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Study of hydration behavior of wood cement-based composite II: effect of chemical additives on the hydration characteristics and strengths of wood-cement composites

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Abstract The influence of the 30 chemical additives on the hydration characteristics of birch wood-cement-water mixture was determined by measuring the maximum hydration temperature (T_{\max}) and the time (t_{\max}) required to reach the temperature. The chemical additives were tested and divided into two types depending on the pattern of exothermic reaction peak within the 24-h observation period. The wood-cement-water mixtures with additions of each of the 11 type I chemical additives showed a two-peak temperature-time curve similar to that for neat cement. CaCl_2 , FeCl_3 , and SnCl_2 reached the highest T_{\max} above 50°C . When the 19 type II chemical additives were included, the mixtures offered only one peak hydration temperature-time curve. Among them, the 10 chemical additives caused an obvious temperature increase at the beginning of the hydration reaction. The most significant effect was with the addition of diethanolamine, where the mixture produced a T_{\max} above 50°C . The strength values (modulus of rupture, internal bond strength) of wood-cement board were tested with separate additions of the 10 chemical additives arranged by the highest T_{\max} . There was a good positive correlation between T_{\max} and the strength values. In addition, the composite chemical additives were preliminarily examined to determine if they accelerated the hydration reaction of blast-furnace slag cement. The results revealed that composite chemical additives evidently accelerated the hydration reaction and the setting of blast-furnace slag cement mixed with wood. Blast-furnace slag cement can thus be

considered for use as an acceptable inorganic bonding material for wood-cement panel manufacture.

Key words Wood-cement composite · Cement hydration reaction · Inhibition · Chemical accelerator · Blast-furnace slag cement

Introduction

Wood-cement panels (WCPs) and their application in the building industry have been rapidly accepted in many countries as a result of their excellent properties. Compared with wood-based particleboard, in which there were conventional problems associated with urea- and phenol-formaldehyde, WCPs have high fire, insect, and fungal resistance in addition to good weatherability and acoustic insulation.¹⁻⁶ These desirable qualities could provide a larger potential market and application field in the predictable future.

However, some problems still impede the development of wood-cement composites, including high variation in the compatibility of wood species mixed with cement due to soluble sugar and extractives⁷⁻¹¹ and the effective chemical additives required to overcome the inhibitory properties of wood.¹²⁻¹⁵ The influence of soluble sugar and extractives in wood results in board strengths being highly sensitive to a change of wood species.¹⁶⁻¹⁸ Furthermore, because ordinary portland cement is more expensive than wood particles, it is a costly component and is responsible for a high proportion of the raw material cost.^{3,4}

Because of the unfavorable effect of water-soluble substances in wood, the addition of chemical additives is believed to be an important, uncomplicated treatment method to improve the compatibility of wood-cement-water mixtures. To deal with the inhibitory differences of wood (e.g., birch) the addition of effective chemical additives would lead to restraints on the inhibitory traits of wood and to the acquisition of good board properties based on the results of comparison and selection of set-accelerating effects in

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terms of the hydration reaction of the wood–cement–water mixture.

Many studies^{19–26} have focused on understanding the inhibitory properties of wood species, the compatibility of wood when mixed with cement, and the effects of chemical additives on set-acceleration of wood species based on the results of hydration reactions of wood–cement composites. However, because WCP is used mainly for building applications, it appears logical to pay more attention to the relation between the hydration process of wood–cement–water mixtures and the strength development of board.

Some reports^{16–18} noted that a correlation existed between hydration characteristics and strength, such as compressive strength and tensile strength, of wood–cement composites. WCPs are usually used as composite wall bodies without load bearing and are especially available for frame-structural buildings, with folding-panel construction as a wall component. With this application, the mechanical strength values [modulus of rupture (MOR) and internal bonding strength (IB)] of board are more important than other mechanical properties of the wood–cement composites.

Blast-furnace slag cement is a group mixture of ordinary portland cement clinker and blast furnace slag, which is a by-produce of the blast furnace process and much less expensive than ordinary portland cement. The chemical composition of blast-furnace slag cement is similar to that of ordinary portland cement. Although it is believed to have a slow hydration process and low initial strength, and so cannot be considered a perfect inorganic bonding material, it has acceptable final strength with no marked difference from ordinary portland cement.^{27,28} The use of blast-furnace slag cement as an acceptable raw material for WCP production will result in a distinct decrease in production cost and a diversity of inorganic bonding material.

The objectives of the present study were to: (1) by means of measuring the hydration characteristics T_{\max} and t_{\max} , evaluate the effects of 30 chemical additives and determine

the improvement of the setting acceleration of wood–cement–water mixtures when the chemical additives are used as accelerators; (2) use correlation to investigate the relation between hydration characteristics and board strength values; (3) gain a preliminary understanding by applying composite chemical additives to improve the compatibility of blast-furnace slag cement mixed with wood, as it was thought not to be available for WCP production.

Materials and methods

Apparatus

The apparatus for testing the hydration reaction and the method used in the study, which were developed by prior investigators such as Weatherwax and Tarkow⁷ and Sandermann et al.,^{8,9} are the same as those described in a previous paper. The effects of chemical additives on the setting acceleration of wood–cement–water mixtures were evaluated in terms of the hydration characteristics T_{\max} and t_{\max} using a thermos flask and thermocouple.

Materials

The addition of an accelerator is the simplest and the most used treatment for manufacturing cement-bonded board. The 30 chemical additives listed in Tables 1 and 2 were used as accelerators in this study to examine the effects on the setting acceleration of the hydration reaction of wood–cement–water mixtures. In addition, the two composite chemical additives $\text{Al}_2(\text{SO}_4)_3 + \text{Na}_2\text{SiO}_3$, and $\text{CaCl}_2 + \text{Na}_2\text{SiO}_3$, referred as composite chemical additives A and B, respectively, were applied to examine improvement in the compatibility of blast-furnace slag cement mixed with wood.

Table 1. Influence of chemical additives on hydration characteristics of wood–cement–water mixtures (type I)

Chemical additive	Temperature T_{\max} (°C)			time t_{\max} (h)		
	Average	SD	Grouping ^a	Average	SD	Grouping
Neat cement (control)	60.3	2.77	A	9.0	0.41	B
CaCl_2	54.3	0.37	AB	8.7	0.24	B
FeCl_3	54.0	1.95	AB	15.7	1.70	DE
SnCl_2	50.0	3.92	A–C	17.8	0.71	EF
$\text{Zn}(\text{NO}_3)_2$	48.5	0.29	A–C	1.3	0.24	A
AlCl_3	47.2	3.33	BC	8.3	0.62	B
$\text{Al}_2(\text{SO}_4)_3$	44.3	1.02	B–D	14.0	0.41	CD
MgCl_2	41.5	1.52	B–D	12.5	1.41	C
CaO	39.3	1.56	CD	17.2	1.25	D–F
Na_2SO_3	38.8	0.00	CD	16.7	0.24	D–F
Al_2O_3	33.5	0.71	D	21.5	0.00	G
BaCl_2	33.3	1.05	D	17.7	1.55	EF

Each value is the average of three replications

SD, standard deviation

^aMeans with the same capital letter are not significantly at the 5% significance level

Table 2. Influence of chemical additives on hydration characteristics of wood–cement–water mixtures (type II)

Chemical additive	Temperature T_{\max} ($^{\circ}\text{C}$)		
	Average	SD	Grouping ^a
$\text{C}_4\text{H}_{11}\text{O}_2\text{N}$ (diethanolamine)	50.3	1.32	A
ZnSO_4	48.8	0.65	A
ZnCl_2	44.4	0.86	B
Na_2S	41.2	0.16	C
NH_4NO_3	40.8	0.21	C
K_2SO_4	40.4	0.43	CD
K_2CrO_4	39.8	0.24	C–E
Na_2SO_4	39.1	0.66	C–F
CaSO_4	38.5	0.47	C–G
NaCl	37.7	0.47	D–H
CuCl_2	37.0	0.16	E–I
CaCO_3	36.4	0.59	F–I
$\text{KAl}(\text{SO}_4)_2$	36.3	0.19	F–I
NaNO_2	36.0	0.54	G–I
FeSO_4	35.8	0.24	G–I
NaNO_3	35.7	0.25	G–I
KNO_3	34.7	0.57	HI
KI	34.5	0.54	I
MgSO_4	34.4	0.45	I

Each value is the average of three replications

^aMeans with the same capital letter are not significantly at the 5% significance level

The wood species included in both the hydration reaction and the board strength test was birch wood (*Betula albo-sinensis* Burkill). It was obtained in northern China based on the consideration that it is a potential raw material for cement-bonded board due to its abundance. It is also believed to have intermediate inhibitory properties according to the results reported in a previous paper (submitted for publication).

Both ordinary commercial portland cement and blast-furnace slag cement (consisting of 35%–65% slag) were used in the study. With a slow hydration reaction and low initial strength, the blast-furnace slag cement was not considered to be available for a bonding material mixed with wood.^{27,28} The improvements in compatibility and early-stage strength development of blast-furnace slag cement when mixed with wood were examined after addition of the composite chemical additives.

Sample preparation and measurement of hydration reaction

The weights of wood, cement, and water in the mixture were, respectively, 15 g (oven-dried), 200 g, and 90 g (including the water in the wood species). The 30 single chemical additives were each added to the wood–cement–water mixtures at 4% of the cement weight. The two composite chemical additives CaCl_2 and $\text{Al}_2(\text{SO}_4)_3$ were added at 4% and Na_2SiO_3 at 2% of the cement weight. Preparation of the sample for the hydration reaction has been described in a previous paper.

The wood–cement–water mixtures combined with the chemical additives were immediately placed in an insulated thermos flask. The temperature changes over a 24-h obser-

vation period were measured with thermocouples and recorded by a plotter. Hydration characteristics were determined for each mixed sample to measure T_{\max} and t_{\max} . A neat cement sample without chemical additives was used as a control sample for comparing the changes caused by a mixture of wood, addition of chemical additives, and change of cement type. The hydration experiment in this study was conducted at ambient temperatures ranging from 20 $^{\circ}$ to 23 $^{\circ}\text{C}$. Three replications were conducted on each specimen for statistic analysis.

Board preparation and measurement of strength values

Among the 30 chemical additives, 10 additives were type I and 10 were type II, with more effective acceleration of the hydration process. In terms of hydration characteristics, T_{\max} and t_{\max} were selected. Board strength values (MOR and IB) were measured to determine if a relation existed between hydration characteristics and board strength values. All wood–cement composite materials were made with a 3:1 weight ratio for cement/wood (c/w) and a 1.00:0.52 weight ratio for cement/water (c/w_a) where the amount of water in the wood was included. For each wood–cement composite, the chemical additives accounted for 4% of the cement weight. As to composite chemical additives, $\text{Al}_2(\text{SO}_4)_3$ and CaCl_2 were added at 4% and the Na_2SiO_2 at 2% of the cement weight, respectively. The board preparation and measurement of strength values were performed as described in a previous paper. Three boards were made from each specimen, and six replications were conducted.

Calculation and data analysis

For statistical analysis of data, Duncan's new multiple comparison procedure²⁹ was used to compare the effects chemical additives on the hydration process in the wood–cement–water mixture by conducting an all pairwise statistical comparison among the means for the samples.

Results and discussion

Comprehensive understanding of hydration reaction of cement

Figure 1 demonstrates the typical hydration temperature curve of cement as a function of time. When water is mixed with cement, the chemical reactions that follow bring about a change in the structure of the cement paste where by the fluid mass becomes rigid and hard, and a considerable amount of hydration heat is liberated. The setting process has been found to be closely associated with the temperature change after the addition of water. The time of the initial set corresponds closely with the time at which a rapid temperature rise occurs, and the final set occurs at the time the temperature reaches a maximum value.²⁷ Sometimes flash set takes place (with in a few minutes) with an unusual

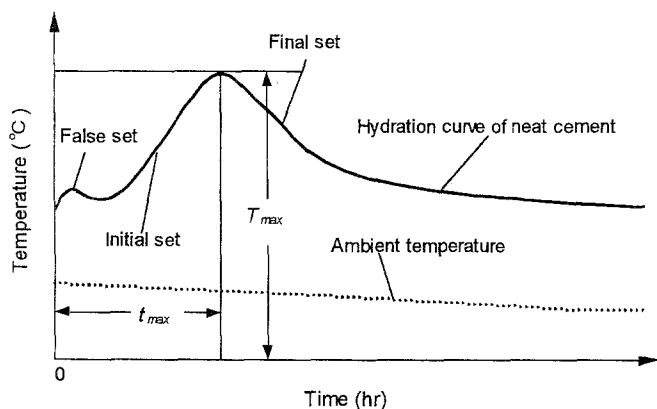


Fig. 1. Representative temperature-time curve of neat cement hydration

temperature increase after the addition of water. In general, two normal peaks associated with hydration of C_3A ($3CaO \cdot Al_2O_3$, tricalcium aluminate) and C_3S ($3CaO \cdot SiO_2$, tricalcium silicate), respectively, could be observed in the hydration temperature-time curves of cement. The major contribution to heat evolution is the hydration of C_3S , which is the largest component of cement.

At an early stage, strength formation and development depends on the content and the completeness of the hydration of C_3S .^{27,28} For neat ordinary portland cement with the same qualities, the difference between the T_{max} and t_{max} of the hydration process should be relatively small if the same experimental conditions pertain. However, any additional materials (e.g., wood, which retards cement hydration owing to its extractives) and any chemical additives used to accelerate setting affect the hydration process and the formation of crystalline hydration products, inevitably leading to changes in heat liberation. The T_{max} and t_{max} could directly reflect these changes.³⁰⁻³² It was for this reason that T_{max} and t_{max} were selected for evaluating the effects of chemical additives on the hydration process of the wood-cement-water mixture in the study.

Inhibitory effect of wood on cement hydration

After 15 g of birch wood power was added to 200 g of ordinary portland cement, inhibiting the hydration process of the cement, as observed in the temperature-time curve (Fig. 2B) compared with the hydration characteristics (T_{max} 60.3°C and t_{max} 9.0 h) of neat ordinary portland cement (Fig. 2A). This was true even though the mixture of wood and cement had a hydration process similar to that of neat ordinary portland cement observed at 24 h, with the presence of two exothermic peaks. There was a shift of the hydration curve in which the T_{max} of the wood-cement-water mixture was greatly decreased to 40.8°C, and the t_{max} was delayed 10.2 h. The hydration temperature (T_{max}), mainly associated with hydration of C_3S , which represented early-stage strength development of cement,²⁷ was greatly reduced. This resulted in an inhibited exothermic peak associated with C_3S that was much lower than that of neat ordi-

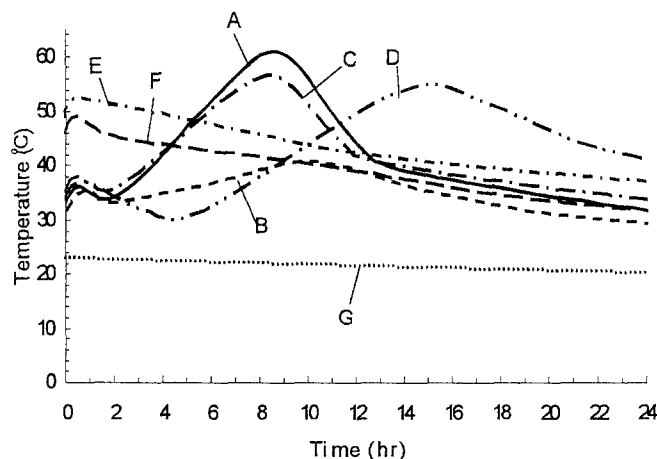


Fig. 2. Influence of chemical additives on hydration characteristics of wood-cement-water mixtures. A, neat portland cement (control); B, Portland cement + wood; C, Portland cement + wood + $CaCl_2$; D, Portland cement + wood + $FeCl_3$; E, Portland cement + wood + $C_4H_{11}O_2N$ (diethanolamine); F, Portland cement + wood + $ZnSO_4$; G, ambient temperature

nary portland cement throughout the hydration process. In accordance with the results reported in our earlier paper, treatment with chemical additives is considered necessary for the wood species because of its intermediate inhibitory effect on cement hydration when used for WCP production.

Accelerated setting action of chemical additives

With the hydration reaction observed, 30 hydration temperature-time curves were obtained based on the mean of the observed data in each group. The hydration characteristics T_{max} and t_{max} for the 30 chemicals added to the wood-cement-water mixtures are listed in Tables 1 and 2, respectively. On the basis of the presence of one or two exothermic peaks during the 24-h reaction time, 30 temperature-time curves were classified as either type I or II.

Eleven chemical additives had type I hydration behaviors when added to the wood-cement-water mixtures. Two exothermic peaks were present in the hydration temperature curves for $CaCl_2$ and $FeCl_3$, as showed in Fig. 2. The most outstanding feature of the hydration phenomenon was that the addition of the type I chemical additives (which raised the T_{max} of the wood-cement-water mixture and effectively overcame the inhibitory influence on C_3S hydration due to extractives in wood) resulted in a hydration process similar to that for neat cement with the presence of a second exothermic peak, characteristic of C_3S hydration.

According to the results of Duncan's multiple comparison (Table 1), the effects of the 11 chemical additives on accelerating set were generally classified into three levels based on the arrangement of the T_{max} . The T_{max} of $CaCl_2$, $FeCl_3$, $SnCl_2$, and $Zn(NO_3)_2$, which ranged from 54.3° to 48.5°C, were grouped in the first level (A-C). $AlCl_3$,

$\text{Al}_2(\text{SO}_4)_3$, and MgCl_2 , with temperatures ranging from 47.2° to 41.5°C, were grouped in the second level (B–D) in which the chemical additives were thought to have intermediate effects on the hydration process. CaO , Na_2SO_3 , Al_2O_3 , and BaCl_2 , with temperatures ranging from 39.3° to 33.3°C, were grouped in the third level (C,D) where with these low hydration temperatures the chemical additives had little accelerating effect on the hydration process. It is remarkable that addition of the four chemicals included in the first level significantly reduced the inhibitory influence of wood with large increases in the T_{max} of the wood–cement–water mixtures. Most of the chemical additives used in the study were inorganic electrolytes, and among them the chlorides had the most significant effect on accelerating the hydration process. Chlorides such as CaCl_2 , FeCl_3 and ZnCl_2 , when added to cement paste, increased the rate of heat liberation and markedly accelerated the hydration process. Thus, the strengths contributed by C_3S and C_2S ($2\text{CaO}\cdot\text{SiO}_2$, dicalcium silicate) were increased under a high hydration temperature.^{27,28} Some studies reported that the chlorides could be used effectively as accelerators to restrain the inhibitory influence of wood species.^{12,13,15}

The hydration characteristics (t_{max}), referred to as a time range for the setting and early-stage strength development of cement, are relatively important, especially during the cold-press process for WCP production. Moreover, the earlier setting of cement with a shorter t_{max} results in reducing the amount of extractives that seep from wood and then rapidly spread into cement paste. The t_{max} of 11 type I chemical additives revealed marked differences. The t_{max} values for $\text{Zn}(\text{NO}_3)_2$ (1.3h), CaCl_2 (8.7h), and AlCl_3 (8.3h) were approximately the same as that (9.0h) for neat portland cement. However, the other eight chemical additives showed a time delay compared with that of neat portland cement, with t_{max} ranging from 12.5h for $\text{Al}_2(\text{SO}_4)_3$ to 21.5h for (Al_2O_3).

Among the type I chemical additives, some of the chlorides (e.g., CaCl_2 , FeCl_3 , SnCl_2 , AlCl_3 , MgCl_2) were found to have a significant effect on cement hydration and setting. This action could be attributed to the fact that the chlorides first reacted with C_3A in cement, forming calcium hydrochloroaluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$), with the result that the solubility of the hydrochloroaluminate in water became greater than that of ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$). The reactions were intensified when water was added, and the first heat peak of cement hydration was observed.¹² In addition, some of the chlorides such as CaCl_2 caused an increase in the alkalis dissolved in the cement. This in turn was believed to accelerate the precipitation of calcium sulfoaluminate, probably accompanied by precipitation of chloroaluminate, resulting in accelerated cement hydration; it led to a sharp increase in heat liberation (second heat peak).²⁸ When some sulfate salts were used as chemical additives in cement, it was found that considerable portions of these sulfates were rapidly dissolved after addition of water. A subsequent reversible reaction was that of the alkali sulfates with $\text{Ca}(\text{OH})_2$, which removed the sulfates from solution. For that reason, they accelerate cement hydration and setting.^{27,28} As shown in

Table 1, these chloride salts were mainly compounds consisting of polyvalent weak alkali or transition metal elements such as Ca^{2+} , Fe^{3+} , Sn^{2+} , Al^{3+} , and Mg^{2+} . Formation of the ranking inorganic salts based on a maximum hydration temperature of cement mixed with a given wood species (birch) can be explained by the fact that in the highly alkaline solution of a cement paste the ionic species would be in hydroxylated state or immediately precipitated as insoluble hydroxides. Thus, the relatively greater or lower solubility of the hydroxides formed by the cations is likely an important factor that results in differences in acceleration of cement hydration.³³

There were 19 type II chemical additives. Within about 30 min after addition of water, the hydration temperatures of mixtures rapidly reached an initial maximum value (T_{max}) and then decreased without an increase in 24h (e.g., for diethanolamine and ZnSO_4), as indicated in Fig. 2. From the results of Duncan's multiple comparison (Table 2), the 10 chemical additives, ranging from diethanolamine to NaCl (A–H), had effects of varying degree on increasing the initial hydration temperatures of the wood–cement–water mixture. Diethanolamine, ZnSO_4 , and ZnCl_2 were considered the best chemical additives; they attained the greatest initial hydration temperatures (T_{max} 50.3°C, 48.8°C, and 44.4°C, respectively), which slowly decreased at a lower rate. However, the other 9 chemical additives, ranging from CuCl_2 to MaSO_4 (E–I), were found to make little contribution to the acceleration of the hydration process owing to less heat liberation. Chemical additives such as diethanolamine, ZnSO_4 , and ZnCl_2 , strengthened hydration of C_3A , and greatly increased the hydration temperatures of the wood–cement–water mixture at the initial hydration stage, where sometimes it was thought that a flash set had occurred. Although no notable exothermic peak resulted from hydration of C_3S , it was still believed that with such a high initial hydration temperature C_3S at least partially participated in the hydration reaction: The hydration of C_3A , unusually accounting for only 9%–10% of cement weight, could not produce as much hydration heat.²⁸

The hydration behavior of type II chemical additives might be characterized as selective. It is suggested that the initial set of ordinary portland cement is due to the formation of hydrated C_3A or hydrated C_3S . Type II chemical additives might be considered to exert a strong influence on hydration of C_3A . The C_3A first went into solution of anhydrous aluminates rapidly; C_3A hydrate formed and quickly led to crystallization of hydrated calcium aluminates, accompanied by a marked rise in hydration temperature immediately upon mixing with water. In this case, the precipitating calcium aluminate hydrate established the structure of cement setting. However, because of the delayed removal of extractives from wood, C_3S would take more time to go into solution and would precipitate as the calcium silicate hydrate, with which cement setting is further developed. Thus the latter situation and the delayed hydration of C_3S would not produce a high hydration temperature.

In this study, according to the maximum hydration temperature (T_{max}) of the wood–cement–water mixtures to

Table 3. Influence of chemical additives on hydration characteristics and strength values of cement-bonded board

Chemical additive	T_{\max} (°C)	t_{\max} (h)	MOR ^a (MPa)	SD	IB (MPa)	SD
Type I						
CaCl ₂	54.3	8.7	13.26	1.53	0.69	1.21
FeCl ₃	54.0	15.7	12.09	1.31	0.62	0.97
SnCl ₂	50.0	17.8	8.28	2.32	0.52	1.30
Zn(NO ₃) ₂	48.5	3.8	7.63	3.68	0.50	1.02
AlCl ₃	47.2	8.3	6.78	1.73	0.56	0.60
Al ₂ (SO ₄) ₃	44.3	14.0	7.65	1.52	0.58	1.44
MgCl ₂	41.5	13.0	6.59	2.35	0.43	1.09
Type II						
C ₄ H ₁₁ O ₂ H	50.3	0.5	10.16	1.78	0.55	0.93
ZnSO ₄	48.8	0.5	8.58	2.24	0.52	1.18
ZnCl ₂	44.4	0.5	6.37	1.44	0.52	1.53
Cement + wood	40.8	10.2	3.53	2.41	0.26	1.13

IB, internal bonding strength

^aModulus of rupture. Each value is the average of six replications

which were added 30 chemicals, the type I and type II chemical additives could be arranged in descending temperature order as shown in Tables 1 and 2. However, this order cannot be considered to hold in all cases. There is a large variety of wood species and the chemical compositions of extractives are not homogeneous regarding their effects on cement hydration. Therefore, it can be believed that the order of the chemical additives can be based only on the hydration reactions of cement when mixed with specified wood species such as (birch wood in this study). When the wood species is changed, the selection and determination of accepted chemical additives should be based on observations of the hydration behavior of the wood–cement–water mixture for that particular wood species. Moreover, it should be verified in terms of the strength values with board testing.

Correlation between hydration characteristics and board strengths

Based on the results of hydration characteristics of wood–cement–water mixtures when 30 simple chemicals were added, the 10 type I chemical additives and the 10 type II additives with the highest hydration temperatures (T_{\max}) were chosen as chemical accelerators. They were used in board strength tests to confirm their effects on accelerating set and to examine the relation between hydration characteristics and board strength values. From the results of these hydration reactions and board test (Table 3), their addition caused different increases in T_{\max} , from 41.5° to 54.3°C, compared with T_{\max} 40.8°C of the wood–cement–water mixture without chemical additives. However, the t_{\max} values were not shown to change consistently (from 0.5 to 17.8 h). There was a positive trend between characteristics and strengths: The higher the T_{\max} , the larger were the strength values of MOR and IB. In Table 4 the MOR and IB values were correlated with the T_{\max} —with relatively high correlations of 0.75 and 0.73; however, similar analysis revealed that the correlation between t_{\max} and MOR and IB values

Table 4. Correlation between hydration characteristics and strength values of cement-bonded board

Parameter	MOR	IB
T_{\max}	0.75	0.73
t_{\max}	0.11	0.15

were small: 0.11 and 0.15, respectively. Similar correlations between hydration characteristics and strength values of wood–cement–water mixture were also found by other researchers.^{16–18} Therefore, under similar experimental conditions, the effect of additional chemical additives and board strength values could be qualitatively predicted in terms of the hydration characteristics of a wood–cement–water mixture when treated with certain chemical additives.

Effect of composite chemical additives on wood/blast-furnace slag cement/water mixture

Although the chemical composition of blast-furnace slag cement resembles that of ordinary portland cement, and its setting and hardening are similar to those of ordinary portland cement, the hydration reaction proceeds slowly with lower heat liberation and a longer hydration time. The slag acts as an inert fine aggregate and may retard the setting and hardening process of cement.²⁷ As can be seen in Fig. 3, the hydration reaction temperature–time curve of neat blast-furnace slag cement is different from that of neat ordinary portland cement. It is characterized by a relatively lower T_{\max} of 39.5°C and a longer t_{\max} of 14.5 h. In general, it is believed that there is not much difference in the final strength values of blast-furnace slag cement, though it has low initial strength.³¹

In this study, two composite chemical additives, A (Al₂(SO₄)₃ + Na₂SiO₃) and B (CaCl₂ + Na₂SiO₃), were added to determine if there is any improvement in the compatibility of wood mixed with the blast-furnace slag cement over the neat ordinary portland cement–wood mix-

Table 5. Hydration characteristics and strength values of cement-bonded board

Composition	T_{\max} ($^{\circ}\text{C}$)	t_{\max} (hr)	MOR ^a (MPa)	IB ^a (MPa)
Neat portland cement	60.3	9.0	–	–
Portland cement + wood	40.8	10.2	3.53	0.26
Portland cement + wood + $\text{Al}_2(\text{SO}_4)_3$	44.3	14.0	7.65	0.58
Portland cement + wood + CaCl_2	54.3	8.7	13.26	0.69
Portland cement + wood + composite (A)	44.3	8.2	8.31	0.58
Portland cement + wood + composite (B)	62.2	2.7	13.62	0.73
Neat slag cement	39.5	14.5	–	–
Slag cement + wood	32.5	2.0	2.25	0.21
Slag cement + wood + $\text{Al}_2(\text{SO}_4)_3$	36.2	2.3	4.47	0.41
Slag cement + wood + CaCl_2	46.3	3.4	6.74	0.48
Slag cement + wood + composite (A)	36.5	1.8	5.85	0.38
Slag cement + wood + composite (B)	54.5	3.0	12.24	0.55

^aEach value is the average of six replications

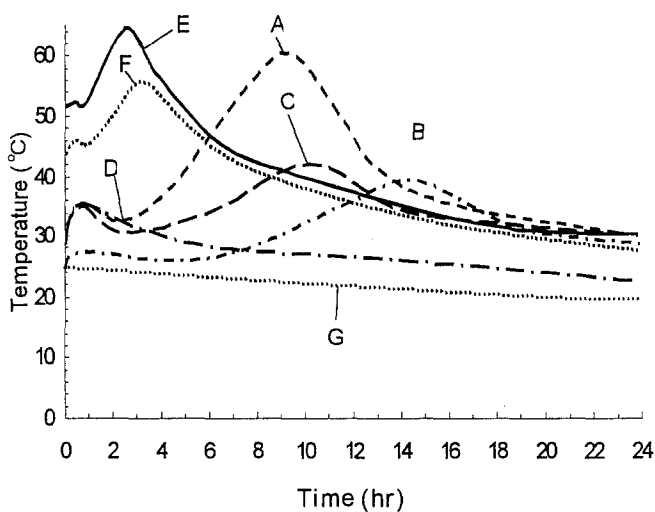


Fig. 3. Effect of composite chemical additives on Portland cement and slag cement mixed with wood. A, neat portland cement; B, neat slag cement; C, Portland cement + wood; D, slag cement + wood; E, Portland cement + wood + composite (B); F, slag cement + wood + composite (B); G, ambient temperature

ture. Table 5 shows that although both of the composite chemical additives (A and B) influenced the hydration characteristics and strength values of ordinary portland cement–wood–water mixtures, only composite chemical additive B had a significant effect on accelerating the set of the wood/blast-furnace slag cement/water mixture, where the T_{\max} increased from 39.5° to 54.5°C, and the t_{\max} decreased from 14.5 h to 3.0 h, compared with the values for neat blast-furnace slag cement. Meanwhile, the boards made with blast-furnace slag cement had higher 28-day mechanical strength values (MOR and IB). This result is probably associated with a major chloride additive such as CaCl_2 in the composite chemical additive (B). It effectively enhanced silica and alumina of slag to react gradually with the calcium hydroxide released during hydration of blast-furnace slag cement. Calcium silicate and calcium aluminate binders were produced as a result of this interaction. During the process, the amount of cement material was increased, improving

the quality of the blast-furnace slag cement. However, the composite chemical additive A seemingly had only a slight effect on the inert compounds in slag. The results also showed that accelerating effects caused by the simple chemical additive $\text{Al}_2(\text{SO}_4)_3$ or CaCl_2 were limited to hydration characteristics and strength values of the wood/blast-furnace slag cement/water mixture. Thus, with the addition of composite chemical additive B, early-stage strength development of blast-furnace slag cement was effectively accelerated, as shown by the increased T_{\max} and shortened t_{\max} . The lower early-stage strength and longer setting time were the greatest obstacles for blast-furnace slag cement to be used as an acceptable inorganic bonding material, especially in a cold-press process for WCP production.

Conclusions

The hydration reaction of a wood–cement–water system can be used as a monitor, taking advantage of hydration heat changes and the hydration characteristics T_{\max} and t_{\max} . These parameters can be used to evaluate qualitatively the result of altering various components in the system, such as the compatibility of cement mixed with a given wood species, accelerating the setting effects from additional chemical additives, and the suitability of cement as a bonding material.

For reducing unfavorable effects caused by water-soluble extractives in birch wood on cement hydration and setting, 30 chemical additives were used as accelerators to examine the effects on accelerating the set of a wood–cement–water mixture. The hydration temperature–time curves of the mixtures revealed significant differences in hydration behavior. In all, 11 and 19 chemical additives were grouped as type I and type II, respectively, in accordance with the patterns of the exothermic reaction peak within the 24-h observation period.

CaCl_2 , FeCl_3 , and SnCl_2 (grouped in type I) were considered acceptable accelerators because they produced maximum hydration temperatures of above 50°C with the addition of 4% (based on cement weight). With the addition

of CaCl_2 , the mixtures reached a T_{\max} of 54.3°C , and the t_{\max} was shortened to 8.7h less than that of neat cement. Among the type II chemicals, the most significant effect was associated with diethanolamine, which resulted in a T_{\max} above 50°C . Because the birch wood used in this study without any treatment had certain inhibitory actions on cement, mentioned previously, these effective accelerators can improve the compatibility between birch wood and ordinary portland cement.

The addition of effective chemical additives as accelerators led to a distinct influence on the hydration characteristics T_{\max} and t_{\max} , resulting in corresponding changes in board strength values (MOR, IB). The good positive correlation indicates that there was remarkable regularity between the hydration characteristics (T_{\max} , t_{\max}) and board strength values (MOR, IB). It implies that in terms of hydration characteristics of mixtures predicting the mechanical behavior of wood–cement–water composites is possible, especially in cases dealing with an understanding of the inhibitory properties of a given wood species. Selection and determination of the chemical additives are required.

Addition of composite chemical additive B caused the hydration reaction and setting of blast-furnace slag cement mixed with wood to be effectively accelerated. The compatibility between birch wood and blast-furnace slag cement was improved, with a marked increase in T_{\max} and a reduction in t_{\max} . Furthermore, the board strength values showed that with certain conditions blast-furnace slag cement can be used as an acceptable inorganic bonding material for WCP production.

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