THE HYDRATION OF CEMENT IN THE PRESENCE OF WOOD AND VARIOUS ADDITIVES

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ABSTRACT

The influence of additives on hydration of neat cement (cement-water mixture) and wood-cement-water mixtures was examined by monitoring hydration temperature profiles over a period of 24 hours. Three series of additives were tested. The first series included sea water and other chloride salts like $CaCl_2$, NaCl, $MgCl_2$ and KCl. In the case of neat cement, there was an accelerated hydration due to the presence of the chloride ions. This effect became inconsistent with the inclusion of wood with the cement. In the second series, sodium silicate, aluminium sulphate (alone or in mixture); and sodium sulphate, aluminium silicate (alone or in mixture) were used. These groups of additives did not show any accelerated effect on cement-wood hydration. The third series included CO_2 releasing compounds. Aluminium sulphate in combination with sodium hydrogen carbonate increased the hydration temperature and reduced the time to reach the maximum temperature as far as cement cure is concerned.

KEYWORDS:

Portland cement; hydration of cement; sea water; carbon dioxide releasing compounds; chloride salts.

INTRODUCTION

Particleboards are commonly made with urea and/or melamine formaldehyde resins and these have limited water resistance. Cement bonded particleboard (CBP), a composite panel manufactured with portland cement as an inorganic binder added to wood or non-wood particles, is a good construction material because it is i) fire resistant (BS EN 13986, 2004), ii) readily machined (Dinwoodie and Paxton 1989) iii) highly resistant to humid weather (Irle and Loxton 1996) and iv) practically rot, fungus and termite proof (Goodle *et al*. 1997]. The major problem that limits CBP development is the compatibility between cement and its wood component. Some wood species produce excellent panels while others do not. Many investigators have attributed such bonding inconsistencies to soluble sugars and extractives in wood (Hofstrand *et al*. 1984; Simatupang *et al*. 1989) that inhibit the setting of cement. The extent of inhibition is more or less pronounced in tropical hardwood species. In order to ensure effective use of any wood or non-wood residues some pre-treatments are required. It is believed that chemical or physical pre-treatment processes minimize the cement and wood components interaction and thus, enhance the compatibility and strength of wood cement products (Simatupang *et al*. 1989; Biblis and Lo 1968; Moslemi *et al*. 1983; Zhenglian and Moslemi 1986). A common useful chemical pretreatment approach to improve wood-cement compatibility is inclusion of chemical additives in the production process. Commonly used additives are $CaCl_2$, $MgCl_2$, Aluminium Sulphate (in combination with either calcium hydroxide or water glass solution). Biblis and Lo (1968) consider that additives improve cement setting by neutralizing the inhibitory substances in wood. However, Moslemi *et al*. (1983) propose that the use of chemical additives speeds up the rate of hydration of plain cement so that there is insufficient time for the unfavourable wood substances to diffuse from the wood in the alkaline environment of the cement. The other barrier that prevents the installation of CPB manufacturing plants is the setting time of the cement binder. Research has shown that this barrier can also be overcome with the addition of powdered carbonates or by the injection of CO_2 gas, where the cement setting time is reduced to a few minutes (Geimer *et al*. 1993; Simatupang and Habigghorst 1993).

The aim of the study presented here is to investigate the effect of a number of cement cure accelerators, some of which have not been tried before, on cement-wood composites formation that will add valuable information regarding the interaction between the accelerator and wood-cement-water mixture.

MATERIALS AND METHODS

The influence of additives on both cement-water and cement-wood-water systems was assessed by measuring the maximum hydration temperature and the time required to reach that maximum. Birch (*Betula spp.)*, which is known to be partially compatible with cement (Defo *et al*. 2004), was used for the study. It was used in the form of fine particles (< 1 mm) with a moisture content of about 13%. A list of the additives used is given in Table 1. The amount of solid additive was equivalent to 1% of the dry cement weight. The additives were added to the samples as solutions. The percentage level of sodium carbonate and sodium hydrogen carbonate was 3% based on cement weight and they were mixed as powders.

Two sets of cement-water samples, with and without wood, were prepared for each additive. The samples without wood will act as controls and provide information regarding influence of the additives on hydration characteristics of cement-water mixture, whereas wood containing samples clarify the effect of wood chemical constituents on hydration temperature.

Table 1 - The list of selected compounds.

First series	Sea water; Calcium Chloride ($CaCl_2$); Sodium Chloride (NaCl); Potassium Chloride (KCl); Magnesium Chloride ($MgCl_2$)
Second series	Aluminium Sulphate ($Al_2(SO_4)_3$); Sodium Silicate (Na_2SiO_3); Aluminium Sulphate and Sodium Silicate (mixture) Sodium Sulphate (Na_2SO_4); Aluminium Silicate (Al_2O_3. $2SiO_2$. $2H_2O$) Sodium Sulphate and Aluminium Silicate (mixture)
Third series	Sodium Carbonate (Na_2CO_3); Sodium Hydrogen Carbonate ($NaHCO_3$) Aluminium Sulphate and Sodium Hydrogen Carbonate (mixture).

For each wood containing sample, 100 g of dry cement was mixed in a plastic bag with 36 g of wood particles (based on oven dry weight) prior water addition. The solid contents of all the samples were adjusted to 50% with the addition of water. Each sample was placed in a Dewar flask and the temperature was measured every 15 minutes with a thermocouple and a computer over a 24 hour period. The method used for measuring hydration temperature was similar to that designed by Irle and Simpson (1993). The hydration temperature of six different samples was measured at each time. All the experiments were conducted at ambient room temperature.

RESULTS AND DISCUSSION

The effect of various additives on the hydration of neat cement and cement-wood samples over a period of 24 hours is presented in Figures 1 to 5. Each line is the average of three replications. The maximum hydration temperature and the time required to reach this temperature for each mixture are presented in Table 2.

Table 2 - Maximum hydration temperature and the time required to achieve this by addition of various additives for both cement-water and cement-wood-water system.

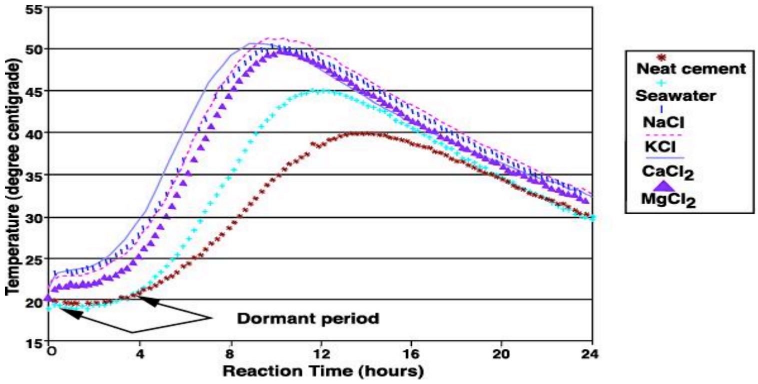
System	Time to max. Hydration temp. (hr.)	Max. Hydration temp. (^oC)
Cement + water	13.50	40.0
Cement + seawater	11.75	45.3
Cement + NaCl	10.00	50.5
Cement + KCl	9.75	51.5
Cement + $MgCl_2$	10.25	49.9
Cement + $CaCl_2$	9.00	50.8
Cement + wood	1.50	26.0
Cement + wood + seawater	14.50	29.9
Cement + wood + NaCl	10.75	31.7
Cement + wood + KCl	12.25	31.7
Cement + wood + $MgCl_2$	10.50	35.9
Cement + wood +$CaCl_2$	10.50	36.3
Cement + Al_2 $(SO_4)_3$	11.25	44.6
Cement + Na_2SiO_3	15.50	35.1
Cement + $Al_2(SO_4)_3$ +Na_2SiO_3	11.25	43.4
Cement + wood + Al_2 $(SO_4)_3$	12.25	31.9
Cement + wood + Na_2SiO_3	2.00	27.8
Cement + wood+$Al_2(SO_4)_3$ + Na_2SiO_3	12.50	33.9
Cement + Al-silicate	12.25	45.5
Cement + Na_2SO_4	13.00	46.5
Cement + Al-silicate + Na_2SO_4	12.00	47.6
Cement + wood + Al-silicate	2.25	29.6
Cement + wood + Na_2SO_4	1.75	28.5
Cement + wood + Al-silicate + Na_2SO_4	2.50	28.8
Cement + $NaHCO_3$	12.50	46.5
Cement + Al_2 $(SO_4)_3$ + $NaHCO_3$	9.25	52.7
Cement + Na_2CO_3	11.75	47.2
Cement + wood + $NaHCO_3$	13.00	33.0
Cement + wood + Al_2 $(SO_4)_3$ + $NaHCO_3$	10.00	35.7
Cement + wood + Na_2CO_3	11.50	29.0

1. First series

Figure 1a shows the effect of seawater and the other chloride salts on cement hydration. The control (cement-water mixture without additives) achieved a maximum hydration temperature of 40ºC after 13.5 hours. Other researchers have reported different maximum hydration temperatures for the controls like 73.7ºC (Zhenglian and Moslemi 1986), 52.2ºC (Irle and Simpson 1993) and 43.5ºC (Weather wax and Tarkow 1964). The differences are mainly due to the amount of cement used (only 100 g used in these experiments compared to 200 g that is often used), its freshness, the cement-water ratio and the hydration conditions.

From the figure it is seen that inclusion of chlorides not only lowered the time to reach the maximum hydration temperature (shifted the peak towards left), but also reduced the dormant period. Of all the chlorides, $CaCl_2$ is the best accelerator followed by KCl, NaCl and $MgCl_2$. Presence of seawater (pH: 7.5 to 8.4) also accelerates cement hydration, but to a lesser extent compared to other chlorides.

Figure 1b shows the effect of additives on the setting of portland cement in presence of birch (*Betula sp*.), a wood species that contains 1.4 to 1.6 % water soluble components and 32.9% of pentosans (Tasypin 1991). A relatively compatible species like spruce contains 0.6 to 0.8% of water soluble components and 11.2% of pentosans (Tasypin 1991). The hydration patterns show that in the absence of chloride additives the cement hydrates slowly. This may be due to higher proportion of pentosan in birch which acts as an inhibitor in cement. In this study, the accelerating effect of $CaCl_2$ is almost equal to that of $MgCl_2$ but higher than that of NaCl and KCl. This accelerating effect may be because of additional metal ions, coming from the salts, react with the wood derived gluconates making the calcium ions present in the cement available for nucleation and crystal growth. Sing (1976) proved that gluconates act as retarders but in a different order. They reported that sodium gluconate retards the cement hydration to a higher degree than calcium gluconates that correlates somewhat with the present investigation. Initially, seawater has no effect on wood cement interaction but after 6 hours temperature increases and it attained a maximum of 29.9ºC at about 14.5 hours. From this result it can be concluded that seawater is also able to overcome the set retarding effect of wood constituent on the hydration of cement.



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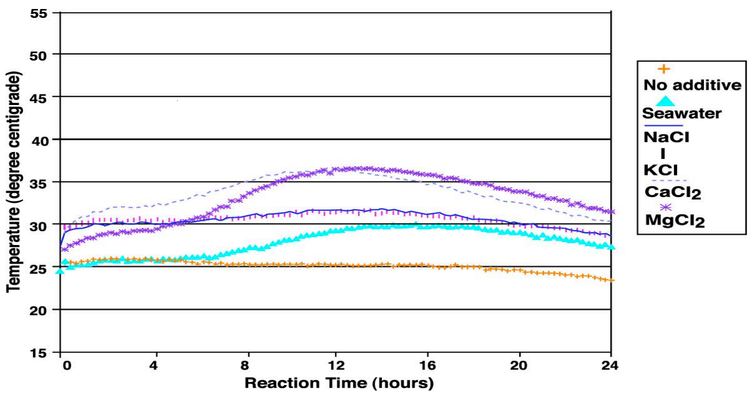

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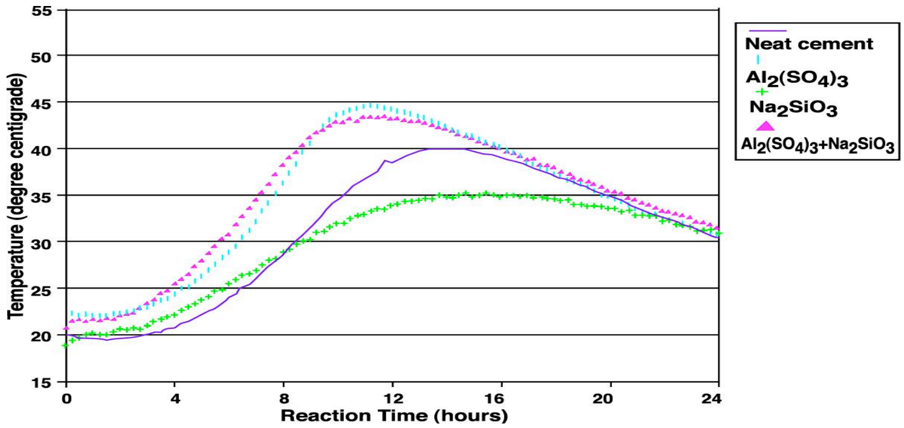
Figure 1 - The influence of NaCl, KCL, $CaCl_2$, $MgCl_2$ and sea water on the hydration of (a) cement samples b) cement-wood samples

2. Second Series

Figures 2a and 2b show the action of Aluminium Sulphate, Sodium Silicate and their mixture on cement-water as well as wood-cement-water systems. It is found that sodium silicate has no effect on cement-water mixture and has only minimum effect on wood-cement mixture. Zhenglian and Moslemi (1985) and Irle (1993) reported that Sodium Silicate did not accelerate the setting of wood-cement mixture. The Aluminium Sulphate works very well both on the cement-water and cement-wood-water system. When Aluminium Sulphate and Sodium Silicate are used together the hydration temperature increased and the time to reach the maximum temperature is reduced. The nature of the curve is more or less similar to Aluminium Sulphate alone.



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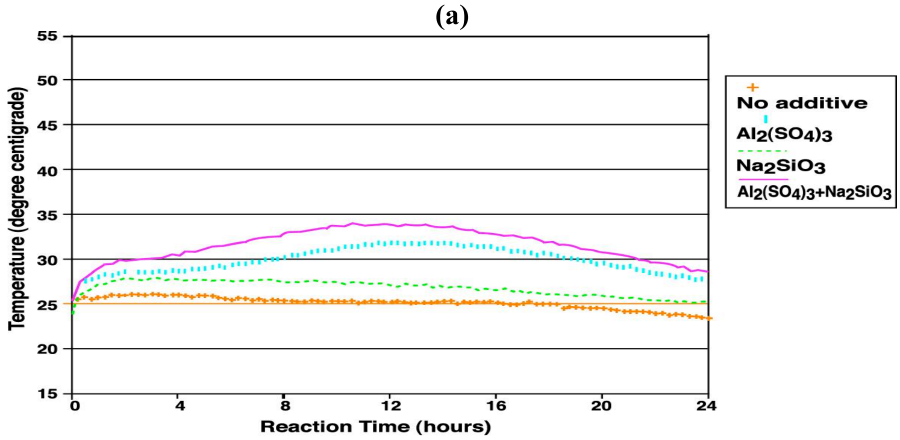

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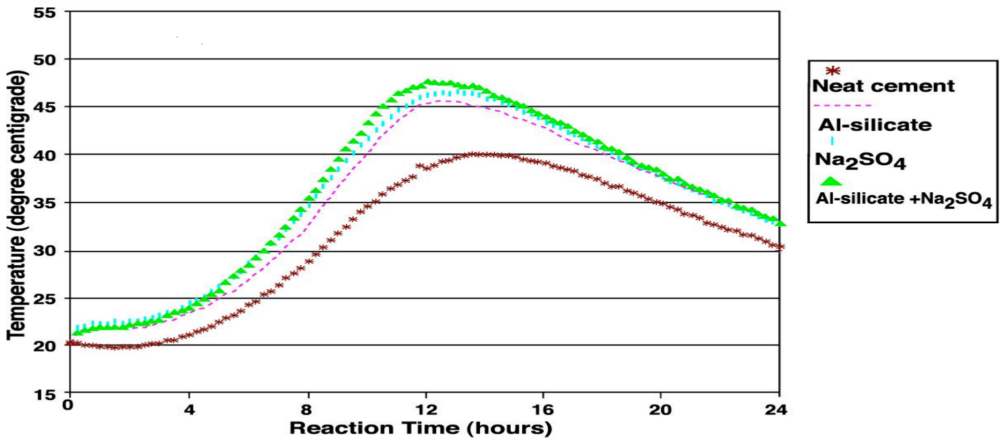
Figure 2 - The influence of $Al_2(SO_4)_3$, Na_2SiO_3, and their mixture on the hydration of (a) cement samples b) cement-wood samples



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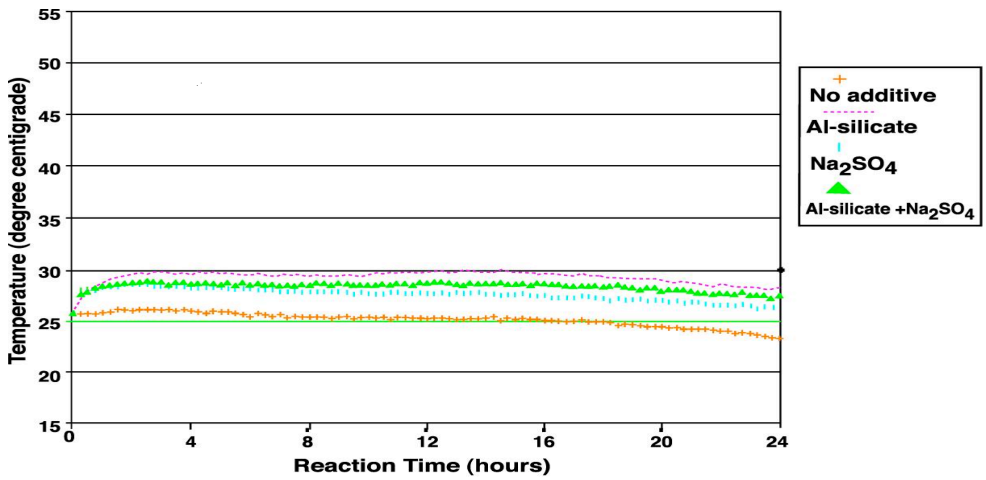


(b)

Figure 3 - The influence of Na_2SO_4, Al-silicate and their mixture on the hydration of

(a) cement samples (b) cement-wood samples

Irle (1993) thought that Aluminium Silicate (China Clay) And and Sodium Sulphate are being formed when Aluminium Sulphate And and Sodium Silicate are mixed together, and these new products cause the accelerating effect. To investigate this hypothesis, individual effect of Aluminium Sulphate and Sodium Silicate as well as their mixture was investigated (Figures 3a and 3b). It can be seen from Figure 3a that the presence of Sodium Silicate, Aluminium Sulphate and their mixture do increase the hydration temperature, it is the highest with their mixtures. However, this effect was less when wood was incorporated in the cement-water mixture (Figure 3b).

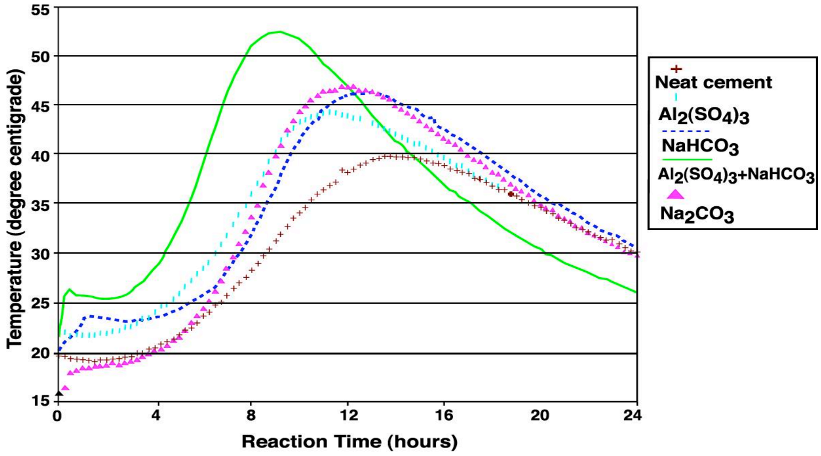
3. Third series

The influence of carbonate salts on hydration temperature is shown in Figures 4a and 4b. Both sodium carbonate and sodium hydrogen carbonate accelerate cement hydration and there is an initial rapid rise in temperature at the start of the dormant period for sodium hydrogen carbonates.

The Aluminium Sulphate combined with Sodium Hydrogen Carbonate system shows a dramatic acceleration in cement hydration (Figure 4a). It attained a maximum temperature of 52.7ºC after about 9.25 hours, which is very rapid as far as cement setting is concerned. From the figure it is seen that after 15 minutes of mixing there is a sharp rise of temperature from 21 to 26ºC. This is different from other additives probably due to the generation of CO_2. The CO_2 participates in converting Calcium Hydroxide present in the mixture to Calcium Carbonate which in turn influences the hydration process. Different authors also agreed that hydration is very fast under the influence of Carbon Dioxide due to the formation of Calcium Carbonate.

Figure 4b shows that it is also possible to improve the hydration of cement in the presence of wood by the addition of Sodium Carbonate and Sodium Hydrogen Carbonate. However, the rate of hydration with Na_2CO_3 was not as intensive as expected. This is probably due to lower amounts of additive added compared to that added by Simatupang (1991). A mixture of Aluminium Sulphate and Sodium Hydrogen Carbonate works very well in cement-wood-water systems. The inhibitory effect of wood is mainly due to the formation of calcium carbohydrate complexes, and the presence CO_2 acted as a calcium scavenger and enhanced hydration (Schubert 1991). Schubert (1991) also mentioned that due to carbonisation, the pH of the pore water decreases that reduces the leaching effect of the alkali on the wood particles. As a result cement-wood bonding is improved.

The efficacy of various additives on the hydration of cement-wood samples is shown in Figure 5. The addition of $CaCl_2$ with wood particles yielded a maximum hydration temperature (about 36.3^{o}C), which is nearly identical with that of Aluminium Sulphate And Sodium Hydrogen Carbonate mixture. The time required to attain this temperature is also comparable. It seems that the Aluminium Sulphate in combination with Sodium Hydrogen Carbonate would be useful additive in CBP manufacture.



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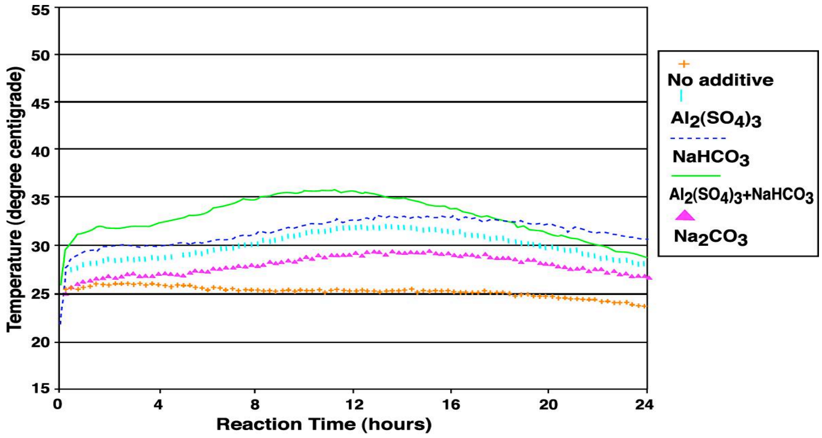

(b)

Figure 4 - The influence of Na_2CO_3, $NaHCO_3$ and the mixture of $Al_2(SO_4)_3$ and $NaHCO_3$ on the hydration of (a) cement samples (b) cement-wood samples

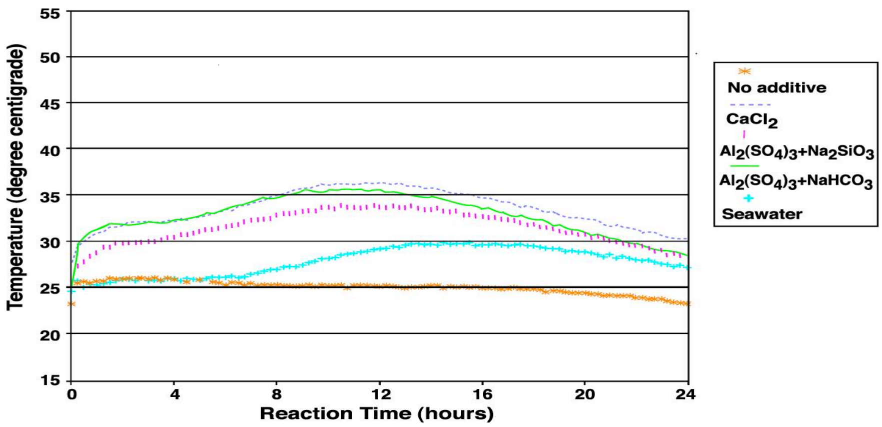

Figure 5 - The comparison of various additives on the hydration of cement-wood samples

CONCLUSION

The addition of additives such as $CaCl_2$, NaCl, $MgCl_2$, increase the setting of cement even in the presence of wood. Seawater also accelerates cement hydration and this may be a useful additive in some parts of the world.

Sodium silicate alone is not a good accelerator for either neat cement or cement-wood mixtures. Once Aluminium Sulphate is added, acceleration occurs. These two additives are often combined in cement bonded particleboard production. Other compounds such as Sodium Sulphate, Aluminium Silicate and their mixtures do not seem to be effective accelerators for wood-cement systems.

Both Na_2CO_3 and $NaHCO_3$ have a considerable affect on the hydration of cement. The addition of Na_2CO_3 does not improve the wood-cement interactions as much as it was hoped. It seems that higher amount of additive is required, which may be feasible for commercial production. A mixture of Aluminium Sulphate in combination with $NaHCO_3$ produces a very strong acceleration. It is clearly evident that CO_2 released by this system could overcome the unfavourable effect of wood substances. In addition, time required to set the cement may reduce. So, it is hoped that this additive (mixture of Aluminium Sulphate with $NaHCO_3$) will open up the possibility of inclusion of woods not previously used in cement bonded particleboard production.

The major drawback of additives containing chloride salts is their corrosiveness on cement composites. In this aspect compounds of third series would be better. Further research is needed to determine whether the inclusion of the additives to the wood prior to mixing them with the cement are worthwhile, considering final board properties, as well as the cost involved and the availability of the additives.

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