a low level of Ca²⁺ will slow the reaction between calcium silicate and water, thereby slowing down the growth of CH. It should be noted that the poplar has much more extractives and soluble sugar than Chinese fir (see Table 2), suggesting a stronger inhibition effect in poplar-cement system.

### 3.3 Simultaneous thermal analysis

It has been shown that the Portland cement hydration products were primarily C-S-H gel, Ca(OH)₂ and ettringite (AFt). The decomposition peak of C-S-H gel and AFt takes place between 100ºC and 120ºC, while the endothermic peak of Ca(OH)₂ lies between 450ºC and 500ºC (Pereira et al. 2006). As shown in Fig. 2a, after being aged for 30min, it can be noticed that there is an obvious endothermic peak appearing between 100 ºC and 120 ºC for the poplar-cement mixture, while it was nearly invisible for the sample containing Chinese fir and neat cement system. This suggests that more AFt is produced for the sample mixed with poplar as compared with neat cement and Chinese fir-cement system at the initial stage of Portland cement hydration. The amount of ettringite formed is enhanced at the initial stage of hydration. And the Aft can be detected at the end of 2h curing in neat cement system and cement-Chinese fir system (see the fig. 2b). In addition, for the decomposition peak of gypsum (the peak located at around 135 ºC), it can be easily detected at poplar-cement system as compared with neat cement and Chinese fir-cement system in Fig. 2a. The peak starts to turn unobvious after the poplar-cement system was cured for 12h, indi-
cating that the addition of poplar flour inhibits the consumption of gypsum. With hydration, the decomposition peak of ettringite will overlap that of C-S-H in the poplar-cement system and Chinese fir-cement system due to the formation of C-S-H gel (see Fig. 2c). Suhua Ma believes that less than 0.03% gluconate promotes the formation of ettringite and stabilizes the AFt at the early age. With the dissolution of the sugar and sugar acid from the wood wastes, the increasing content of these organic molecules will significantly retard the reaction between C₃A and gypsum. Some studies also confirmed that the soluble sugar acid and soluble sugar will prevent the dissolution of gypsum and be adsorbed on the surface of C₃A after their complexion with Ca²⁺ (Milstone, 1979; Ma et al. 2015).

Neat cement displays an endothermic peak between 450 °C and 500 °C after 2h of hydration, indicating the formation of Ca(OH)₂. Compared with neat cement, the endothermic peak appeared after 8h for the cement-Chinese fir system and after 1d for the cement-poplar system (see Fig. 2d to Fig. 2f). In the same hydration period, neat cement exhibits the largest endothermic

![Fig. 2 DTA curves of cement-poplar mixture, cement-poplar mixture and neat cement hydration, a: 30min, b: 2h, c: 4h, d: 8h, e: 12h, f: 24h.](image-url)
peak of Ca(OH)$_2$ while the cement-poplar showing the smallest one. Meanwhile, the Ca(OH)$_2$ endothermic peak of cement-poplar mixture increase slightly more slowly than that of other systems (see Fig. 3), indicating that the poplar wood powder has more noticeable restricting effect on the generation of Ca(OH)$_2$ (or on cement hydration) relative to Chinese fir. Obviously, the STA result is well consistent with the results obtained from XRD measurements.

3.4 Spectroscopic analysis

FTIR spectra of neat cement, Chinese fir-cement and poplar-cement at the different hydration ages are shown in Fig. 4. At the initial stage of hydration, two obvious vibration peaks at 925 cm$^{-1}$ and generate rapidly, which are associated with the absorption peaks of C-S-H (Peschard et al. 2004; Mollah et al. 2000), respectively. With the progress of hydration, the absorption peak at around 970 cm$^{-1}$ becomes growingly wider, suggesting that the ratio of n(Ca)/n(Si) during the formation of C-S-H increases gradually. After hydration for 4h, the absorption peak shifts from 925 cm$^{-1}$ to 970 cm$^{-1}$ gradually, indicating the formation of C-S-H (Ylmén et al. 2009). In addition, at the of 4h of curing the absorption peak at 3640 cm$^{-1}$ belonging to the stretching vibration of hydroxyl groups (O-H) appears and the intensity increases (see Fig. 4a) with hydration, clearly indicating the content of the Ca(OH)$_2$ gradually increases in the neat cement system. Obviously, the FTIR result is well consistent with the results obtained from XRD and STA measurements.

Figures 4b and 4c show the FTIR spectra of the wood-cement mixture during different hydration periods. Although the hydration process of the wood-cement mixture is similar to that of neat cement, the wood-cement mixture exhibits a much slower transformation speed evidenced by the absorption peak at 925 cm$^{-1}$ to the one at around 970 cm$^{-1}$, especially exhibited in the cement-poplar system. Besides, the absorption peak at 3640 cm$^{-1}$ belonging to the stretching vibration of hydroxyl groups (O-H) appears much later than the one at neat cement system. Thus, FTIR results obviously show that the presence of two wood species do have an inhibiting effect on cement hydration.

3.5 Scanning electron microscopy analysis

As previously stated, the primary hydration products of the Portland cement is calcium aluminate hydrate (C$_3$A·6H$_2$O), calcium silicate hydrate (C-S-H), calcium hydroxid (Ca(OH)$_2$), calcium ferrite hydrate (C$_3$F·6H$_2$O) and calcium sulfoaluminate hydrates. And there are two types of hydrated calcium silicate, namely the gel and crystalline one. Among all hydration products, approximately 70% is C-S-H gel with the unfixed chemical component. Fig. 5 shows SEM micrographs of general appearances of neat cement system in different hydration periods. At the initial stage of hydration, the coral-like and/or flower-like C-S-H gel has appeared on the surface of cement particles. Meanwhile, a few rod-like crystals of Aft (Wei et al. 2003; Zhou et al.
2000) can be also clearly observed on the surface of cement particle because of the fast hydration speed between C₃A and gypsum. Moreover, the amorphous C-S-H gel can cross-link with the rod-like AFt crystal to form a large but loose skeleton network structure with high porosity. After 12h of hydration, the entire surface of cement particles is basically covered with the hydration products, the crystalline AFt disappeared, and various shapes of C-S-H can be observed. However, after aging 3d, C-S-H gels are transformed into layered sheet crystals. Fig. 6 shows the global appearances of wood-cement system (Chinese fir filled cement) during the different hydration periods. The hydration process is similar to that of neat cement. However, the rod-like AFt crystal can be still observed even after 12h of hydration, obviously indicating that the hydration speed of
the cement-Chinese fir mixture is slower than neat cement. Upon hydration 1d, the surface morphology of the mixture looks similar to that of neat cement.

Figure 7 shows SEM micrographs of appearances of poplar filled cement in the different hydration periods. After 12h of hydration, the rod-like AFt crystal can be still observed on the surface of hydration products. The C-S-H gel does not form in the majority of cement surface until 12h of hydration, clearly means the slower formation of C-S-H gel in the cement-poplar mixture. However, the micro-morphology of cement surface in the cement-poplar mixture is the similar to that of neat cement after 1 or 3d hydration. This indicates that at the initial stage of hydration there are certain compounds that can to some extent inhibit the growth of the crystalline hydration products in the cement-poplar system. Moreover, these compounds can also restrict the formation of the cross-linking C-S-H gel, thus resulting in a weaker intensity of the curved cement. The SEM results also confirm that the sugar and sugar acid in the wood are effective retardation agents for cement hydration.

4. Conclusions

Effects of two typical waste wood flours from Chinese fir and poplar on the hydration of Portland cement were investigated systematically in this work. Two types of wood species have different impacts on the hydration and condensation of Portland cement, especially at the early stage of hydration. Because of the much higher content of sugar and sugar acid in the poplar-cement system, the poplar flour inhibits the hydration process more than the Chinese fir at the initial stage of hydration.

Besides, due to the small amount of sugar and sugar acid in Chinese fir, addition of Chinese fir does not inhibit significantly the growth of crystalline hydration products and the formation of network structure of C-S-H gel, but promotes the formation of AFt crystal. In comparison, the evolution of crystalline products is to some extent inhibited and the network structure of C-S-H gel is more difficult to form in the poplar-cement system. This work helps understand and clarify how different types of waste wood species affect the hydration of Portland cement, and thus contributes to creating advanced green cement-wood composites in the near future.

Acknowledgment

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Reference


