

**STUDY ON HYDRATION MECHANISM OF LOW DENSITY
MAGNESIA-BONDED WOOD WOOL PANEL**

BIN NA, ZHIPENG WANG, ZHIQIANG WANG, TAO DING, RONG HUANG, XIAOLING L.
NANJING FORESTRY UNIVERSITY, COLLEGE OF MATERIALS SCIENCE
AND ENGINEERING
NANJING, CHINA

(RECEIVED AUGUST 2012)

ABSTRACT

Low density magnesia-bonded wood wool panel (MWWP) is an inorganic-bonded panel product in which wood excelsior is bonded with magnesia. The hydration reaction between magnesia (main content: MgO) and $MgCl_2$ directly influences the performance of the product, and is therefore the key factor to the improvement of MWWP quality. In this study, DSC, SEM, XRD and XPS analyses were applied to explore the mechanism of the hydration reaction. The results showed that the reaction products were more stable when the following parameters were chosen: magnesia-to-wood powder ratio was 100:25; the magnesia-to- $MgCl_2$ solution ratio was 100:90; the specific gravity of $MgCl_2$ solution was 1.26 and ferric alum and $(NH_4) H_2PO_4$ were chosen as additives. Prolonged reaction time also helped further the reaction and made the reaction product more stable. The optimum hydration temperature was 80°C.

KEYWORDS: Magnesia; wood wool panel; hydration; DSC; SEM; XRD; XPS.

INTRODUCTION

With higher living standards and awakening of environmental consciousness, people are trying to develop new building materials with both nice appearance and good environmental, thermal, and acoustic properties (China Building Material Academy 2003; Jiang et al. 2002). Low density magnesia-bonded wood wool panel (MWWP) is a panel product composed of wood excelsior as reinforcing material and magnesia as bonding adhesive, and is considered a product that can meet all the demands. It has been applied as soundproofing and thermal insulation material in industrial and residential buildings (Zhang et al. 2002; Yang et al. 1999). In recent years, wood wool panel has also been used in some public buildings in China as decorative and soundproofing material (An et al. 2006; Tu et al. 2007). Due to its good physical and mechanical properties (Ashori et al. 2011; 2012) and modern decorative appearance, it has earned itself wider acceptance and broader application.

The hydration reaction between magnesia (main content: MgO) and MgCl₂ solution is a very complex physicochemical process and its products are the binder of the panel. It has been investigated by many studies and can be briefly described as a process of forming 5 Mg(OH)₂.MgCl₂.8 H₂O (5-phase crystal) and 3 Mg(OH)₂.MgCl₂.8 H₂O (3-phase crystal) at room temperature (Barnes 1983). Studies on the formation of magnesium oxychloride cement can be summarized as follows: It was first believed that both 5-phase crystal and 3-phase crystal were formed by reaction between Mg(OH)₂ and MgCl₂ solution. Ved et al. (1976) described the hydrates as a complex with a core of [Mg(H₂O)_n]²⁺ and a shell of [Cl(-O-Mg-OH)m]⁻, and believed that the formation of the hydrates was the result of linkage between these ions. This opinion was questioned by Bilinski et al (1984), who compared the MgO-MgCl₂-H₂O system and the NaOH-MgCl₂-H₂O system and concluded that the hydrates were formed by reactions among Mg²⁺, OH⁻, and Cl⁻. A similar conclusion was drawn by Zhang et al. (1991) based on thermodynamics calculations, who concluded that the hydrates were formed by reaction between MgCl₂ solution and MgO or Mg²⁺. Since various hypotheses and theories exist on the mechanism of the reaction, further studies are needed to make it clear. In this study, differential scanning calorimetry (DSC) was conducted during the hydration reaction. The hydrates were analyzed by means of X-ray diffraction (XRD), scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). (Ma et al. 2010; Stark 2011; Plekhanova et al. 2007) The aim was to further explore the mechanism of the hydration reaction.

MATERIAL AND METHODS

Measurement of hydration reaction heat by DSC

Magnesia with 60 % of MgO (size: 120 mesh) was supplied by Shandong Laizhou Hongda Building Material Factory. Wood powder (150-200 mesh) was prepared by grinding poplar wood in a Wiley mill. Four types of MgCl₂ solutions (Tab. 1) were prepared from analytically pure MgCl₂ crystal. The additives chosen were talc, aluminum powder, NH₄H₂PO₄, ferric alum (FeSO₄) and milky-white glue. The materials were well mixed according to Tab. 2, and then heated in a differential scanning calorimeter (NETZSCH, DSC 200F3). In all experiments, the heating rate was 5 °C.min⁻¹, and the temperature ranged from 10 to 170 °C.

XRD, SEM and XPS analysis

Magnesia and MgCl₂ solution were mixed and heated in an oven (Beijing Zhongke Ring Test Apparatus Co. Ltd, DHG-9030A) at 80 °C for 2 hours. After conditioned at room temperature, the reaction products were ground and analyzed by an X-ray diffractometer (ARL, X'TRA), scanning electron microscope (Hitachi, S-3400N II) and X-ray photoelectron spectrometer (ULVAC-PHI, PHI5000 VersaProbe) respectively.

Tab. 1: Parameters of MgCl₂ solution.

Baume degree (°Bé)	28	30	32
Specific gravity	1.24	1.26	1.28
MgCl ₂ (%)	26.06	27.77	32.77
H ₂ O (%)	71.94	70.23	65.23

Tab. 2: Methods and results of DSC experiment.

No.	Magnesia/ wood powder	Specific gravity of MgCl ₂	Magnesia / MgCl ₂	Additives**	Peaks (°C)	DSC heat output (j.g ⁻¹)
1	100:15	1.26	100:100	/	97.1	784.6
2	No wood powder	1.26	100:100	/	64.4	886
3	100:15*	1.26	100:100	/	79.9	719.1
4	100:20	1.26	100:80	/	79.9	482.7
5	100:20	1.26	100:90	/	84.2	701.7
6	100:20	1.26	100:100	/	84.1	564.4
7	100:20	1.26	100:110	/	87.8	596.7
8	100:20	1.24	100:90	/	84.1	547.1
9	100:20	1.28	100:90	/	84.1	574
10	100:15	1.26	100:90	/	87.7	525.7
11	100:25	1.26	100:90	/	70.8	476.3
12	100:20	1.26	100:90	Al	86.9	483.5
13	100:20	1.26	100:90	Al+(NH ₄)H ₂ PO ₄	81.4	476.7
14	100:20	1.26	100:90	talc+ Al+(NH ₄)H ₂ PO ₄	83.7	549.7
15	100:20	1.26	100:90	Ferric alum+ Al+(NH ₄) H ₂ PO ₄	80.9	563.9

* 15: digested solution of poplar

** The weight ratio of magnesia to additives was 100:1

RESULTS AND DISCUSSION

DSC analysis of hydration reaction

Fig. 1 shows the influence of poplar wood powder and digested solution of poplar on the hydration reaction. In this figure and the following figures till Fig. 5, the curve numbers correspond with the serial numbers in Tab. 2. The exothermic peak was found at 97.1°C (curve 1) when poplar wood powder was chosen as reactant. It was shifted to 79.9°C (curve 3) when

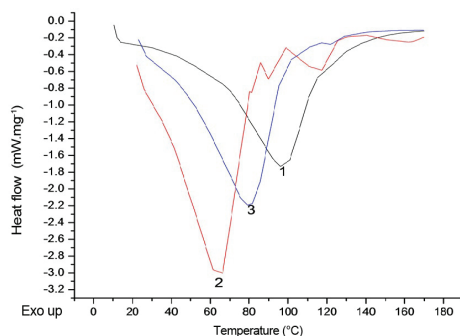


Fig. 1: Influence of poplar wood powder and digested solution of poplar on hydration reaction.

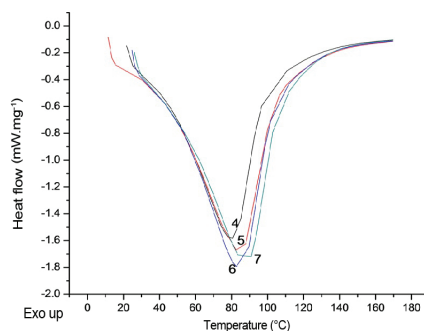


Fig. 2: Influence of MgCl₂ solution content on hydration reaction.

digested solution of poplar was adopted, indicating that poplar wood powder retarded the hydration reaction. Compared to curve 2, cure 1 and cure 3 exhibited less heat release, but the differences were modest, implying limited influence of wood powder on the hydration reaction. The pH value of the digested solution was 5.3. Since it promoted the hydration reaction, it can be concluded that the hydration process can be promoted by acid substances.

As shown in Fig. 2, when the amount of wood powder and specific gravity of $MgCl_2$ solution was kept unchanged, excessive $MgCl_2$ solution content would retard the exothermic peak, which appeared at 79.9, 84.2, 84.1 and 87.8°C corresponding to the magnesia-to- $MgCl_2$ ratio of 100:80, 100:90, 100:100 and 100:110. Higher $MgCl_2$ content also resulted in lower heat release. That's because higher $MgCl_2$ content caused higher $MgCl_2$ -to- MgO ratio, which in turn resulted in unstable reaction products other than the expected 5-phase or 3-phase products and retarded the hydration process.

Fig. 3 shows the influence of specific gravity of $MgCl_2$ solution on the hydration reaction. It can be found that when the content of wood powder and $MgCl_2$ solution were kept unchanged, specific gravity exerted no pronounced influence on the reaction, which was also proved by Karimi and Monshi (2011). However, when the specific gravity was 1.26, the heat release was found the highest, indicating this specific gravity the most suitable one for the hydration reaction.

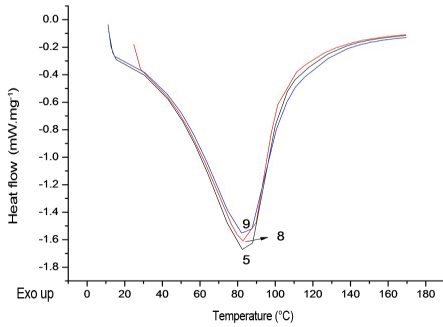


Fig. 3: Influence of specific gravity of $MgCl_2$ solution on hydration reaction.

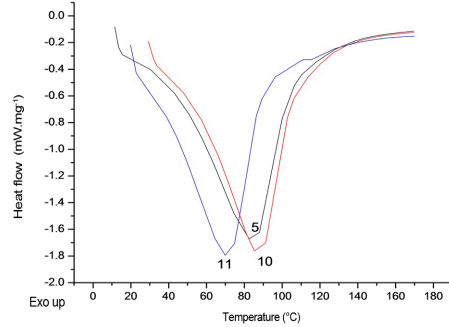


Fig. 4: Influence of wood powder content on hydration reaction.

According to Fig. 4, when the magnesia-to-wood powder ratio was 100:25, the reaction peak was lowered to 70.8°C, which indicated that higher content of wood powder accelerated the hydration reaction.

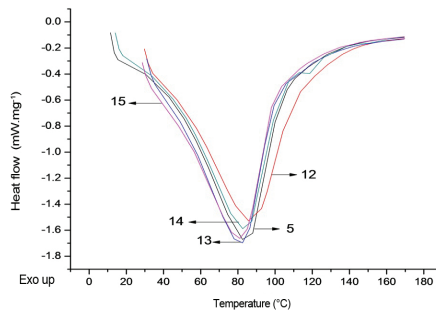


Fig. 5: Influence of additives on hydration reaction.

According to Fig. 5, additives had significant influence on the hydration reaction. The adding of aluminum powder or talc retarded the hydration reaction, without which, the exothermic peak was at 84.2°C compared to 86.9°C when aluminum powder was added. Meanwhile, the mixture of ferric alum and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ was found beneficial to the reaction. That's because ferric alum and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ can react with Mg^{2+} to form MgSO_4 and $\text{Mg}_3(\text{PO}_4)_2$ as precipitates.

Microstructure analysis

Microstructure analysis on hydration reaction products

Hydration reaction products were ground and analyzed by XRD. It was found that the reaction products were mainly composed of $\text{Mg}_3\text{Cl}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$, MgCO_3 , MgO , talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$), chlorite, and trace amount of unknown substances (Fig. 6). Magnesia is the calcined magnesite (MgCO_3). When it is placed at room temperature for a long time, complex physicochemical reactions will occur. That's why MgCO_3 , $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, and chlorite were found in the reaction products.

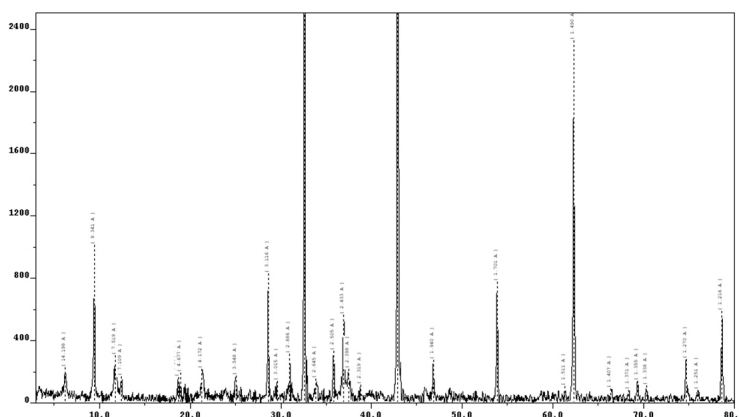


Fig. 6: XRD spectrum of reaction products from hydration without additives.

Elemental analysis was performed on hydration products when no additives were added. The results are listed in Tab. 3, from which it can be concluded that MgCO_3 occupied a higher percentage in the reaction products while the content of $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ and chlorite was relatively low. Given the lower activity of MgO , only part of it participated in the hydration reaction and formed the 5-phase crystal. The unreacted part was left in the reaction products. Zhang et al. (1991) analyzed the formation of the 5-phase crystal, and suggested the following mechanisms :

- (1) MgO and MgCl_2 were the initial reaction products.

$$\text{MgO} + \text{Mg}^{2+} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Cl}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$$
- (2) Mg^{2+} , OH^- and MgCl_2 solution were the initial reaction products.

$$\text{Mg}^{2+} + \text{Cl}^- + \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Cl}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$$
- (3) $\text{Mg}(\text{OH})_2$ and MgCl_2 were the initial reaction products.

$$\text{Mg}(\text{OH})_2 + \text{Mg}^{2+} + \text{Cl}^- + \text{H}_2\text{O} \rightarrow \text{Mg}_3\text{Cl}(\text{OH})_5 \cdot 4\text{H}_2\text{O}$$

Since there was no $\text{Mg}(\text{OH})_2$ present in the hydration products, the 5-phase product may be the result of reaction (1) and (2).

Tab. 3: Chemical element percentage of hydration reaction products.

Element	C	O	Mg	Si	Cl
Percentage (%)	17.34	52.06	21.55	1.32	7.72

Mechanism analysis on hydration reaction with additives

XRD and SEM analyses were made on hydration products when ferric alum, aluminum powder and $(NH_4)H_2PO_4$ were added as additives.

According to Fig. 7, when the reaction temperature was $60^\circ C$, the main reaction products were the 5-phase crystal, MgO , $MgCO_3$, and $Mg_3Si_4O_{10}(OH)_2$, among which MgO and $MgCO_3$ accounted for the majority, while the content of 5-phase crystal was relatively low. The low content of 5-phase crystal was attributed to the low activity of MgO . It can be found from Fig. 7 that the content of the 5-phase crystal increased with prolonged reaction time, while the height of the characteristic peak of MgO decreased with reaction time, indicating that the reaction process was not from MgO to $Mg(OH)_2$ and that no $Mg(OH)_2$ was formed as reaction product. Peak D in the XRD spectra indicated a minor amount of α -Fe, which was due to the adding of ferric alum.

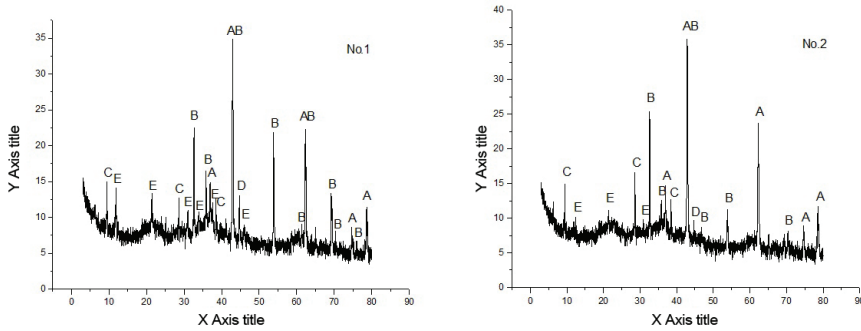


Fig. 7: XRD spectrum of hydration products (reaction temperature: $60^\circ C$, reaction time: 2 hours(left) and 4 hours(right)).
 A- MgO B- $MgCO_3$ C- $Mg_3Si_4O_{10}(OH)_2$ D- α -Fe E- 5-phase crystal

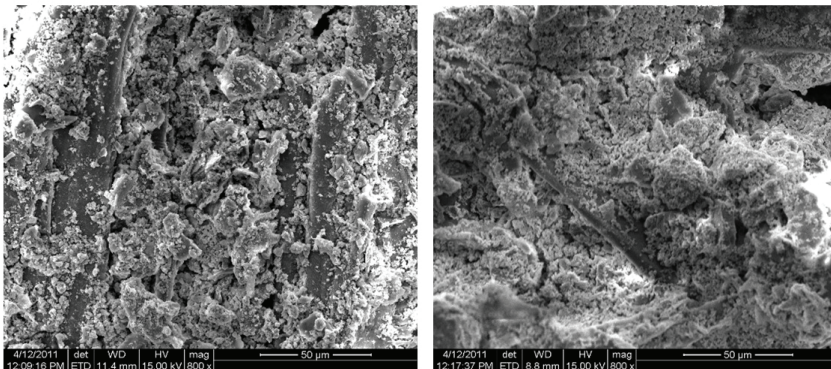


Fig. 8: SEM micrograph of hydration products (reaction temperature: $60^\circ C$, reaction time: 2 hours (left) and 4 hours (right)).

Fig. 8 shows SEM photos of the reaction products. When the reaction time was 2 hours, minor amount of 5-phase crystal was formed. Their needle or leaf-like appearance indicated low hydro-stability. The amount of the 5-phase crystal increased when the reaction time was prolonged to 4 hours. Their gel appearance was the indicator of better hydro-stability. Therefore, it can be concluded that a 4-hour reaction is superior to a 2-hour one. The prolonged reaction time resulted in the complete reaction of the active MgO and more 5-phase crystal as reaction product.

According to Fig. 9, the reaction temperature influenced the relative contents of hydration products, i.e., 5-phase crystal, MgO, MgCO₃, Mg₃Si₄O₁₀(OH)₂ and α-Fe. The content of 5-phase crystal decreased with the increase of temperature. The temperature rise from 60 to 80°C led to the increase of MgCO₃ content and the decrease of MgO content. That may partly be explained by the reaction between MgO and CO₂ in the air, in which, MgCO₃ is formed as reaction product. Another reason is that the ferric alum and (NH₄)₂HPO₄ in the additives reacted with MgO, forming minor amount of unknown substances.

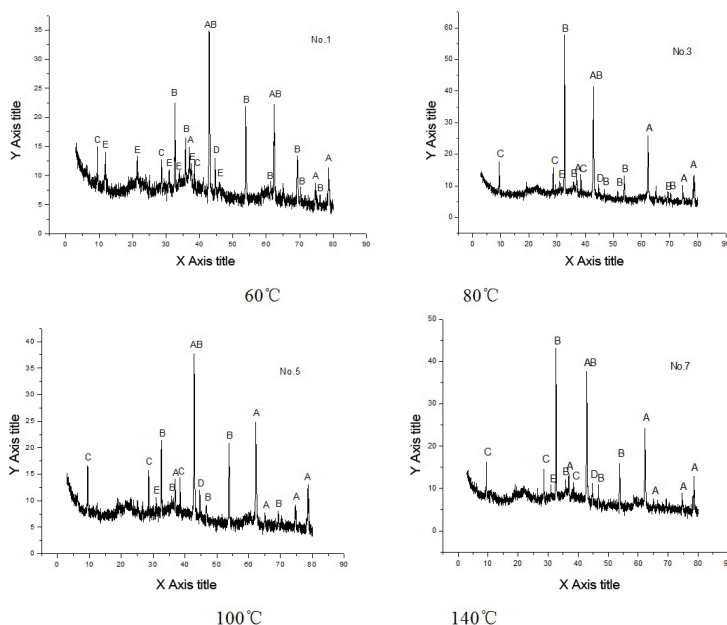


Fig. 9: XRD spectrum of hydration products (reaction time: 2 hours, temperature: 60, 80, 100, 140°C). A-MgO B-MgCO₃ C-Mg₃Si₄O₁₀(OH)₂ D-α-Fe E-5-phase crystal.

The contents of the reaction products changed reversely when the reaction temperature rose from 80 to 100°C. In this case, the content of MgCO₃ decreased, while the content of MgO increased. Such reversal may be attributed to the degradation of MgCO₃ at higher temperatures. MgO was formed as the reaction product. The content of MgCO₃ increased again when the reaction temperature climbed to 140°C. It was also due to the reaction between MgO and the CO₂ in the air. The content of α-Fe increased with the rise of temperature, indicating that it underwent reaction during the hydration.

Fig. 10 shows the SEM micrographs of hydration products from reactions at 60, 80, 100 and 140°C. It could be found that when the temperature was 60°C, the 5-phase crystal exhibited

a leaf-like appearance. When the temperature increased to 80°C, its appearance changed to a gel-like form, implying better stability. Surface fractures were observed when the reaction temperature was 100°C, and greater needle-like fractures were found when it reached 140°C. The content of the 5-phase crystal at the surface decreased with climbing temperature. Therefore, it can be concluded that the optimum reaction temperature is between 60 and 80°C.

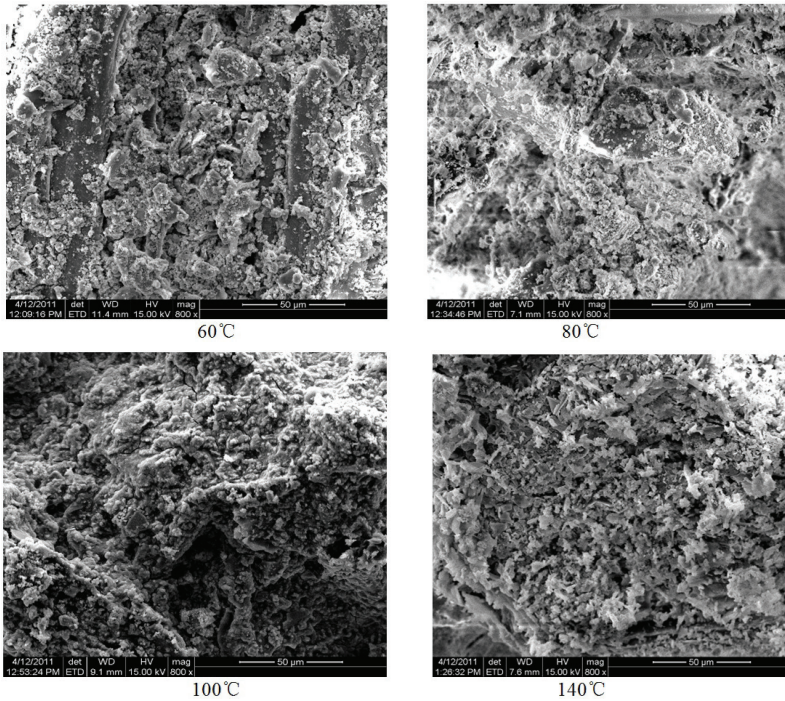


Fig. 10: SEM micrograph of hydration products (reaction time: 2 hours, reaction temperature: 60, 80, 100, 140°C).

According to Fig. 11, when the reaction time was 4 hours, the content change of the hydration products with rising reaction temperature was similar to that in the 2-hour reaction.

Fig. 12 shows the SEM micrographs of the hydration products. When the reaction temperature was 60°C, the surface of the reaction products showed gel-like appearance dotted with unevenly distributed blocks, which was turned to densely distributed blocks when the reaction temperature rose to 80°C. It can be concluded that the microstructure formed at 80°C was better than that formed at 60°C in terms of stability and strengths. As the reaction temperature climbed to 100°C, needle-like appearance dominated the surface and only a small part looked like gel. Hydration at 140°C led to leaf-like reaction product with a small part of gel-like area. Both microstructures were poor in terms of hydro-stability and mechanical strengths. So, it can be concluded that the optimum reaction temperature is 80°C.

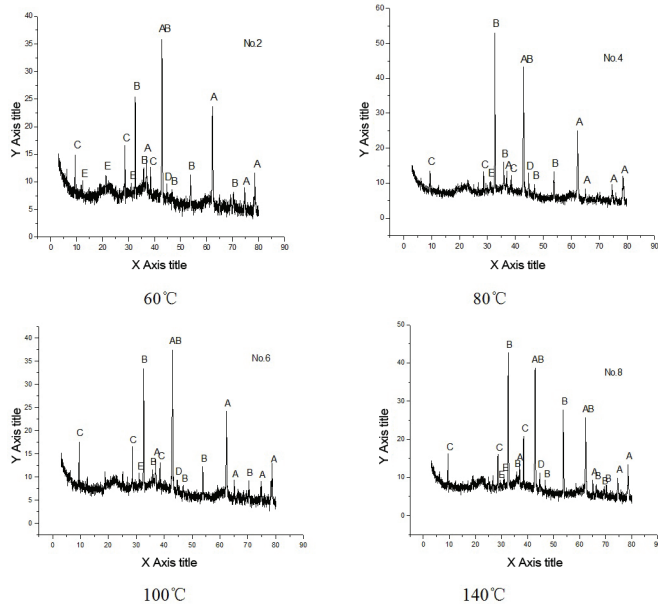


Fig. 11: XRD spectrum of hydration products (reaction time: 4 hours, reaction temperature 60, 80, 100, 140°C).

A-MgO B-MgCO₃ C-Mg₃Si₄O₁₀(OH)₂ D-α-Fe E-5-phrase crystal

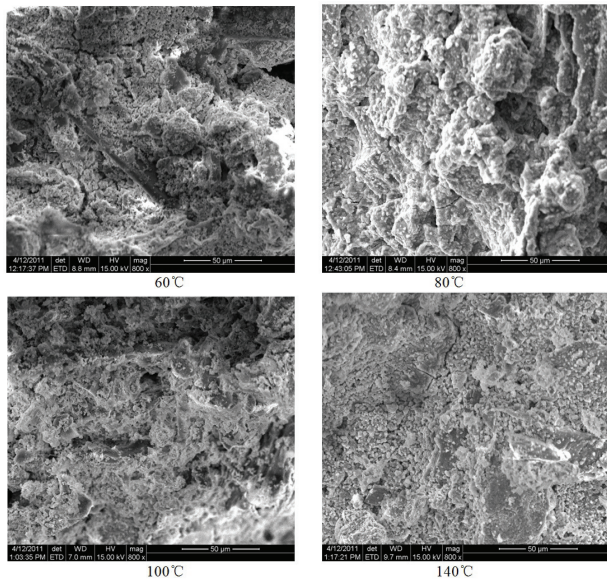


Fig. 12: SEM micrograph of hydration products (reaction time: 4 hours, reaction temperature: 60, 80, 100, 140°C).

CONCLUSIONS

DSC analysis showed that more 5-phase crystal was formed and the hydration products were more stable when the following reaction parameters were adopted: Magnesia-to-wood powder ratio was 100:25; magnesia-to-MgCl₂ solution ratio was 100:90; specific gravity of MgCl₂ solution was 1.26, and additives chosen were ferric alum and (NH₄)H₂PO₄. XRD and SEM analyses showed that more 5-phase crystal was formed when the reaction time was prolonged from 2 to 4 hours. Therefore, it can be concluded that more reaction time means more sufficient hydration and more stable reaction products. The optimum reaction temperature was 80°C, at which, more 5-phase crystal was found.

ACKNOWLEDGMENT

This study was funded by National Natural Science Foundation of China (31070502) and Public Farewell Project of National Forestry Bureau of China (201104042). The authors would also like to thank the support of northern Jiangsu scientific and technological development plan of China (BC2012417).

REFERENCES

1. An, G., 2006: A review on cement-bonded wood panel. *Liaolin Building Mater.* (3): 33-37.
2. Ashori, A., Tabarsa, T., Azizi, K., Mirzabeygi, R., 2011: Wood-wool cement board using mixture of eucalypt and poplar. *Industrial Crops and Products* 34(1): 1146-1149.
3. Ashori, A., Tabarsa, T., Sepahvand, S., 2012: Cement-bonded composite boards made from poplar strands. *Construction and Building Materials* 26(1): 131-134.
4. Barnes, P., 1983: Structure and performance of cement. Applied Science Publishers Ltd, London and New York.
5. Bilinski, H., Matkovic, B., Mazuravic, C., Zunic, T.A., 1984: The formation of magnesium oxychloride phases in the system MgO-MgCl₂-H₂O and NaOH-MgCl₂-H₂O. *J. Am. Ceram. Soc.* 67(4): 266-274.
6. China Building Material Academy, 2003: Green building material and technologies reaching it. Chemical Industry Press, Beijing.
7. Jiang, J., Luo, Y., Lan, X., 2002: Novel thermal insulation and soundproofing building material. Chemical Industry Press, Beijing.
8. Karimi, Y., Monshi, A., 2011: Effect of magnesium chloride concentrations on the properties of magnesium oxychloride cement for nano SiC composite purposes. *Ceramics International* 37(7): 2405-2410.
9. Ma, J., Zhao, Y., Wang, J., Wang, L., 2010: Effect of magnesium oxychloride cement on stabilization/solidification of sewage sludge. *Construction and Building Materials* 24(1): 79-83.
10. Plekhanova, T.A.; Keriene, J.; Gailius, A.; Yakovlev, G.I., 2007: Structural, physical and mechanical properties of modified wood-magnesia composite. *Construction and Building Materials* 21(9): 1833-1838.
11. Stark, S., 2011: Recent advances in the field of cement hydration and microstructure analysis. *Cement and Concrete Research* 41(7): 666-678.

12. Tu, P., 2007: Cement excelsior board and its manufacture technology. *China Forest Products Industry* 34(2): 34-37.
13. Ved, E.I., Zharov, E.F., Phong, H.V., 1976: Mechanism of magnesium oxychlorides formation during the hardening of magnesium oxychloride cements. *Zh Prikl Khim* 49(10): 2154-2162.
14. Yang, M., 1999: Thermal insulation and soundproofing building material. China Planning Press, Beijing.
15. Zhang, S., Shui, B., Wang, H., 2002: Manufacture and application of chemical building material. Chemical Industry Press, Beijing.
16. Zhang, Z., Dai, C., Zhang, Q., Guo, B., Liu, W., 1991: Study on the formation of 5-phase and 3-phase crystal. *China Sci.* (1): 82-89.

BIN NA*, ZHIPENG WANG, ZHIQIANG WANG, TAO DING, RONG HUANG, XIAOLING L.
NANJING FORESTRY UNIVERSITY
COLLEGE OF MATERIALS SCIENCE AND ENGINEERING
NANJING, 210037
CHINA
Corresponding author: nabin8691@126.com

