INTERFACIAL PROPERTIES OF CHEMICAL BONDED PHOSPHATE CERAMICS AND SUGAR MAPLE (*Acer saccharum*)

By

HENGXUAN CHI

A thesis submitted in partial fulfillment of

The requirements for the degree of

Master of Science in Material Science and Engineering

WASHINGTON STATE UNIVERSITY

School of Mechanical and Materials Engineering

December 2012

To the Faculty of Washington State University,

The members of the Committee appointed to examine the thesis of HENGXUAN CHI find it satisfactory and recommend that it be accepted.

_____

Karl R. Englund, Ph.D, Chair

_____

Vikram Yadama, Ph.D

_____

Donald A. Bender, Ph.D

ACKNOWLEDGEMENTS

First and foremost I offer my sincerest gratitude to my chair, Dr. Karl Englund, who has supported me though out my thesis with his patience and knowledge. I attribute the level of my Master's degree to his encouragement and effort; and without his outstanding help and advice, this thesis would not have been completed or written. One simply could not wish for a better or friendlier supervisor. I am grateful to him for bring me into this project and give me so many valuable advices on this thesis. Also I would like to offer my special thanks to my committee member Dr. Vikram Yadama, for his guidance in my experimental design and research objective; he also helped me a lot in this project. As well as Dr. Donald Bender, thanks a lot for his advice and help.

I would like to acknowledge the USDA grant (USDA NIFA 2010-34158-20938) that paid for the research project.

I would also like to extend my thanks to the CMEC personnel for their unlimited support and help. Thanks to Robert Duncan and Scott Lewis, for their useful support and encouragement. I wish to thank various people at CMEC for their contribution to this research. Thank you also goes to all stuffs, graduate students and under graduate students working of worked in CMEC for their kindness help and encouragement.

Finally, I wish to thank my whole family for their encouragement and support throughout my study.

INTERFACIAL PROPERTIES OF CHEMICAL BONDED PHOSPHATE CERAMICS AND SUGAR MAPLE (*Acer saccharum*)

ABSTRACT

By Hengxuan Chi, M.S.
Washington State University
December 2012

Chair: Karl Englund

The research within this thesis focused on the interfacial bond between magnesium phosphate ceramics (MPCs) and sugar maple (*Acer saccharum*). A pull-out test method was investigated and utilized for evaluating the interfacial mechanical properties. A variety of aggregates and binder component ratios were incorporated into MPC formulations that were evaluated for their bond performance with wood. A 3:1 weight ratio of monopotassium phosphate (MKP) and magnesium oxide (MgO), the binder system, was found to have the best binder performance. A Mixture Design model was used to understand the influence the levels of MPC binder, and aggregates; Portland cement, wollastonite and VCAS, had on the interfacial properties. The statistical results show that MPC binder level is the primary factor which influences the interfacial properties, while wollastonite and VCAS can mutually promote the interfacial property. But the bond strength is decreased when Portland cement is mixed with the two other

aggregates. Polyvinyl alcohol (PVA) fiber was used as a reinforcement of the MPC and was also found to influence the interfacial strength of MPC with maple. The interfacial mechanical properties with the maple dowel rods are enhanced by PVA in a wollastonite-based MPC but a decrease was seen in cement-MPC/maple and VCAS-MPC/maple. Treatments of 90% RH conditioning and water immersion were utilized to evaluate the environmental durability of MPCs. The type of aggregates utilized in the MPCs exhibit different moisture durability performance; the VCAS-MPC/maple has very poor moisture performance, while the Portland cement-MPC/maple and wollastonite-MPC/maple had reduced had reduced interfacial shear stress, but still maintained bond integrity unlike the VCAS based MPC.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF NOMENCLATURE

CBPC	Chemical bonded phosphate ceramics
ZPC	Zinc phosphate ceramics
MPC	Magnesium phosphate ceramics, MgO based CBPCs
MKPC	Magnesium potassium phosphate ceramics, a type of MPC
MKP	Monopotassium phosphate, H_2KPO_4
MgO	Magnesium oxide
Mg	Magnesium
VCAS	Vitrified calcium aluminio-silicate, white pozzolan
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
WCC	Water content coefficient
τ_f	Failure shear stress
τ_i	Initial crack shear stress
DOE	Design of experiment
VCAS-MPC	MPC of 60 wt.% MPC binder and 40 wt.% VCAS
W-MPC	MPC of 60 wt.% MPC binder and 40 wt.% wollastonite
C-MPC	MPC of 60 wt.% MPC binder and 40 wt.% Portland cement
RH	Relative humidity

CHAPTER ONE
INTRODUCTION

1.1 Chemical bonded phosphate ceramics

1.1.1 Chemical bonded phosphate ceramics

Chemical bonded phosphate ceramics (CBPCs) is a class of inorganic materials also called phosphate cements [24] or phosphate "Ceramicrete" [20]. They are synthesized through the chemical reaction of metal cations with phosphate anions at room temperature [18]. The metal cations of CBPCs can be provided by many metal oxides, such as ferric (Fe_2O_3), aluminum (Al_2O_3), zinc (ZnO), ferrous oxide (FeO), magnesium (MgO) and calcium oxide (CaO) [20]. Therefore, the CBPCs can be grouped according to metal cations, such as zinc phosphate ceramics (ZPCs) magnesium phosphate ceramics (MPCs) to name a few. Fabrications of CBPCs were initially started in the 19^{th} century, where ZPCs were used in dental applications [1]. In 1939 Prosen [14] utilized MPCs in foundry operations for casting metals.

Because of their unique properties, CBPCs are also classified as ceramic cements, where they contain the attribute of ceramics and hydraulic cements. The microstructure of CBPCs is similar to ceramics, with highly crystalline structures, however, unlike ceramics CBPCs can be formed at room temperature and utilize water to initiate chemical reactions to set the material, which is analogous to fabrication of hydraulic cements [18]. Table 1.1 compares some of the basic characteristics and attributes of CBPCs, Portland cement, and traditional ceramics [3, 11, and 18]. Due to their highly crystalline structure, CBPCs are generally stronger and have improved mechanical properties to that of

Portland cement. Unlike the pH of Portland cement, which is usually around 12 [4], CBPCs generate a final pH that is neutral, making them non-invasive to the aggregates utilized in the final cement formulation. The highly alkalinity of Portland cements can destroy the interfacial bonding when in contact with wood or other lingo-cellulosic materials [16].

Table 1.1 Comparisons between chemical bonded phosphate ceramics (CBPCs), Portland cement, and traditional ceramics

Properties	**CBPCs**	**Portland cement**	**Clay ceramics**
Setting process	Acid-base reaction, hydration and crystallization	Hydration and crystallization	Sintering
Setting temperature	- 0˚C + (can set below freezing)	0˚C +	High temperature
Acidity and alkalinity	Neutral (depending on formulas)	Strong alkaline	Neutral
Crystallinity	Highly	Lowly	Highly
Potential bonding with wood	Strong	Weak	N/A

1.1.2 Magnesium phosphate ceramics

Magnesium phosphate ceramics (MPCs) are most common CBPCs and are currently used in mending or repairing Portland cement structures [7], stabilization of hazardous wastes [18] and architectural markets. MPC is a general term for all MgO based CBPCs, which can react with multiple phosphate salts chemically and form several phases. Phases found in MPCs are listed in Table 1.2 [18].

Table 1.2 Phases found in magnesium phosphate ceramics [18]

Formula	Name
$Mg(H_2PO_4)_2 \cdot 2H_2O$	Magnesium dihydrogen phosphate
$Mg(H_2PO_4)_2 \cdot 4H_2O$	Magnesium dihydrogen phosphate
$MgHPO_4 \cdot 3H_2O$	Newberyie
$MgHPO_4 \cdot H_2O$, $MgHPO_4 \cdot 2H_2O$	Haysite
$Mg(NH_4 \cdot HPO_4)_2 \cdot 4H_2O$	Schertelite
$MgNH_4PO_4 \cdot 4H_2O$	Struvite
$MgNH_4PO_4 \cdot H_2O$	Dittmarite
$MgKPO_4 \cdot 6H_2O$	Magnesium potassium phosphate
$Mg_3(PO_4)_2 \cdot 4H_2O$	Magnesium phosphate

Monopotassium phosphate (MKP) is a commonly used form of phosphate for the manufacture of magnesium potassium phosphate ceramics (MKPC) [18] as a type of MPCs. The major chemical reaction of MKP and MgO in aqueous solution has three steps: rapid dissolution of acid MKP, dissolution of the alkaline MgO and crystallization [18].

Because MgO does not dissolve in an aqueous system at a neutral pH [19], the first step of the reaction is the dissolution of MKP, which creates an acidic environment. The solubility in water of MKP is approximately 22g/100ml at room temperature, the pH for 1% MKP aqueous solution is 4.6 and shows a weak acid property. The dissociation reaction of MKP can be expressed as [18],

$$KH_2PO_4 = K^+(aq) + H_2PO_4{}^-(aq)$$

$H_2PO_4{}^-$ has the ability to dissociate where the major product is $HPO_4{}^{2-}$at a pH of 4.6

$$H_2PO_4{}^-(aq) = H^+(aq) + HPO_4{}^{2-}(aq)$$

$$HPO_4{}^{2-}(aq) = H^+(aq) + PO_4{}^{3-}(aq)$$

MgO becomes soluble in the acidic slurry created by the dissociation of MKP, resulting in the following dissolution reaction:

$$MgO + 2H^+ = Mg^{2+}(aq) + H_2O$$

The final step of this reaction is crystallization

$$Mg^{2+}(aq) + K^+(aq) + PO_4{}^{3-}(aq) + 6H_2O = MgKPO_4 \cdot 6H_2O$$

The complete reaction which includes the three primary reactions above is given by [5]

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O$$

Because of MgO is the proton acceptor as base and MKP is the proton donator as acid, this reaction is also considered an acid-base reaction [18].

Wagh [19] determined that the dissolution of MgO is a very important step which could influence the reaction rate of the MKP-MgO reaction. The dissociation constant *K* witch refers the dissolution rate of MgO is defined as

$$K = \langle Mg^{2+}(aq)\rangle / \langle MgO\rangle \langle H^+\rangle^2$$

And K here is also related with the Gibbs free energy changing (ΔG) of the dissolution

$$K = exp[\beta(-\Delta G)]$$

$$\beta = 1/k_B T$$

Where k_B and T are, the Boltzmann constant and the absolute temperature of the system [19]. By using calcined MgO the dissolution can be reduced because of the particle size of MgO is increased via calcination [18].

Wescott et al. [22]monitored the temperature variation of the MKP/MgO reation at a 55-gal scale, Wagh utilized a similar procdure with a lower volume of 2 liters [18]. The tests by Wagh [18] showed that the MPC slurry cools by about 3℃ in 10 min initially, during which MKP dissolves and makes the slurry slightly acidic. Later, the solution dissolves MgO partially, and the acid-base reation initiates. The slurry sets at 55℃, while the now hardened CBPC continues to heat until a theoretical maximum of 82℃ in about 1.5 hours.

The microstructure of magnesium potassium phosphate cement (MKPC) was explored by Chau et al [5]. Their research showed that the major crystalline phase observed in MKPC is magnesium potassium phosphate hexahydrate. The MKPC has a similar structure as struvite ($MgNH_4PO_4{\cdot}4H_2O$); it is needle shaped polycrystals with small cross section but large aspect ratio. And the hexahydrate poly crystals generally grow along the longitudinal direction of the crystal. The final forms of the crystals depend upon the molar ratio of magnesium to phosphate. With a molar ratio of magnesium to phosphate as low as 2, it is needle shaped polycrystals with small cross section but large

aspect ratio. As the molar ratio of magnesium to phosphate increases, the polycrystals grow much larger and turn into prismatic (Fig 1.1). This phenomenon indicates the possibility of the varying of the mechanical properties by changing the molar ratio of magnesium to phosphate in these magnesium based phosphate cements.

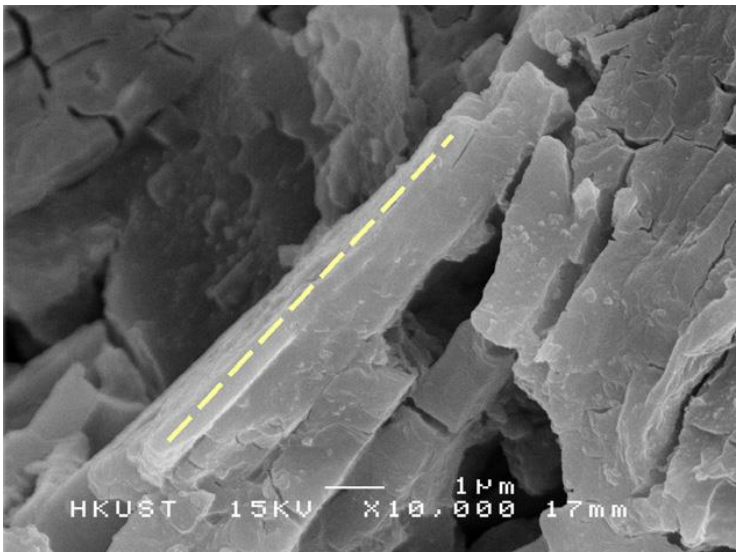


Fig 1.1 A prismatic MKPC polycrystal covered with subhedral surfaces [5]

Jovannovski et al. [9] studied the crystal structure of MKPC monohydrate ($MgKPO_4 \cdot H_2O$) in 1997. The results of this research indicate that the Mg atoms are coordinated to five oxygen atoms belonging to PO_4 groups and one oxygen atom oxygen atom H_2O, while K atoms are surrounded by eight oxygen atoms.

1.2 Background on inorganic binders in wood composites

There are unique attributes of CBPCs that make it an ideal binder for wood and natural fiber composites. CBPCs can have a rapid setting time (MPCs set in 20-60 minutes), have good adhesive properties with many materials, low water sorption, and impart improved flame and fire retardency [18].

Natural fiber/inorganic composite materials, such as wood fiber/cement composite materials, have advantages over traditional wood composites. When compared to many polymeric binder-wood composites, natural fiber/inorganic composite materials can be durable, impart toughness in frozen environments, improved flame retardant potential, have higher moisture resistance, lower susceptibility to biodegradation, and improved noise isolation [23]. Many researchers in this area have focused in Portland cement-based wood composite materials, but have found the compatibility of wood and cement is often compromised [8, 12, 21]. The cellulose chain length is sensitive to alkali attack, it can be decreased via peeling and hydrolytic reactions [3, 15], also called alkaline degradation of cellulose [13]. In research by Roffael and Sattler [16] the interaction between sulphate pulps made from rice straw and cement, showed that the cellulosic pulps were degraded to soluble carbohydrates by cement due to its highly alkalinity. This research indicates that the materials made from cement with lower alkaline buffering capacity have higher mechanical strength values. Moreover, the research also showed two ways to increase the mechanical properties of inorganic/natural fiber composite, decreasing the alkalinity and changing the binder systems. Unlike Portland cement/wood composites, CBPCs/wood composites have the potential of better composite performance primarily due to their neutral pH.

There is limited information at this time on the development of natural fiber/CBPC composites. In studies by Laufenberg and Aro [10], they found that CBPCs as a binder in wood composites has the potential for lower minimum binder loading, shorter process time, non-thermal processing, better mechanical properties, improved fire resistance properties, and lower energy consumption than Portland cement. One distinctive

disadvantage of MPCs is the price MKP. Phosphates are often used in many applications in the chemical industry [17] and fertilizers in agriculture applications [2]. The expensive price of MKP makes the cost of MPC much higher than Portland cement.

Donahue and Aro [6] studied MPC as a binder for oriented strand board (OSB). For the MPCs in this research, a 3/1 weight ratio of MKP/MgO was utilized and fly ash was the primary aggregate. They tested four formulas of the boards with different binder, fly ash, residue and water levels. The density, water absorption, thickness/volume swelling, modulus of rupture (MOR), screw withdrawal strength and internal bond strength of these boards were tested. The results indicated that the performance of these MPC/wood board is eligible for many construction applications. A preliminary market assessment shows there is potential for these products to be utilized as interior door core and door stile and rail material.

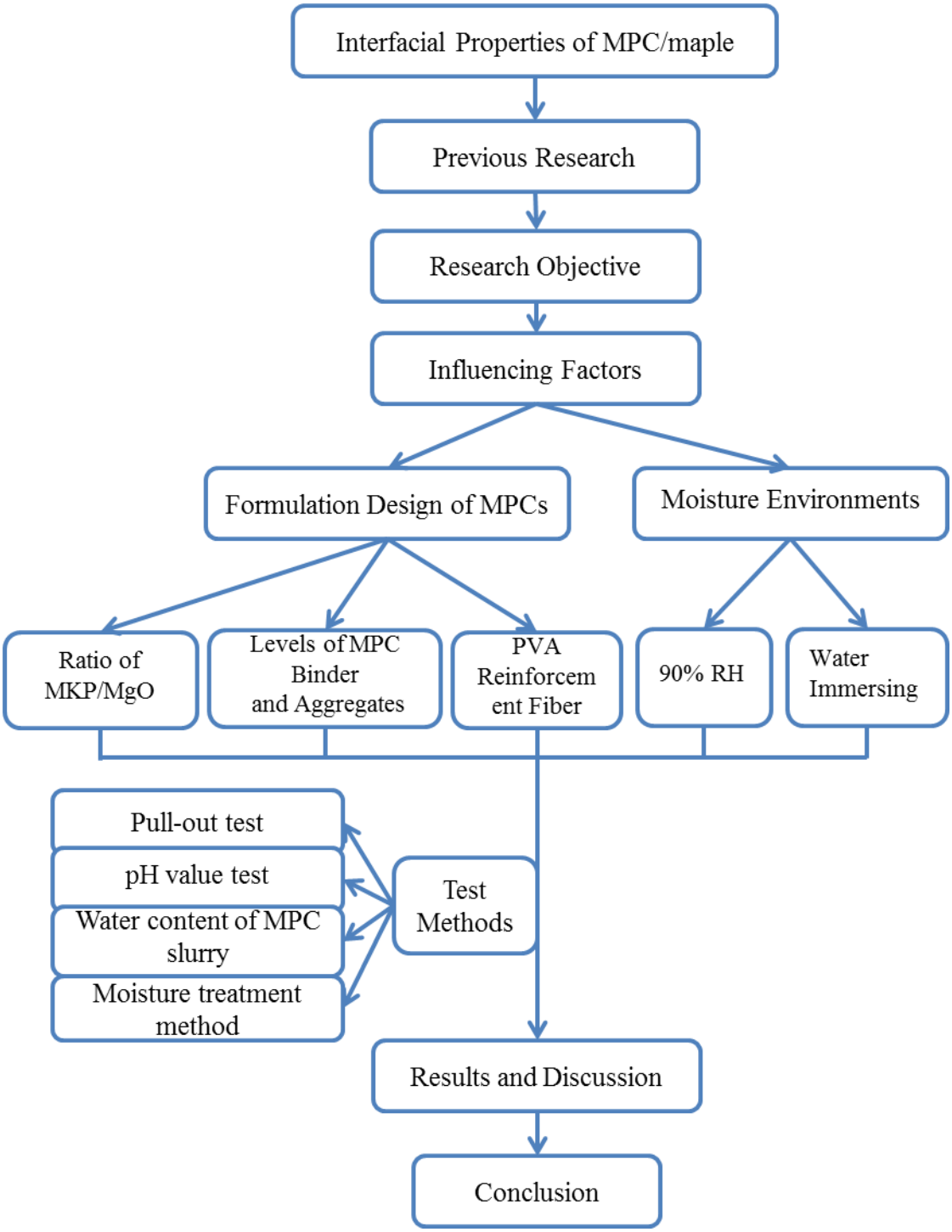
1.3 Research Objectives

The overall goal of this project is to evaluate the interfacial mechanical properties of chemical bonded phosphate ceramics and sugar maple. Due to the unique properties of MPCs, the objectives of the thesis are:

- Determine a standard of water content level for maintain various formulas MPCs slurries have similar fluidity.
- Evaluate how formulas of binder influence the strength of MPC/maple interface.
- Evaluate the influences of different binder level with different aggregates types, and different aggregates level and reinforcement by polyvinyl alcohol (PVA) fibers, on MPC/maple interface.

- Evaluate the influence of different moisture environment on the interfacial bonding performance and MPCs properties

1.4 Research structure



References

1. Ames, W. (1893). Oxyphosphates. *Dental Cosmos, 35*, 869-875.
2. Barranco, D., Arquero, O., Navarro, C., & Rapoport, H. F. (2004). Monopotassium phosphate for olive fruit abscission. *HortScience, 39(6)*, 1313-1314.
3. Bezerra, E., Joaquim, A., Jr., H. S., John, V., & Agopyan, V. (2006). The effect of different mineral additions and synthetic fiber contents on properties of cement based composites. *Cement and Concrete Composites, 28*, 555-563.
4. Birchall, J. D., Howard, A. J., & Bailey, J. E. (1978). On the hydration of Portland cement. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 360(1702)*, 445-453.
5. Chau, C., Qiao, F., & Li, Z. (2011). Microstructure of magnesium potassium phosphate cement. *Construction and Building Materials, 25*, 2911–2917.
6. Donahue, P. K., & Aro, M. D. (2006). Durable Phosphate-Bonded Natural Fiber Composite Products. *10th International Inorganic-Bonded Fiber Composites Conference*, (pp. 79-88). S ão Paulo – Brazil.
7. El-Jazairi, B. (1982). Rapid repair of concrete pavings. *Concrete, (London), 16*, 12-15.
8. Jorge, F. C., Pereira, C., & Ferreira, J. M. (2004). Wood-cement composites: a review. *Holz als Roh- und Werkstoff, 62(5)*, 370-377.
9. Jovannovski, G., Pocev, S., & Kaitner, B. (1997). Crystal Structure of Magnesium Potassium Phosphate Monohydrate (MgKPO4·H2O). *Bulletin of the Chemists and Technologists of Macedonia, 16(1)*, 59-63.
10. Laufenberg, T. L., & Aro, M. (2004). Phosphate-Bonded Ceramic – Wood Composites : R & D Project Overview and Invitation to Participate. *Ninth International Conference on Inorganic-Bonded Composite Materials*, (pp. 1-12). Madison, Wisconsin.
11. Lee, W. E., Souza, G. P., McConville, C. J., Tarvornpanich, T., & Iqbal, Y. (2008). Mullite formation in clays and clay-derived vitreous ceramics. *Journal of the European Ceramic Society, 28(2)*, 465-471.
12. Miller, D. P., & Moslemi, A. A. (1989). Wood-cement composites: effect of model compounds on hydration characteristics and tensile strength. *Wood and Fiber Science, 23(4)*, 472-482.

13. Pavasars, I., Hagberg, J., Borén, H., & Allard, B. (2003). Alkaline degradation of cellulose: mechanisms and kinetics. *J Polym Environ, 11 (2)*, 39–47.

14. Prosen, E. M. (1939). *Patent No. 2,152,152.* United States.

15. R. D. Toledo Filho, K. S. (2000). Durability of alkali-sensitive sisal and coconut fibres in cement mortar composites. *Cement and Concrete Composites, 22*, 127-143.

16. Roffael, V. E., & Sattler, H. (1991). Studies on the interaction between lignocellulosics (straw pulps) and cement. *Holzforschung, 45(6)*, 445-454.

17. Van Pilsum, J. F., Martin, R. P., Kito, E., & Hess, J. (1956). Determination of creatine, creatinine, arginine, guanidinoacetic acid, guanidine, and methyl-guanidine in biological fluids. *Journal of Biological Chemistry, 222(1)*, 225-236.

18. Wagh, A. S. (2004). *Chemically Bonded Phosphate Ceramics.* Oxford: Elsevier.

19. Wagh, A. S., & Jeong, S. Y. (2003). Chemically bonded phosphate ceramics: I, a dissolution model of formation. *Journal of the American Ceramic Society, 86*, 1838–1844.

20. Wagh, A. S., Singh, D., Jeong, S. Y., & Strain, R. (1997). *Ceramicrete stabilization of low-level mixed wastes - A complete story, ANL/ET/CP-92843.*

21. Wei, Y. M., Zhou, Y. G., & Tomita, B. (2000). Hydration behavior of wood cement-based composite i : evaiuation of wood species effects on compatibility and strength with ordinary portland cement. *Journal of Wood Science, 46*, 296-302.

22. Wescott, J., Nelson, R., Wagh, A., & Singh, D. (1998). Low-level and mixed radioactive waste in-drum solidification. *Practice periodical of hazardous, toxic, and radioactive waste management, 2*, 4-7.

23. Wolfe, R. W., & Gjinolli, A. (1996). Cement-Bonded Wood Composites as an Engineering Material. *The Use of Recycled Wood and Paper in Building Applications,* (pp. 84-91). Madison, Wisconsin.

24. Yang, Q., Zhu, B., Zhang, S., & Wu, X. (2000). Properties and applications of magnesia–phosphate cement mortar for rapid repair of concrete. *Cement and concrete Research, 30(11)*, 1807-1813.

CHAPTER TWO
THE INFLUENCE OF FORMULATION DESIGN OF MAGNESIUM PHOSPHATE CERAMICS (MPC) ON THE INTERFACIAL BONDING PROPERTIES WITH SUGAR MAPLE (*Acer saccharum*)

2.1 Introduction

As a type of chemical bonded phosphate ceramics (CBPCs), magnesium phosphate ceramics (MPCs) have found uses in architectural and some construction applications [10, 26]. Due to their highly crystalline structure, MPCs are generally stronger and have improved mechanical properties to that of Portland cement [26]. Moreover, Portland cement-based wood composite materials have been researched in previous studies and have found that compatibility of wood and Portland cement is often compromised [17, 20, 28]. Unlike Portland cement/wood composites, MPCs/wood composites have the potential of better composite performance. To prove this potential, studies on the interfacial bonding properties between MPC and wood are necessary. There are many factors which have the potential to influence the interfacial bonding properties between MPC and wood; such as pH value and water content of MPC slurries, aggregates used in the MPC and formulation design of the MPCs.

MgO has a very low solubility in an aqueous system at a neutral pH; and this solubility and dissolution rate increase with the increasing pH value [27]. The reaction rate of MKP and MgO highly depends on the MgO dissolution rate [27]. Therefore, this reaction rate is closely related with pH value of the aqueous system and it also has a great potential to influence the microstructure and mechanical properties of the product. From

another perspective, many organic chemical reactions are initiated by strong acid and alkali, such as the strong alkalinity of Portland cement can initiate the alkaline degradation of cellulose [21]. This alkaline degradation has a highly potential to influence the interfacial properties between wood and inorganic material. Tol êdo Filho et al. [25] reported the mechanical property of natural fiber can be influenced by alkaline attack; similarly, this alkaline attack has the possibility to influence the interfacial property of MPC and wood.

Another important factor with hydraulic cements, such as Portland cements and our CBPCs is the water content of the slurries. The water content influences the fluidity and workability of all hydraulic cements. In the early 20th century, Duff A. Abrams [1] developed the slump test method which utilized to indicate the different fluidity and workability of cement slurries; the slumps are different with different water/cement ratio for a certain formula of cement. The relation between strength of cement and water content was also figured out in Abrams's book [1]; the strength of cement decrease with the increasing water content. As a type of hydraulic cement, there is a potential that CBPCs have similar workability properties as with Portland cement.

The water content in CBPCs slurry was mentioned in previous studies. In Formosa, et al.'s research [11], a water to solid (W/S) ratio (water content) of 0.24 was used to study the MPC slurry which mixed with MgO, MKP and boric acid. In Donahue and Aro's research [9], 3 parts MKP, 1 part MgO, and 2 parts water (by weight, water content = 0.5) was used to produce MPC typically. However, the use of different binder ratios and aggregate types will impart different slurry properties, such as water absorption ability, fluidity and workability. The reasons for these different properties can be

chemical composition, different particle size and shape, and their microstructure. Therefore, water contents for consistent slump values need to be addressed.

In MPCs, the MKP and MgO are the primary binders or adhesive component of the cement. The weight ratio of MKP to MgO is strongly related to the mechanical and physical performance of the MPC. The crystal size and shape are different between high and low MKP/MgO ratio [7], the MPC crystal tends to be smaller and needle shaped at molar ratio of magnesium to phosphate of 2, but are larger and turn into bladed and prismatic structures with wrinkled surface at molar ratio of magnesium to phosphate of 1.11:0.96. In Formosa, et al.'s research [11], an MKP/MgO weight ratio of 77/23 was utilized; an MKP/MgO weight ratio of 3/1 was utilized in Donahue and Aro's research [9]. These MKP/MgO weight ratios were determined as best ratios of MPC compression strength, however little or no research has looked at binder ratios and their influence on interfacial bonding properties.

Many aggregates and additives used in concrete and traditional ceramics have the potential to be used in MPCs. Previous research by Yang et al. [29] reported a successful rapid repair of concrete by utilizing MPCs. This success was measure by the good compatibility of MPC with Portland cement. A source which provides soluble silica in the CBPC systems has the potential to enhance the mechanical properties of CBPC product [26]. Therefore, Portland cement has a great potential to enhance CBPC because of it is a typical material containing soluble silica [5]. MPCs have lower alkalinity than Portland cement [4, 26], therefore, Portland cement/MPC mixtures will likely have lower alkalinity than native Portland cement. The lowered pH of this mixture will potentially avoid the interfacial cellulosic degradation [24] when bonded with wood.

Vitrified calcium aluminio-silicate (VCAS) also called white pozzolans has a general chemical and mineralogical composition similar to that of Class C fly ash. VCAS generally contains 52%-62% silicon dioxide (SiO_2), 12%-16% aluminum oxide (Al_2O_3), and 16%-25% calcium oxide (CaO). There are several benefits of using VCAS in concrete products which include; workability of cement with lower water content demands; reduction in heat of hydration reducing the incident of thermally induced stress cracking; increased durability, improved surface quality, and no color change [14, 15].

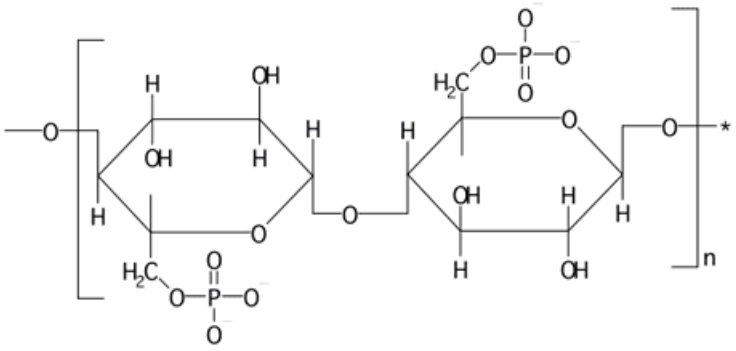
Wollastonite is calcium inosilicate mineral ($CaSiO_3$) and is found in crystalline limestones [26]. The particle of wollastonite which used in construction industry is usually acicular or short fiber. In an aqueous system, wollastonite is slightly soluble and hence participates in the setting reaction as a source of soluble silica during formation of CBPC products and provides better toughness and flexural properties [26].

Polyvinyl alcohol (PVA) fibers are utilized to modify the mechanical properties of cementitious materials. Çavdar [6] evaluated the mechanical properties of fiber reinforced cement composites at 21 ℃, 100 ℃, 450 ℃ and 650 ℃. The results indicate PVA fiber increased flexural strength of cement at these temperatures, but decreased the compressive strength of cement. In Kim and Lee's research [18], PVA fibers decreased the tensile and compressive strength of fiber-reinforced concrete slightly.

There are some potential bonding mechanisms of the interfacial MPC/wood bonding, such as mechanical interlock and chemical adhesion. In the field of wood adhesives, of the preparation of the wood surface is usually done via sawing, knife-planning followed by finishing sanding. In de Moura's study [31], the adhesion

mechanisms of maple wood treated by two surfacing processes have been evaluated by pull-off adhesion test and accelerated aging. These processes are peripheral straight-knife planning and sanding with a 120- 180-grit sandpaper. Because of different mechanical interlock properties of these processes, the adhesive characteristics of maple wood surfaces have distinct properties. As a result, pull-off adhesion was significantly higher on sanded (7.1 MPa) than on planed surfaces (4.5 MPa).

One of the main components of wood is cellulose, and cellulose is able to react with phosphate and form cellulose phosphate [32]. The chemical structure of cellulose phosphate can be described as,



Cellulose phosphate from oil palm empty fruit bunches microcrystalline cellulose is synthesized and characterized by Wanrosli [33]. The cellulose phosphate gel was synthesized from oil palm empty fruit bunch microcrystalline cellulose (OPEFB - MCC) by using the $H_3PO_4/P_2O_5/Et_3PO_4$/hexanol method, and a 30℃ reaction temperature and 72h reaction time has a highly yield percentage. Because of the reaction temperature and time are similar than the CBPC curing process, there is a highly possibility that cellulose phosphate forms on the interface of CBPC/wood; even it is a minor reaction.

Interfacial mechanical properties test methods usually address the evaluation of crack energy release rate and shear strength. To evaluate interfacial crack energy release rate, wedge test [12], three-point bending [16] and four-point bending [22, 23] are commonly utilized. To evaluate shear strength, shear-block test [3] and pull-out test [8, 16] are often utilized. In this study, a pull-out test was used to evaluate the interfacial shear strength of MPCs and wood.

2.2 Research Objective

The overall goal is to evaluate the relationship between formulas of MPC and their influence on the interfacial strength when bonded to sugar maple. To reach this goal, an effective mechanical test method for evaluate the interfacial strength has to be investigated. Moreover, there are many factors which have the possibility to influence the interfacial properties of MPC and sugar maple; workability or slurry water content, MKP/MgO ratio, reinforcement fiber, levels of MPC binder and aggregates (Portland cement, wollastonite, VCAS). The specific objectives are as follows:

- Determine the pH and water content requirements of MPC slurries with different aggregates.
- Utilize a pull-out test to evaluate the interfacial performance of MPC and maple utilizing different binder ratios (MKP/MgO) and binder levels.
- Evaluate the relationship between different aggregates and fiber reinforcement in the MPC and their influence on the interfacial strength of MPC/maple.

2.3 Raw Materials

In this research, sugar maple (*Acer saccharum*) was used as the wood species throughout all of the testing protocols. Wooden dowel rods were purchased through Cincinnati Dowel & Wood Products Co. The MPC mixture is comprised of binder (MKP/MgO), water, and various aggregates; Portland cement (Type I/II), wollastonite (NYCO Minerals Inc., short micro fiber) and VCAS (VCAS 160, Vitro Minerals, Inc.,). Synthetic polyvinyl alcohol (PVA) fibers, 8mm in length, (RECS15, 8 denier, monofilament, Nycon Corporation) were also used in some of the formulations. The MPC binder is made from calcined magnesium oxide (MgO) and monopotassium phosphate (MKP) both supplied by Ecologically Responsible, LLC.

2.4 Test methods

2.4.1 Test methods for interfacial mechanic properties of CBPCs and wood

Previous studies have evaluated interfacial shear strength by using a dowel pull-out method [8, 16]. The structure, shape and size of pull-out test specimens in this study for evaluating interfacial shear strength of MPCs and wood are shown in Fig 2.1. A sugar maple rod was bond in the center of an MPC cylindrical block. The diameter of the wood dowel was 6.35mm (0.25 inch); the total length was 114.3mm (4.5 inch). The diameter of the CBPC block was 31.75mm (1.25 inch); the length was 25.4mm (1 inch), which is the length of the MPC/wood interface. The wood rod was pulled out in positive x-axis direction; and the CBPC block was held by a frame shown in Figure 2.2.

For casting the specimens, a custom mold was designed. The mold was made from polyvinyl chloride (PVC) tubes and 3 holders which held the rod in the center of the mold. The mold was coated by semisolid lubricant grease to provide a release property.

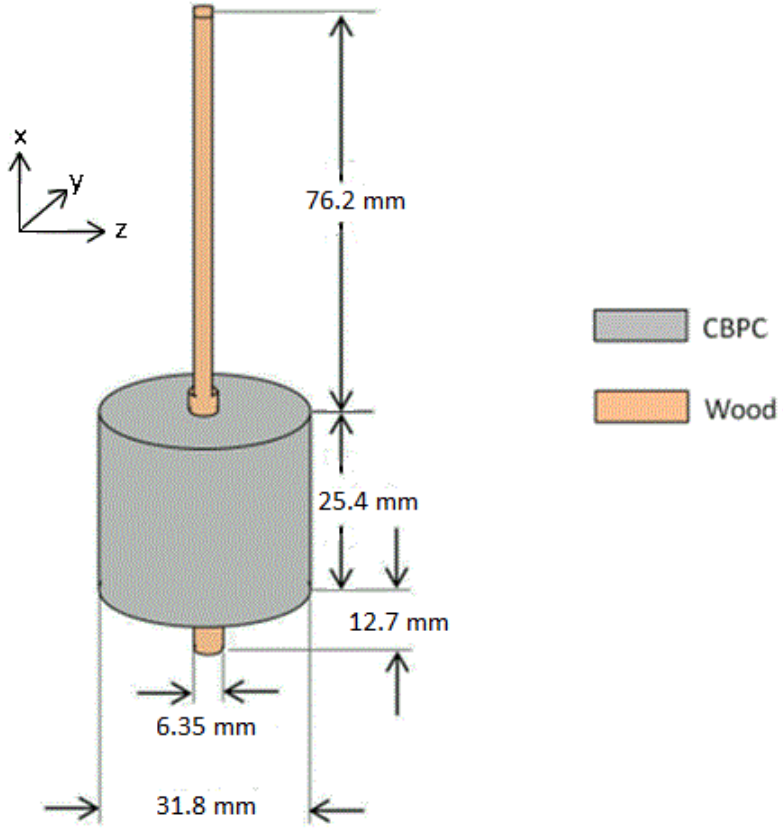


Fig 2.1 Structure, shape and size of pull-out MPC/maple specimen

The maple wood rods were cut into 114.3mm (4.5 inch) lengths and conditioned at 64% RH, 22 ℃ for at least 7 days. After the conditioning, the wood rods were cleaned and sanded by using 200 mesh sand paper. The molds were assembled and the rods were inserted into the molds. The dry solid raw materials of the MPC were weighed and dry mixed in a polyethylene plastic bowl for 10 minutes by hand. For the specimens containing PVA fibers, the fibers were used to reinforce and potentially toughen the MPC.

The PVA fibers were initially separated by rubbing them in a clean plastic bag; added into the MPC dry powder mixture; and mixed by hand with the MPC powder for 10 minutes until the PVA fiber was separated in the mixture uniformly before adding water. Water was then added to the dry ingredients and mixed for an additional 10 minutes. The slurry was filled into the molds and vibrated on a vibration table for 10 minutes to minimize air pockets and voids in the cement or at the interface. Once the MPC solidified (24 hours), the specimens were conditioned at 64% RH, 22 ℃ for at least 7 days prior to any testing.

Once the specimens were conditioned for least 7 days the molds were disassembled. A file was used to eliminate any build-up on the MPC and to create a flat parallel surface for testing.

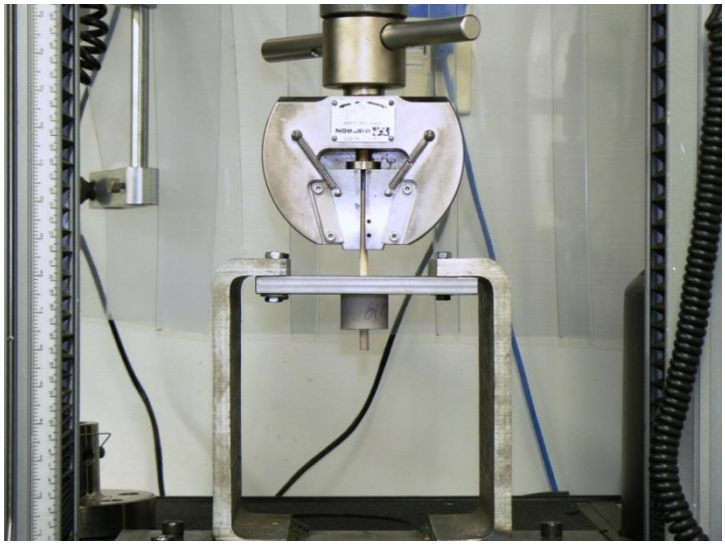


Fig 2.2 Mechanical test of a pull-out MPC/maple specimen

An image of the set-up for the pull-out test procedure is shown in Fig 2.2. A holding plate and 30 kN wedge action grips were utilized on a 8.90 kN (2 kip) electromechanical universal test frame system to apply the tensile load through the

wooden dowel of the specimen. The specimens were pulled in tension with a 1.27 mm (0.05 inch) per minute displacement rate until failure. And the load- crosshead displacement data collection rate was 15Hz. The displacement of these data was the relative displacement between the specimen holder and the wedge action grips.

Calculating the interfacial shear strength for the pull-out test is described in Hwang, Hse and Shupe's [16] research through the following equation:

$$T = \frac{F}{\pi \times \mathrm{d} \times \mathrm{l}}$$

Where,

T, interfacial shear strength

F, debonding force

l, interfacial length

d, wood rod diameter

π, circular constant

2.4.2 Test method for pH value of CBPC slurries

A pH meter (OAKTON® pH15 Meter) with a glass electrode was utilized to measure the alkalinity of MPC slurries. The test procedure utilized followed the same procedure outlined by Zhong, Ni and Li [30]. The pH meter was calibrated by using pH=4, pH=7 and pH=10 buffer solutions before testing. 10g dry MPC samples which may contain MKP, MgO, Portland cement, VCAS and wollastonite were mixed in a plastic container for 4 minutes, then 100g water were filled into the container, the MPC

samples were mixed with water for 30 seconds. Subsequently, the electrode and temperature sensor were put into the solution and mixed for 30 seconds until the reading of pH meter becomes stable. Because of the pH value of MPC is not only depending on formula but also reaction time, the pH values were measured at the beginning of MPC's reaction and are classified as "starting pH value". The reading was accurate to 0.1 pH. A replicate test was utilized for each formula to verify the reliability of the pH measurement.

The pH values of the individual aggregated; Portland cement, VCAS and wollastonite without MKP or MgO were also evaluated; similarly, the pH values of the mixture containing binder only (2.5 g MgO, 7.5 g MKP and 100 g water) was also evaluated.

2.4.3 Water content in MPC slurries

To maintain a similar MPC slurry workability or fluidity when different aggregates are added to the system, the relationship between water content and MPC formulas has to be evaluated. In this research, all effective factors were assumed and approximated as linear factors. Then, the water content of an MPC slurry with certain workability and formula can be described as,

$$WC_{MPC} = \sum_{i=1}^{n} WCC_i \times C_i$$

Where,

WC_{MPC}, Water content of an MPC slurry

WCC_i, Water content coefficient of component i

C_i, Content of component i, and

$$\sum_{i=1}^{n} C_i = 100\%$$

The WCC is a coefficient to describe the water content requirement of a certain component in MPC slurries. A higher WCC indicates this component requires higher water content to reach a certain fluidity. To evaluate the WCC, a slump test was utilized similar to the procedures outlined in ASTM C143 [2], however, a smaller slump cone with the base 76 mm (3 inch) in diameter, the top 48 mm (1.9 inch) in diameter, and the height 91 mm (3.6 inch) was used to minimize material usage. The cone was placed on a plastic board, the slurry was filled fully in the cone. Then the cone was carefully lifted vertically upwards, and the difference between the top of the mold and the displaced original center of the top surface of the slurry was measured immediately.

2.5 Results and discussion

2.5.1 pH value of MPC slurries

Table 2.1 pH values of the mixture containing MPC binder, Portland cement, wollastonite or VCAS and water

Formula	pH
Portland cement	11.7
Wollastonite	8.6
VCAS	7.7
MPC Binder (MKP:MgO=3:1 by weight)	5.1

The results for the pH tests on in the individual aggregates and the binder are shown in Table 2.1. These results show that the alkalinities of these components vary and may have the potential to influence the interfacial bond strength. Further results of the complete formulations are found in Tables 2.5 and 2.7. As expected Portland cement showed the highest alkalinity, while the MKP/MgO binder system had an acidic slurry and a lower pH.

2.5.2 Water content in MPC slurries

In this research, there are four components added in MPC slurry, MPC binder (a mixture with 3 parts MKP and 1 part MgO, by weight), VCAS, Portland cement and wollastonite. Therefore, the water content coefficient of MPC binder (WCC_{binder}), the VCAS (WCC_{VCAS}), Portland cement (WCC_{cement}), and wollastonite ($WCC_{wollastonite}$), have to be assessed. Because of slurry containing MPC binder reacts very rapid and does not allow for sufficient time for slump test, an estimated value of 0.27 was utilized as WCC_{binder}. This estimate is based on laboratory experiences with the binders. To assess the aggregate slump without any binder, Portland cement, wollastonite and VCAS were mixed with water separately and tested by using this method. The test results are shown in Fig 2.3 and it quite clear from these results that the aggregate type plays an important role in the amount of water needed to make a slurry that is workable for this composite structures.

A 8 mm (0.32 inch) slump was found has the best workabilty for preparing pull-out specimens. The water content coefficients of the three components for this slump were calculated by extending trendlines to 8 mm slump in Fig 2.3. The final results of *WCC*s for these four components were listed in Table 2.2.

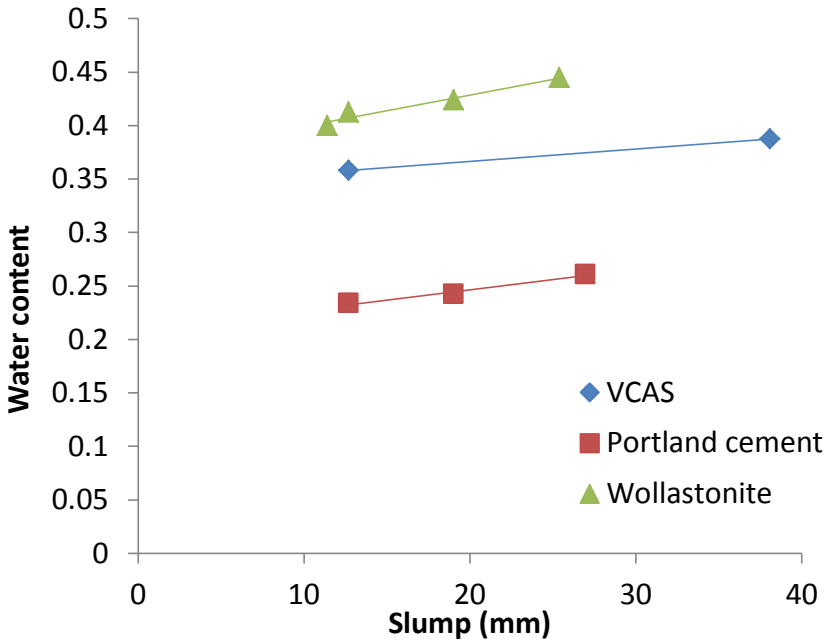


Fig 2.3 Water content-slump curves

Table 2.2 The water content coefficients of the components in MPCs

Component	Water content coefficient
VCAS	0.35
Portland cement	0.22
Wollastonite	0.39
MPC binder (MKP:MgO = 3:1 by weight)	0.27

2.5.3 Pull-out test of CBPCs and sugar maple

In this research, many trials with different test methods were explored, such as pull-out test, shear-block test [3] (more details of shear block test were introduced in APPENDIX C) and four-point bending test [22, 23]. Shear-block test for MPCs had low accuracy and high coefficients of variation; the specimens of four-point bending test are easily to failure due to the difficulty to exhaust the air form thin layer of MPC in the

casting processing. However, the pull-out test method had the best feasibility in these test methods.

Table 2.3 Test results of the five pull-out test specimens

Specimen	A	B	C	D	E	Average (coeff. of variation)
Max Load (kN)	1.797	1.873	1.886	1.853	1.835	
Diameter (mm)	6.502	6.528	6.528	6.604	6.299	
Length (mm)	27.66	27.69	25.65	29.11	30.35	
Area (mm2)	565.0	567.8	526.1	603.9	600.7	
Max Stress (kPa)	3180	3298	3584	3069	3055	3237 (194)

To verify the feasibility of the test method, an initial trial formulation that included 17.5 wt.% MgO, 52.5 wt.% MKP, 10 wt.% Portland cement, 10 wt.% wollastonite, 10 wt.% VCAS, with a water content of 28.5 wt.% was used. The results of the five pull-out specimens can be seen in Figure 2.4and Table 2.3.

The load-displacement curves (Fig 2.4) show that all the interfacial failure is brittle fracture. Max stresses of these specimens are calculated and analyzed the results shown in Table 2.3. There are three types of failure modes of pull-out test reported in previous study, split failure, rod break off and interfacial bond failure [19]. The types of failure modes are depending on the strength of CBPC block, wood rod and interfacial strength. The displacements before failure are likely the deformation of the sugar maple rods and initial displacement is from the specimen settling into the holder. The load after failure is the remaining friction force between sugar maple rod and MPC block.

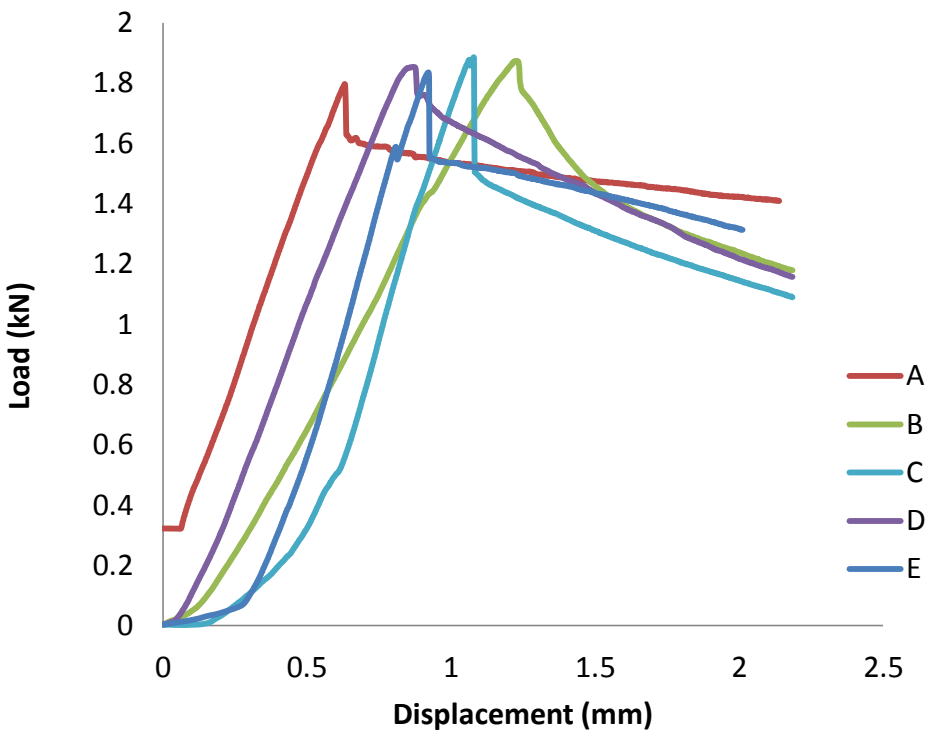


Fig 2.4 Load-displacement curves of the five pull-out test specimens

2.5.4 Weight ratio of MKP/MgO in MPC binder and interfacial strength

Table 2.4 The formulas of MPC binder with different MKP/MgO ratios

MKP/MgO (weight ratio)	MKP/MgO (mole ratio)	MKP (wt. %)	MgO (wt. %)
1.0	0.30	21.50	21.50
1.5	0.44	25.80	17.20
2.0	0.59	28.67	14.33
2.5	0.74	30.71	12.29
3.0	0.89	32.25	10.75
3.5	1.04	33.44	9.56
4.0	1.18	34.40	8.60

The formulas for evaluating the MPC binders are shown in Table 2.4. All of these MPC slurries contain 43 wt.% MPC binder, 19 wt.% Portland cement, 19 wt.% wollastonite, and 19 wt.% VCAS. The water content of all these slurries was 0.27 and 5 specimens for each formula were tested for statistical validation.

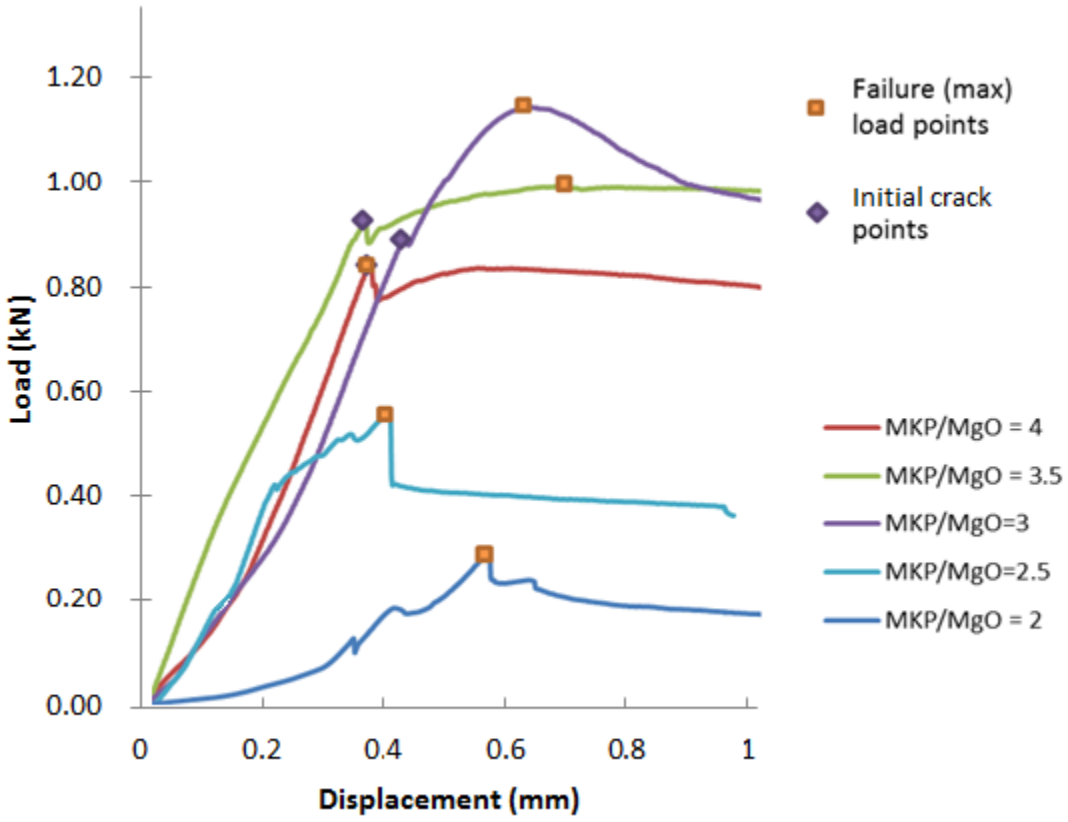


Fig 2.5 The load-displacement curves of some MPC specimens with different MKP/MgO ratios

Figure 2.5 shows the load-displacement curves for the various MKP/MgO binder ratios. At the low ratios of 1.0 and 1.5 the specimens showed very poor quality and did not accumulate much load. On the load-displacement curves of 3 - 4 MKP/MgO ratios,

"Initial crack load points" were assigned to the distinct disruptions in the curves near the maximum load.

Table 2.5 The stresses and pH values of MPCs with different MKP/MgO ratios

MKP/MgO (weight)	Failure stress (τ_f, kPa)		Initial crack stress (τ_i, kPa)		Starting pH values
	Average	Coeff. of variation	Average	Coeff. of variation	
1.0	193	236	–	–	6.4
1.5	301	188	–	–	6.3
2.0	488	100	–	–	6.3
2.5	1111	528	–	–	6.2
3.0	2024	189	1863	164	6.2
3.5	1818	240	1718	216	6.2
4.0	1837	297	1805	305	6.1

The failure and initial crack shear stresses of these specimens and the starting pH values of these MPC slurries are shown in Table 2.5 and Fig 2.6. The starting pH value of these MPC slurries decrease slightly with the increasing of MKP/MgO ratio; this is because of the MKP has weak acidity and MgO has weak alkalinity. The differences of average failure stress values (τ_f) and average initial crack stress values **(**τ_i) are shown in Fig 2.7. This data shows that the interfacial bond shear strength is poor at binder ratios of 1, 1.5 and 2 and reaches a maximum stress at 3. As the binder ratio increases past 3 the strength begins to lower. In Fig 2.7, the value of $\tau_f - \tau_i$ decrease with the increasing of MKP/MgO ratio. This $\tau_f - \tau_i$ decreasing may imply that the mechanism of the interfacial bonding is changing.

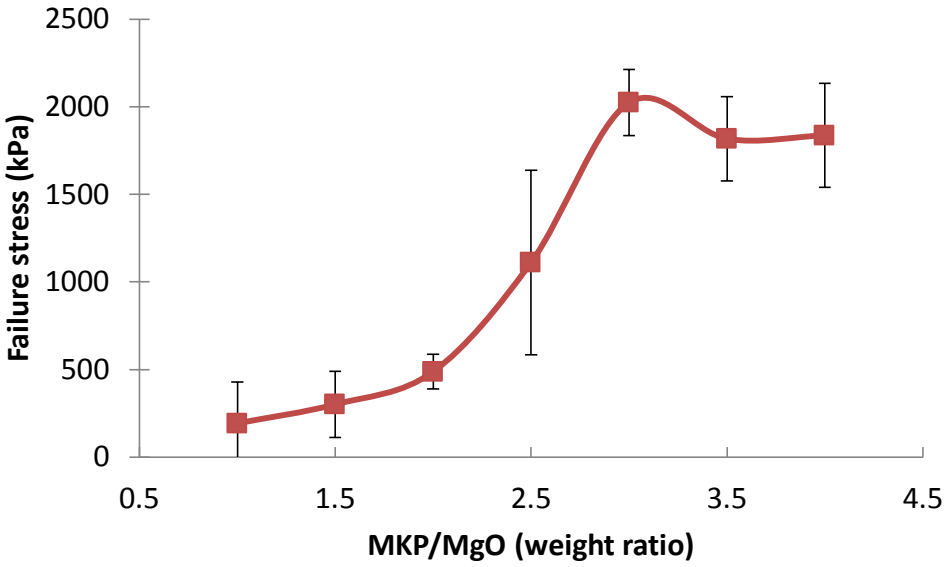


Fig 2.6 The failure shear stresses of MPC specimens with different MKP/MgO weight ratios

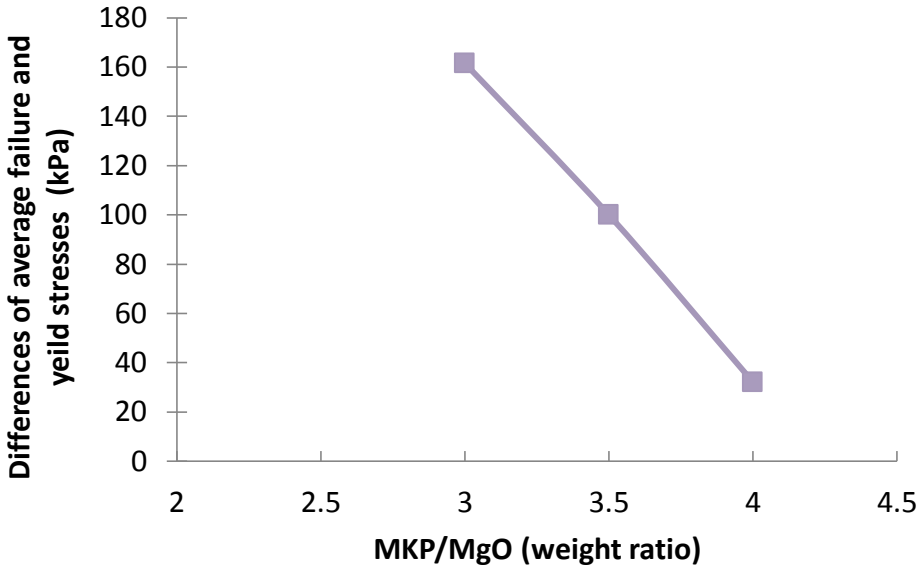
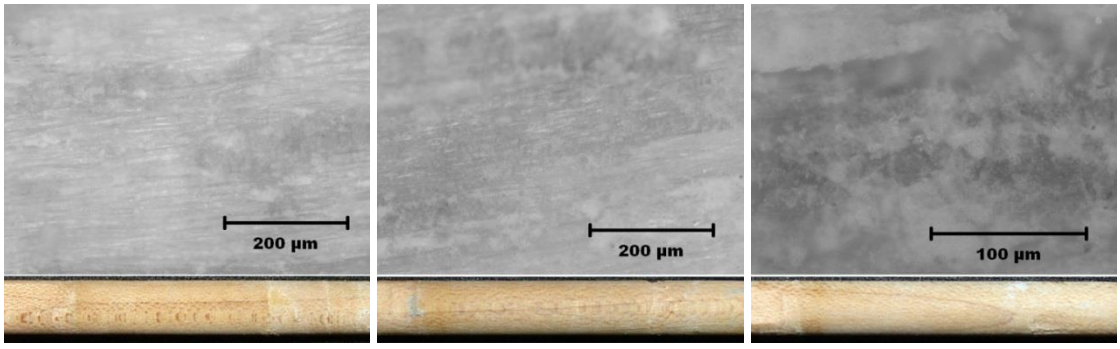


Fig 2.7 The differences of average failure stress values and average initial crack stress values of MPC specimens with different MKP/MgO ratios

The 3:1 weight ratio of MKP/MgO was found to have the best interfacial binder performance, and had a mole ratio approximate equal to 0.89. This is less than the 1.0

mole ratio indicated in the chemical reaction formula. At a binder ratio of 3.5, our mole ratio was close to 1 (1.04) and showed a slightly lower maximum stress.



(a) (b) (c)

Fig 2.8 The fracture surfaces of some pull-out specimens with different MKP/MgO weight ratios ($\boldsymbol{\beta}$) (a) $\boldsymbol{\beta = 1.0}$, (b) $\boldsymbol{\beta = 3.0}$ and (c) $\boldsymbol{\beta = 4.0}$

An Olympus® BX51 optimal microscope was utilized to observe the fracture surface of these specimens as shown in Fig 2.8. Every picture includes a camara photo and a microscope photo. These picture show that the fractures of these specimens are generally because of interfacial failure. There is only small amounts of MPC particles left on the sugar maple rod surface and very little evidence of sugar maple incorporated into the MPC surface.

2.5.5 Aggregate type and level influence on the interfacial strength

To evaluate the aggregates and their influence on the interfacial strength properties between MPC and sugar maple an Optimal-IV mixture design for special cubic model (does not contain AB(A-B), AC (A-C), AD (A-D), BC(B-C), BD(B-D) and CD(C-D) terms than normal cubic model) generated by Stat-Ease® software with 22 runs including 4 replicated runs and 4 runs for estimate lack of fit was utilized to evaluate the relationship between these factors and the interfacial shear strength. Portland cement, wollastonite VCAS and binder levels in MPC are the four variables in the design of

experiment (DOE). And Table 2.6 indicates the lower and upper limit of these four factors for this DOE. The lower limit for the binder was set at 20%.

Table 2.6 The range of the 4 factors for the DOE of the interfacial strength test of various MPC binders Portland cement, wollastonite and VCAS's level

Factor	Code	Content range (wt.%)	
		Lower boundary	Upper boundary
MPC Binder (%)	A	20	100
Portland Cement (%)	B	0	80
Wollastonite (%)	C	0	80
VCAS (%)	D	0	80

MPC formulations that contain 100% MPC binder reacts very rapid and does not allow for sufficient time for specimen processing. To slow the reaction down, 1% boric acid was added into this formula to allow for sufficient working time [13]. To account for this change an extra run with the formula of 90% MPC binder and 3.33% Portland cement, 3.33% wollastonite and 3.33% VCAS was added in this DOE to add another data point in the high binder region. The water content of these MPC slurries was calculated by using the method introduced earlier. The MKP formulas of these 23 runs are listed in Table 2.7.

Table 2.7 The MPC formulas of the 23 DOE runs with different MPC binder Portland cement, wollastonite and VCAS levels and their test results

Run code	MPC Binder (wt.%)	Portland Cement (wt.%)	Wollastonite (wt.%)	VCAS (wt.%)	Water content	Average failure stress (kPa)	Coeff. of variation (kPa)	Starting pH values	Fracture type
1	20.00	0.00	0.00	80.00	0.33	0	0	5.7	Split
2	30.00	10.00	50.00	10.00	0.33	208	95	6.1	Split
3	20.00	0.00	40.00	40.00	0.35	430	167	5.7	Split
4	60.00	0.00	0.00	40.00	0.30	2834	323	5.4	Interfacial
5	46.67	0.00	26.67	26.67	0.32	2642	221	5.4	Interfacial
6	20.00	0.00	80.00	0.00	0.37	915	71	5.8	Split
7	20.00	40.00	0.00	40.00	0.28	0	0	6.7	Split
8	46.67	26.67	26.67	0.00	0.29	1341	386	6.3	Interfacial
9	30.00	50.00	10.00	10.00	0.27	73	20	6.7	Interfacial
10	60.00	0.00	40.00	0.00	0.32	2260	379	5.4	Interfacial
11	100.00	0.00	0.00	0.00	0.27	1330	72	5.1	Interfacial
12	20.00	40.00	40.00	0.00	0.30	3	4	6.8	Split
13	20.00	26.67	26.67	26.67	0.31	41	35	6.8	Split
14	20.00	80.00	0.00	0.00	0.23	203	26	7.1	Split
15	46.67	26.67	0.00	26.67	0.28	1098	161	6.2	Interfacial
16	46.67	26.67	26.67	0.00	0.29	1539	264	6.3	Interfacial
17	70.00	10.00	10.00	10.00	0.29	3237	194	5.8	Interfacial
18	30.00	10.00	10.00	50.00	0.32	558	164	6.0	Interfacial
19	60.00	40.00	0.00	0.00	0.25	3084	255	6.4	Interfacial
20	46.67	0.00	26.67	26.67	0.32	3496	161	5.4	Interfacial
21	20.00	26.67	26.67	26.67	0.31	30	23	6.8	Split
22	46.67	26.67	0.00	26.67	0.28	1605	252	6.2	Interfacial
23	90.00	3.33	3.33	3.33	0.28	2971	299	5.5	Interfacial

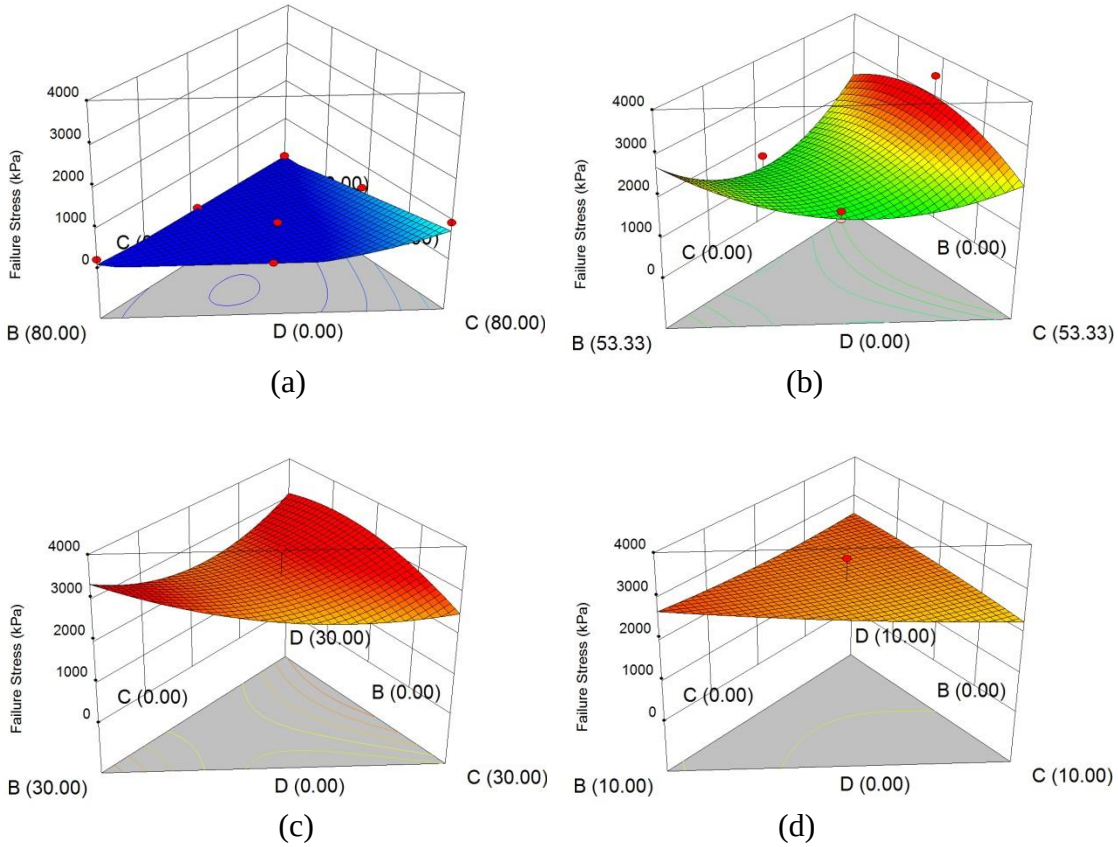
* 1% Boric acid added for decrease the reaction rate

The average stress and starting pH values were analyzed by using Stat-Ease® software, while Table 2.7 shows the average values and formulations. For evaluating the primary factor which influences the bond strength, a linear model fitting by using Stat-Ease® software was analyzed with based upon the pull-out stress. Coefficient estimates of 5.15 for factor of MPC binder, -1.40 for Portland cement, and 0.19 for wollastonite, and -0.28 for VCAS levels. These results indicate that the MPC binder level is the primary factor which influences the MPC/maple interfacial bond shear strength in MPC slurries. However, to estimate any non-linear responses, a cubic model was fitted to the data.

A cubic model containing A-MPC binder (A), Portland cement (B) , wollastonite (C), and VCAS(D) weight percentages was developed to determine the weighted effects of each component. The model F-value of 7.55 implies the model is significant. The model adequate precision of 7.814 indicates an adequate signal, this model can be used to navigate the design space. The R^2 value (coefficient of determination) of this model is 0.916 indicates that the model fits the data well.

An equation based on these results is obtained for estimating the interfacial debonding strength (τ_f) with the four factors, A, B, C and D, via this special cubic model fitting (all units in kPa).

$$\tau_f(kPa) = 19.00A - 31.88B - 9.23C - 32.10D + 9.71AB + 4.60AC + 9.08AD + 3.44BC + 8.68BD - 5.39CD - 1.96ABC - 3.08ABD + 1.87ACD - 0.39BCD$$

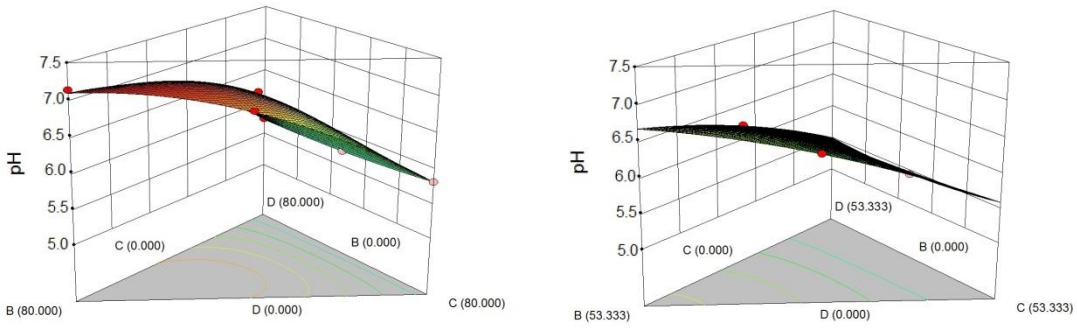


* Axis B = Portland cement (wt.%), axis C = wollastonite (wt.%) and axis D = VCAS (wt.%):

Fig 2.9 The cubic model fitting of the average specimen interfacial shear strength with 20 wt.% (a), 46.67 wt.% (b), 70 wt.% (c) and 90 wt.% (d) binder content and different aggregates levels

Response surface graphics at binder levels of 20, 46.67, 70 and 90 wt.% are shown in Fig 2.9 (All other binder levels are shown in Appendix A). These plots indicate that MPC binder level is one of the primary factors influencing the interfacial bond strength. The interfacial strength increases with the increasing of the MPC binder content when the MPC binder level is below 70 wt.%, but decreases with the increasing of the MPC binder content when the MPC binder level is over 70 wt.%. The reduction in interfacial strength at the 90% and higher binder ratio may be attributed to the quick reaction time. The MPC may be beginning to set before the specimen is fully placed in the casting mold. In

the test run of 100% MPC binder contained in MPC formula, many cracks were observed on the MPC block and these cracks decreased the bond strength between MPC and maple wood. Wollastonite and VCAS can mutually promote the interfacial property, but the bond strength is decreased when Portland cement is mixed with the other two aggregates. However, when Portland cement is used as an aggregate by itself, the interfacial bond strength is quite high as long as there is sufficient binder in the system.



(a) (b)

* Axis B = Portland cement (wt.%), axis C = wollastonite (wt.%) and axis D = VCAS (wt.%)

Fig 2.10 The cubic model fitting of the pH value with 20 wt.% (a) and 46.67 wt.% (b) binder content and different aggregates levels

Starting pH values of these MPC slurries are close related with bond strength, the cubic plot of these pH values are shown in Fig 2.10 (All other binder levels are shown in Appendix B). Comparing Fig 2.9 and Fig 2.10, the interfacial strength generally decrease with increasing pH value. This indicates an MPC which only contains MgO, MKP, Portland cement, wollastonite and VCAS has a stronger interfacial strength with sugar maple if it has lower pH value (in the pH range 5.5-7.2). A potential reason for this result is the MgO dissolute more quickly and completely in acidic environment than alkaline, and makes the MgO reacted with MKP more completely [27]. This would indicate that

the pH does not cause any negative effects to the sugar maple surface but more likely is due to the kinetics of dissolution of the MgO in an acidic environment.

There are three types of fracture that commonly exist in the pull-out test, split failure, rod break off and interfacial bond failure [16]. If the strength of CBPC block is weaker, a block split failure will likely occur; if the strength of wood rod is weaker, a wood rod failure will result; and if the strength of CBPC/wood interface is weaker, an interfacial bond failure is often observed. The MPC block split failure (expressed as "Split" in Table 2.7) and MPC/maple interfacial bond failures (expressed as "Interfacial" in Table 2.7) are usually obtained in this study. In general, Table 2.7 indicates that the split failure was related with a poor MPC, and interfacial failure was related with a good MPC and improved interfacial strength. Therefore, the strength of MPC block is an important factor which influences the interfacial strength. The split failure is usually observed in low MPC binder level specimens. Fig 2.11 displays the microscope images and photographs of the fracture surface on some specimens. Fig 2.11 (a), (b) and (c) are formulas with 20 wt.% MPC binder, (d), (e) and (f) are formulas with 60 wt.% MPC binder, (g) is the 100 wt.% MPC binder formula. In Fig 2.11 (a), (b) and (c), the split MPCs remain on the fracture surface. But in Fig 2.11 (d), (e), (f) and (g), the fracture surfaces are pretty clean. Fig 2.12 shows the fracture surfaces on the MPC blocks of (a) Run 4 and (b) Run 10. Some sparse wood fiber in brown color can be found on these fracture surfaces. This can also illustrate that these specimens fail because of interfacial fracture and that there is likely some mechanical interlocking or other strong adhesive mechanism working at the interface.

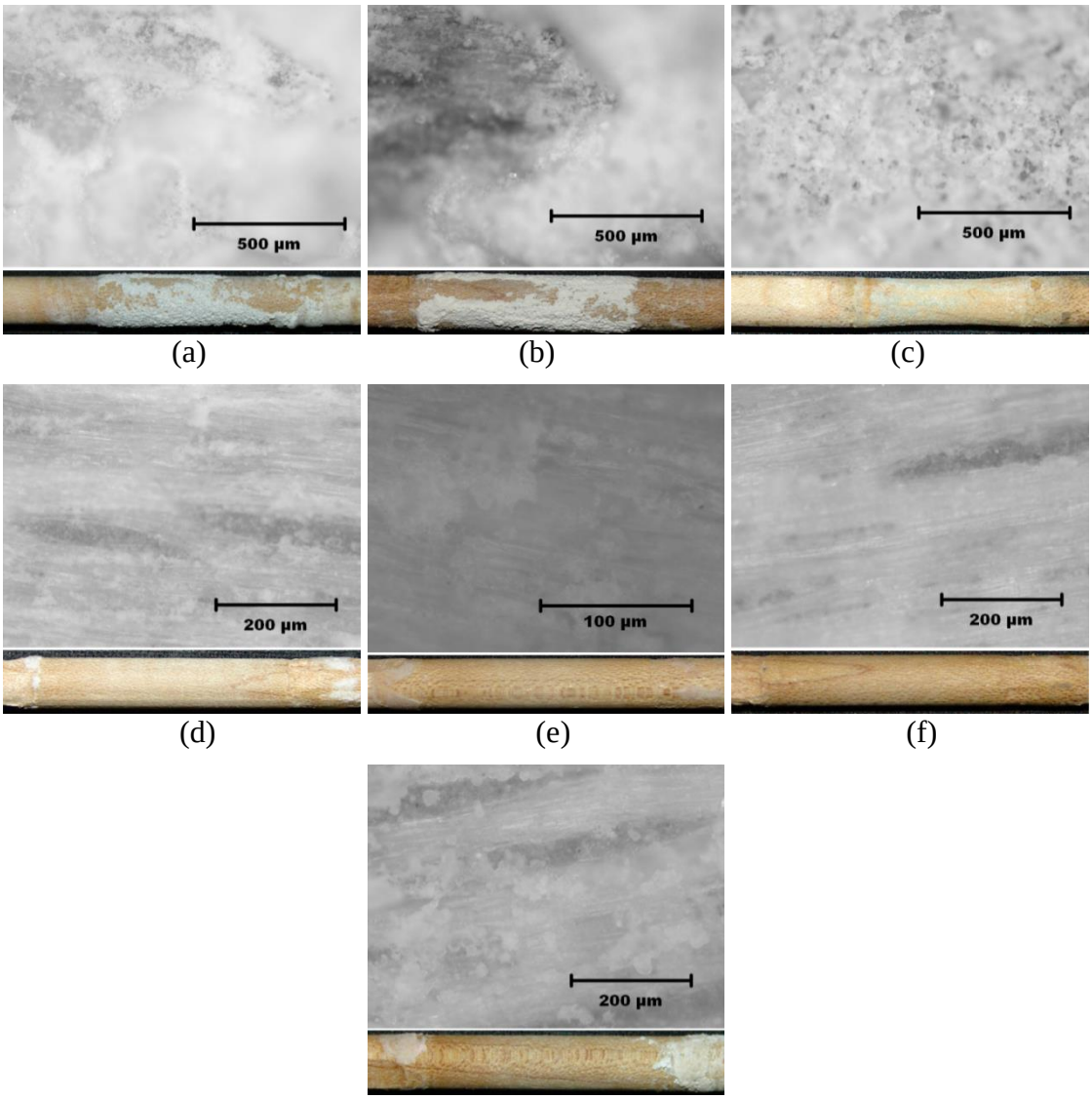
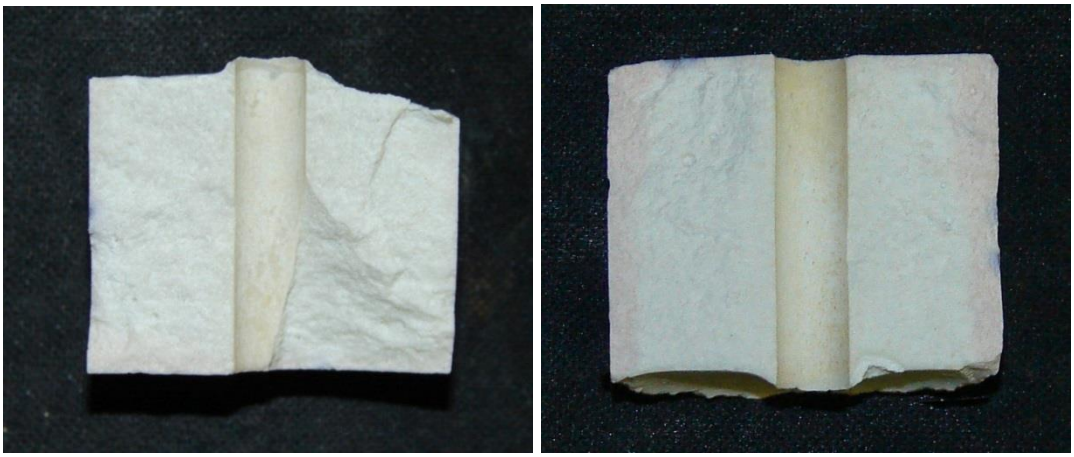


Fig 2.11 The fracture surfaces of pull-out specimens with varying MPC binder and Portland cement, wollastonite and VCAS levels, (a) Run 1, (b) Run 6, (c) Run 14, (d) Run 10, (e) Run 4, (f) Run 19 and (g) Run 11



(a) (b)

Fig 2.12 The fracture surfaces on the MPC blocks with different MPC binder and Portland cement, wollastonite and VCAS levels, (a) Run 4 and (b) Run 10

2.5.6 PVA reinforcement fiber of MPC and interfacial strength of MPC and sugar maple

For preparing the MPC slurries, the water content of PVA fiber (WCC_{PVA}) was estimated as 2.0. This estimate is based on laboratory experiences by comparing WCC_{PVA} values of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 in slurry preparation. Water content of these MPCs was calculated by using the *WCC*s in the water content test. Three types of MPCs were utilized in this test: PVA reinforced VCAS-MPC (0-1 wt.% PVA fiber content, 60 wt.% MPC binder and 40 wt.% VCAS), PVA reinforced W-MPC (0-1 wt.% PVA fiber content, 60 wt.% MPC binder and 40 wt.% wollastonite) and PVA reinforced C-MPC (0-1 wt.% PVA fiber content,60 wt.% MPC binder and 40 wt.% Portland cement). The formulas of PVA reinforced MPCs are listed in Table 2.8. The pull-out test method was utilized to test these specimens.

The pull-out test results of these specimens are shown in Table 2.8 and Fig 2.13. These results indicate that these PVA fiber reinforced MPCs have different MPC/maple interfacial properties. The reinforcing PVA fiber decreased the MPC/maple interfacial

strength of VCAS and Portland cement aggregate-based MPC (VCAS-MPC and C-MPC), and increased the interfacial strength of 40 wt. % wollastonite contained MPC (W-MPC). There is a possibility that wollastonite, which is short fiber mineral, can be interlocked with PVA fiber. However, the influence of PVA fiber on the MPC/maple interface is minimal.

Table 2.8 The formula design and interfacial shear strength of MPC pull-out specimens with different PVA fiber levels and formulas

MPC type	PVA fiber content (wt.%)	Water content (wt.%)	Average interfacial shear strength (kPa)	Coeff. of variation (kPa)
VCAS-MPC	0	0.30	2834	323
W-MPC	0	0.32	2260	379
C-MPC	0	0.25	3084	255
VCAS-MPC	0.5	0.31	2360	108
W-MPC	0.5	0.33	2899	445
C-MPC	0.5	0.26	2797	302
VCAS-MPC	1.0	0.32	1620	121
W-MPC	1.0	0.34	2699	226
C-MPC	1.0	0.27	2533	315

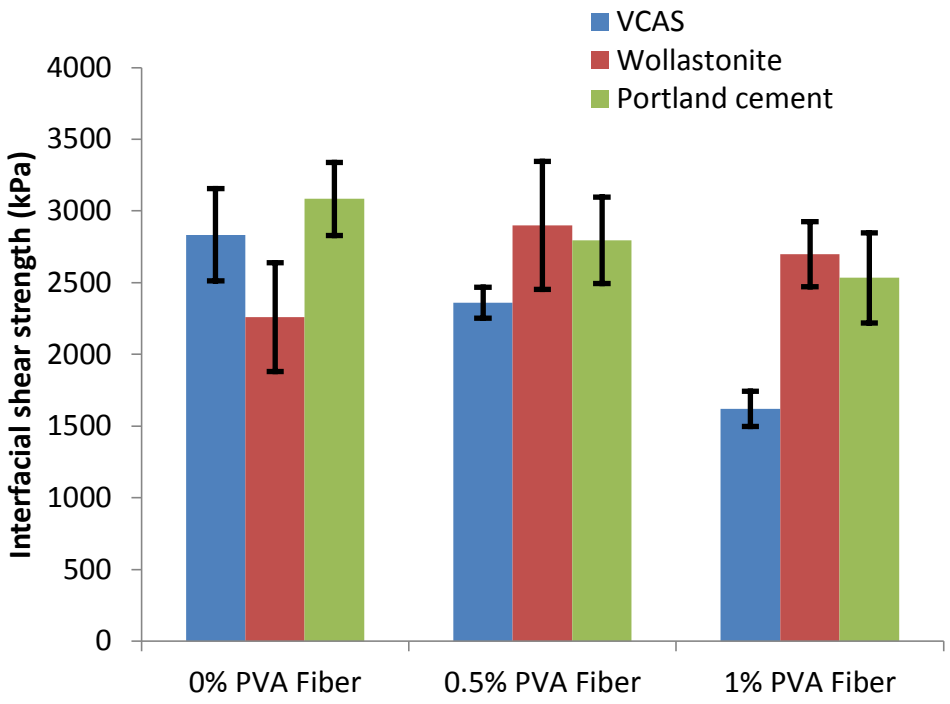
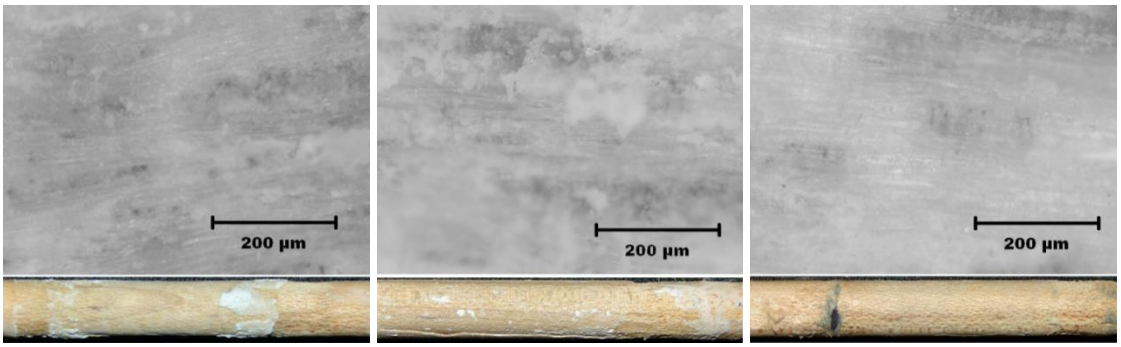


Fig 2.13 The interfacial shear strength of MPC pull-out specimens with different PVA fiber levels and formulas



(a) (b) (c)

Fig 2.14 The failure surfaces of MPC pull-out specimens with 1% PVA fiber and different formulas, (a) Run 7, (b) Run 8 and (c) Run 9

Fig 2.14 shows the microscopic images and photographs of the surfaces of MPC pull-out specimens with 1% PVA fiber and different MPCs formulations. Comparing these pictures with Fig 2.11 (d) (e) and (f), there are no identifiable differences between

the fractured surfaces. This indicates that PVA reinforcement fiber in MPC did not change the interfacial failure mechanism significantly and likely was a bond inhibitor which decreased the shear stress.

2.6 Conclusion

In this chapter, the alkalinity and the workability and fluidity of binder ratios and MPC formulations has been evaluated. Using a pull-out test procedure to evaluate the interfacial properties between MPC and sugar maple, various MKP/MgO ratios and MPC formulations were tested in this study. The results show that a 3:1 weight ratio of MKP and MgO has the best binder performance. The differences of average failure stress values and average initial crack stress values decreased with the increase of the MKP/MgO ratio; the starting pH value of MPC slurries decrease slightly with the increasing of MKP/MgO ratio, which is a result of a higher amount of the acidic MKP. The fractures of these specimens are generally because of interfacial failure.

Mixture design analysis was used to evaluate the MPC/maple interfacial shear properties with different aggregate levels. Portland cement, Wollastonite and VCAS were used as aggregates within the MPC system. The test results indicates that MPC binder level is the primary factor which influences the interfacial properties, while wollastonite and VCAS can mutually promote the interfacial property , but the bond strength is decreased when Portland cement is mixed with the wollastonite and VCAS. The interfacial strength of these MPCs increased with the increasing of MgO dissolution and decreasing of the starting pH value. The fracture type analyses shows there are two types of fracture usually observed on the fracture surfaces, MPC block split failure and

MPC/maple interfacial bond failure. These two types of failure are close related with the interfacial strength and MPC binder level.

The MPCs were also reinforced by 0 wt. %, 0.5 wt. % and 1 wt. % PVA fiber and prepared for pull-out test. The test results indicate that these PVA fibers decreased the MPC/maple interfacial pull-out strength of VCAS and Portland cement containing MPCs, but increased pull-out strength when the MPC aggregate was wollastonite. The interfacial failure mechanism of PVA reinforced MPCs is similar than non-reinforced MPCs.

Reference

1. Abrams, D. A. (1919). *Design of concrete mixtures (Vol. 1).* Structural Materials Research Laboratory, Lewis Institute.

2. ASTM C143. *Standard Test Method for Slump of Hydraulic-Cement Concrete*.

3. ASTM D905-08. *Standard Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading*.

4. Birchall, J. D., Howard, A. J., & Bailey, J. E. (1978). On the hydration of Portland cement. *Proceedings of the Royal Society of London. A. Mathematical and Physical Sciences, 360(1702)*, 445-453.

5. Bye, G. C. (1999). *Portland cement: composition, production and properties.* Thomas Telford Services Limited.

6. Çavdar, A. (2012). A study on the effects of high temperature on mechanical properties of fiber reinforced cementitious composites. *Composites Part B: Engineering, 43(5)*, 2452–2463.

7. Chau, C., Qiao, F., & Li, Z. (2011). Microstructure of magnesium potassium phosphate cement. *Construction and Building Materials, 25*, 2911–2917.

8. Chen, Y., Davalos, J. F., Ray, I., & Kim, H.-Y. (2007). Accelerated Aging Tests for Evaluations of Durability Performance of FRP Reinforcing Bars for Concrete Structures. *Composite Structures, 78*, 101-111.

9. Donahue, P. K., & Aro, M. D. (2006). Durable Phosphate-Bonded Natural Fiber Composite Products. *10th International Inorganic-Bonded Fiber Composites Conference*, (pp. 79-88). São Paulo – Brazil.

10. El-Jazairi, B. (1982). Rapid repair of concrete pavings. *Concrete, (London), 16*, 12-15.

11. Formosa, J., Chimenos, J., Lacasta, A., & Niubo, M. (2011). Interaction between Low-grade Magnesium Oxide and Boric Acid in Chemically Bonded Phosphate Ceramics Formulation. *Ceramics International, 38*, 2483–2493.

12. Guo, S., Dillard, D. A., & Nairn, J. A. (2006). Effect of Residual Stress on the Energy Release Rate of Wedge and DCB Test Specimens. *International Journal of Adhesion and Adhesives 26 (4)*, 285–294.

13. Hall, D. A., Stevens, R., & El-jazairi, B. (2001). The effect of retarders on the microstructure and mechanical properties of magnesia-phosphate cement mortar. *Cement and Concrete Research, 31*, 455-465.

14. Hemmings, R. T., Nelson, R. D., Graves, P. L., & Cornelius, B. J. (2004). *Patent No. 6776838.* United States.

15. Hemmings, R. T., Nelson, R. D., Graves, P. L., & Cornelius, B. J. (2006). *Patent No. 7070131.* United States.

16. Hwang, C., Hse, C., & Shupe, T. F. (2008). Effects of raw materials on the properties of wood fiber-polyethylene composites-Part 3: Effect of a compatibilizer and wood adhesive on the interfacial adhesion of wood/plastic composites. *Forest Products Journal, 58(5)*, 66-72.

17. Jorge, F. C., Pereira, C., & Ferreira, J. M. (2004). Wood-cement composites: a review. *Holz als Roh- und Werkstoff, 62(5)*, 370-377.

18. Kim, B., & Lee, J. (2012). Relationships between mechanical and transport properties for fiber reinforced concrete. *Journal of Composite Materials, 46(13)*, 1607-1615.

19. Lee, M.-G., Chiu, C.-T., & Wang, Y.-C. (2005). The Study of Bond Strength and Bond Durability of Reactive Powder Concrete. *Journal of ASTM International, 2*, No. 7.

20. Miller, D. P., & Moslemi, A. A. (1989). Wood-cement composites: effect of model compounds on hydration characteristics and tensile strength. *Wood and Fiber Science, 23(4)*, 472-482.

21. Pavasars, I., Hagberg, J., Borén, H., & Allard, B. (2003). Alkaline degradation of cellulose: mechanisms and kinetics. *J Polym Environ, 11 (2)*, 39–47.

22. Qiao, P., & Chen, F. (2011). On the Compliance and Energy Release Rate of Generically-unified Beam-type Fracture Specimens. *Journal of Composite Materials,45*, 65-101.

23. Qiao, P., Chen, F., Hamey, C. S., & Wang, J. (2011). Mixed-Mode Fracture of Hybrid Material Bonded Interfaces under Four-Point Bending. *Journal of aerospace engineering, April*, 218-226.

24. Roffael, V. E., & Sattler, H. (1991). Studies on the interaction between lignocellulosics (straw pulps) and cement. *Holzforschung, 45(6)*, 445-454.

25. Toledo Filho, R. D., Scrivener, K., England, G. L., & Ghavami, K. (2000). Durability of Alkali-sensitive Sisal and Coconut Fibres in Cement Mortar Composites. *Cement and Concrete Composites, 22(2)*, 127–143.

26. Wagh, A. S. (2004). *Chemically Bonded Phosphate Ceramics.* Oxford: Elsevier.

27. Wagh, A. S., & Jeong, S. Y. (2003). Chemically Bonded Phosphate Ceramics:I, A Dissolution Model of Formation. *Journal of the American Ceramic Society, 86*, 1838-1844.

28. Wei, Y. M., Zhou, Y. G., & Tomita, B. (2000). Hydration behavior of wood cement-based composite i : evaiuation of wood species effects on compatibility and strength with ordinary portland cement. *Journal of Wood Science, 46*, 296-302.

29. Yang, Q., Zhu, B., Zhang, S., & Wu, X. (2000). Properties and Applications of Magnesia–Phosphate Cement Mortar for Rapid Repair of Concrete. *Cement and Concrete Research, 30*, 1807–1813.

30. Zhong, S., Ni, K., & Li, J. (2012). Properties of Mortars Made by Uncalcined FGD Gypsum-Fly Ash-Ground Granulated Blast Furnace Slag Composite Binder. *Waste Management, 32*, 1468–1472.

31. de Moura, L. F., & Hernández, R. E. (2005). Evaluation of Varnish Coating Performance for Two Surfacing Methods on Sugar Maple Wood. *Wood and Fiber Science, 37(2)*, 335-366.

32. Sjostrom, E. (1993). *Wood chemistry, second edition.* San Diego: Academic Press.

33. Wanrosli, W., Rohaizu, R., & Ghazali, A. (2011). Synthesis and characterization of cellulose phosphate from oil palm empty fruit bunches microcrystalline cellulose. *Carbohydrate Polymers, 84*, 262-267.

CHAPTER THREE
DURABILITY OF THE MAGNESIUM PHOSPHATE CERAMICS (MPC)/SUGAR MAPLE (*Acer saccharum*) INTERFACE IN MOISTURE ENVIRONMENTS

3.1 Introduction

Magnesium phosphate ceramics (MPCs)/wood composite have the potential to be utilized in variety of markets. However, as with all wood-based composites the durability and performance in high humidity and water immersed environments is always a concern and needs to be understood. Cement and inorganic binder wood composite systems are not immune to this problem and their moisture performance needs to be addressed.

Previous research by Donahue and Aro [1], evaluated a series of panel products made from paper mill waste residue, MPC, fly ash, water and additives as an inorganic-bonded composite building product. This research assessed mechanical properties of the composite board including screw withdrawal, internal bond strength, and bending strength. These properties indicate that the MPC composite board is acceptable to be used as a construction particleboard. The water absorption of the MPC composite is at the level of 25.2% - 31.4%, the volume swelling is at the level of 1.2%-2.6% after a 24-hour water soak treatment. These results show that this type of MPC composite has lower water absorption and swelling in water than traditional wood materials [1, 2]. However, this research did not mention how the water absorption influences the mechanical properties of this product.

Inorganic/wood composite materials were developed to enhance the environmental durably of wood. This environmental durability includes climatic, chemical, biological and mechanical. As an important type of climatic environmental durably, moisture durability was evaluated by many different methods for wood/inorganic composite. A study was conducted to investigate the strength and durability of Para wood (also called rubberwood) particle wastes and cement composite in 2011 [9]. This research treated the samples by using three different conditioning scenarios; seawater immersion at room temperature, alkaline solution immersion at room temperature, and elevated temperatures. The average compressive strengths of these composites aged in alkaline and salt solutions was observed to follow the same trend as the specimens curing at room temperature. The durability to chloride penetration and the corrosion of concrete containing bagasse-rice husk-wood ash was tested in 2011by Horsakulthai et al. [3]. The measurement of non-steady state chloride diffusion coefficient by accelerated salt-ponding was used to evaluate the chloride penetration resistance of this material. An accelerated corrosion test by impressed voltage was utilized to evaluate the initial current corrosion of this material. The chloride penetration and corrosion rate was decreased with the increasing content of bagasse-rice husk-wood ash. Cement and hornbeam wood particles composite particleboards were proven to prevent the attack of fungi in work done by Papadopoulos in 2009 [6]. These cement-based particleboards were exposed to brown and white rot fungi; and the results indicate both fungi failed to attack the cement-based boards. In a study by John et al. [4], aged panels came from internal and external walls of a 12-year-old house were prepared to test specimens. These panels were produced using blast-furnace slag, lime, gypsum, and coir fiber. After SEM examination, fibers removed from

the 12-year-old samples seem to be undamaged. The lignin contents of wood fibers from these aged panels are also evaluated in this research. The results indicate that guaiacyl lignin contents were decreased by this 12 year-old aging, and the lignin content levels of external and internal walls are similar.

As fillers and aggregates can influence the environmental durability of cement [8], they can also impart change when used as an inorganic binder. Soroushian et al. [7] utilized extruded fiber cement for their moisture durability study in 2006. This in organic composite material was made with silica sand and expanded shale as fillers, and reinforced with softwood, hardwood, and recycled fibers. The data of this research indicated that silica sand and expanded shale filler can improve moisture resistance and durability performance of this extruded fiber cement.

3.2 Research Objective

The overall goal of this study is to evaluate the moisture performance of the interfacial properties of CBPC and wood (sugar maple). To meet this goal, the following objectives were addressed:

- Expose specimens to water and humidity by using various treatment methods.
- Evaluate the water sorption of the different aggregate-based MPCs when exposed to high humidity and water immersion conditions.
- Evaluate the interfacial strength of three types of MPC/maple pull-out specimens which are exposed to moisture environments by using pull-out method.

3.3 Methods and Materials

Three types of MPCs were utilized in this environmental durability test: VCAS-MPC (40 wt.% vitrified calcium aluminio-silicate, 60 wt.% MPC binder), W-MPC(40 wt.% wollastonite, 60 wt.%, MPC binder), and C-MPC (40 wt.% Portland cement, 60 wt.% MPC binder). The raw materials and sample preparation of these exposure tests are the same as outlined in Chapter 2. These formulations and water contents of the MPC slurries are listed in Table 3.1.

Table 3.1 The three MPC formulas which utilized in environmental durability test

	MPC binder (wt. %)	Portland cement (wt. %)	Wollastonite (wt. %)	VCAS (wt. %)	Water content of MPC slurry
VCAS-MPC	60.00	0.00	0.00	40.00	30.02
W-MPC	60.00	0.00	40.00	0.00	31.94
C-MPC	60.00	40.00	0.00	0.00	25.03

Five treatment methods including high humidity conditioning and water immersion were utilized. These treatments are listed in Table 3.2; all specimens were cured at 64%RH, 22 ℃ for at least 7 days before moisture treatments and reconditioned at 64%RH, 22 ℃ for at least 10 days after the moisture treatments. A humidity test chamber (G series temperature/humidity test chamber, Russells Technical Products) was utilized to condition the specimens at 90% relative humidity (RH) conditioning. The specimens to be water soaked were submerged in water at 20 ℃. Weights of the specimen were recorded periodically throughout the test procedure. A piece of non-wood MPC block

with similar thickness of the MPC section of the pull-out test was prepared for a water sorption reference in every test group.

Table 3.2 Treatment methods of specimens

Treatment code	Moisture Treatment processing
A	Conditioning at 90%RH, 20 ℃ for 7 days
B	Soaking in water for 1 day
C	Soaking in water for 3 days
D	Soaking in water for 7 days
E	Soaking in water for 14 days

3.4 Test results and analysis

3.4.1 Moisture sorption of the MPC/maple specimens

Fig 3.1 indicates the relative weight changing of the MPC/maple pull-out specimens and non-wood MPC blocks which were conditioned at 90%RH, 20 ℃. Due to moisture sorption in the MPCs and the maple, the weights of all specimens all increased in the 90% RH conditioning. The relative weight changing of maple wood from 64% RH to 90% RH is about 8% [2]. The relative weight change of MPC block with no maple from 64% RH to 90% RH is about 0.5%-1.5%. The moisture sorption of VCAS-MPC specimens is much higher than W-MPC or C-MPC specimens.

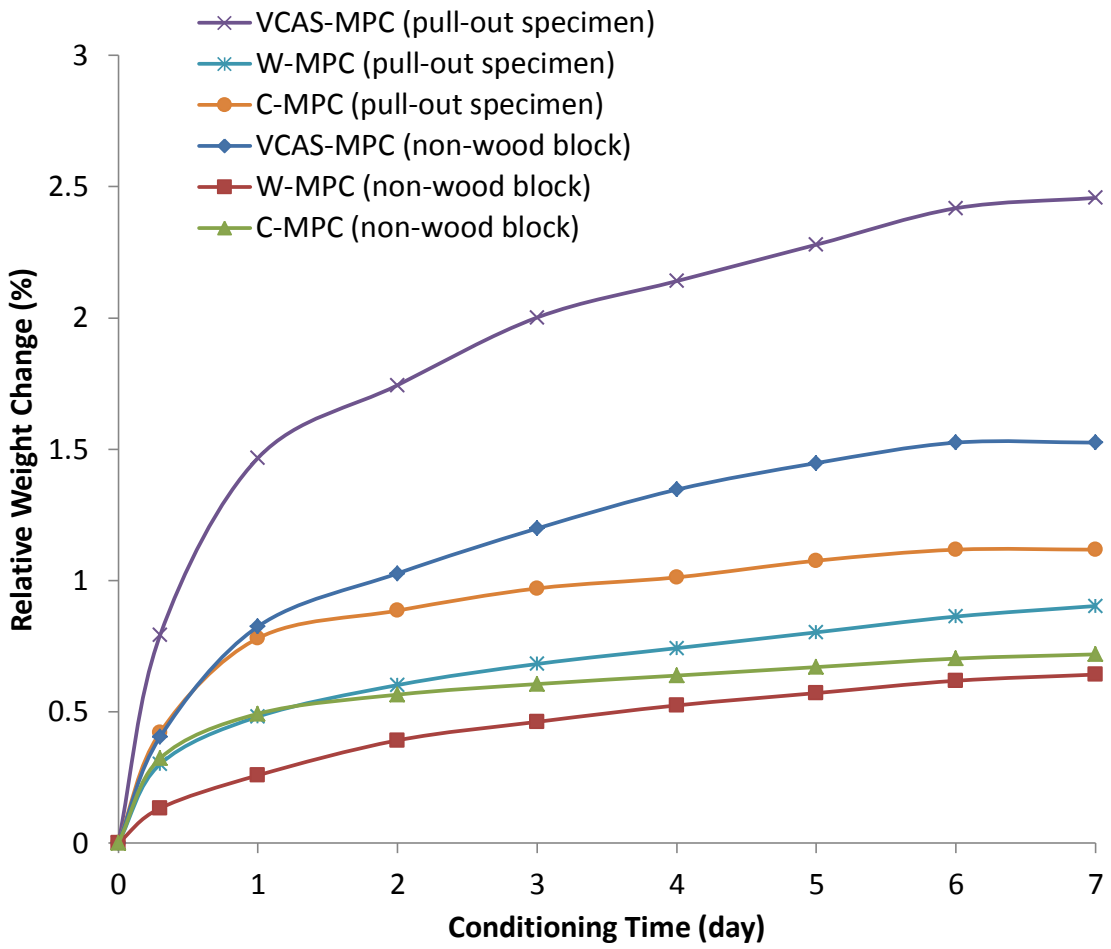


Fig 3.1 Relative weight change – conditioning time curve of MPC/maple pull-out specimens and non-wood MPC blocks at 90% RH 22 ℃ condition

Fig 3.2 shows the relative weight changing of the MPC/maple pull-out specimens and non-wood MPC blocks when immersed in water at 20 ℃. After 14 days of immersion, the weight change of MPC blocks are 4.4 % for VCAS-MPC, 3.6% for W-MPC and 2.2% for C-MPC; the weight gain of MPC/maple pull-out specimens are 7.8% for VCAS-MPC, 6.8% for W-MPC and 5.7% for C-MPC. The weight change of VCAS-MPC is larger than W-MPC; C-MPC specimens following the same trend as with the high humidity tests. After 7 days of water immersion the VCAS-MPC appears to have reached saturation, however the remaining W-MPC and C-MPC continue to gain

moisture. This is indicates the water diffusion kinetics in MPC blocks is dependent upon the aggregate utilized.

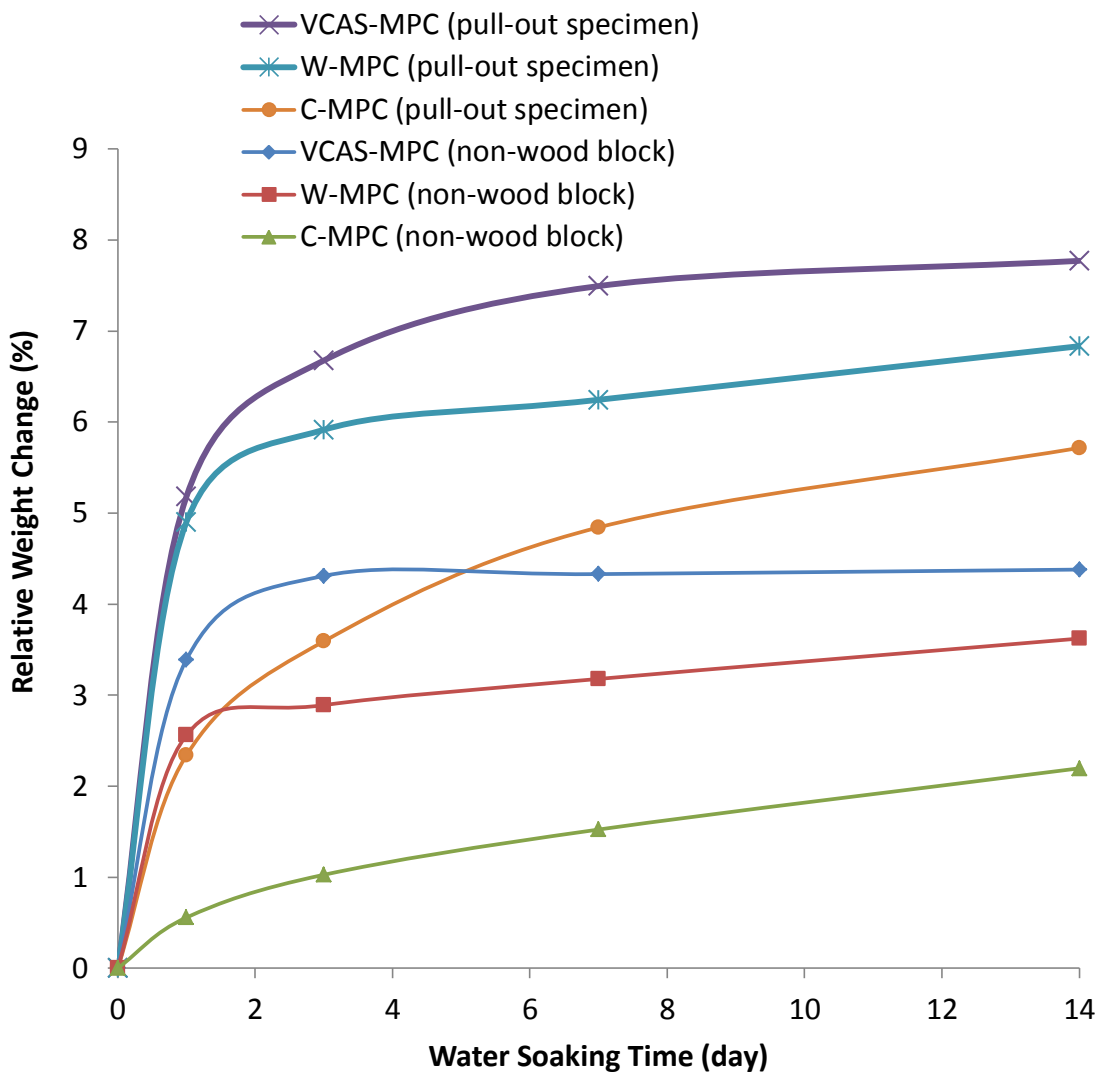


Fig 3.2 Relative weight change – water soaking time curve of MPC/maple pull-out specimens and non-wood MPC blocks

3.4.2 Interfacial bond performance of the MPC/maple pull-out specimens

All the pull-out test results for the moisture exposed and their controls are listed in Table 3.3. Comparing with the results of non-exposed (control) specimens in Chapter 2, the interfacial shear strengths of MPC/maple pull-out specimens with conditioning at 90%

RH for 7days is shown in Fig 3.3. All specimens showed a decrease in interfacial shear strength with the VCAS-MPC specimens having the greatest reduction in bond strength. This reduction coincides with the higher water sorption characteristics of the VCAS-MPC specimens.

Table 3.3 Failure stresses of MPC/maple pull-out specimens with different environmental treatment

Treatment	Failure stress (kPa)					
	VCAS-MPC		W-MPC		C-MPC	
	Average	Coeff. of variation	Average	Coeff. of variation	Average	Coeff. of variation
Without treatment	2834	323	2259	379	3083	255
90% RH, 7 days	285	73	1753	232	2113	503
Water soaking 1 day	65	130	1262	352	1671	223
Water soaking 3 days	0	0	1025	330	1079	379
Water soaking 7 days	0	0	1108	405	765	104
Water soaking 14 days	0	0	829	359	869	245

The MPC/maple interfacial bond of VCAS-MPC specimens can be greatly influenced through water immersion. Fig 3.4 shows the reduction in bond strength of the various MPC specimens over time, while immersed in water. The interfacial shear strength decreased significantly during the first 3 days of water immersion, with the VCAS-MPC having no bond integrity after 1 day of immersion. The W-MPC and C-

PMC both appeared to level-off or converge to a minimum shear strength during the remaining 3-14 days of immersion. The interfacial shear strength of W- MPC/maple specimens decreased 22.4% after 7-day conditioning at 90% RH, and decreased 63% after 14-day water soaking; for C- MPC/maple specimens, these two values are 32% and 75%. These results also indicate that the environmental durability of VCAS-MPC/maple interface is quite compromised when VCAS-MPC/maple exposed to any moisture environment, especially water immersion.

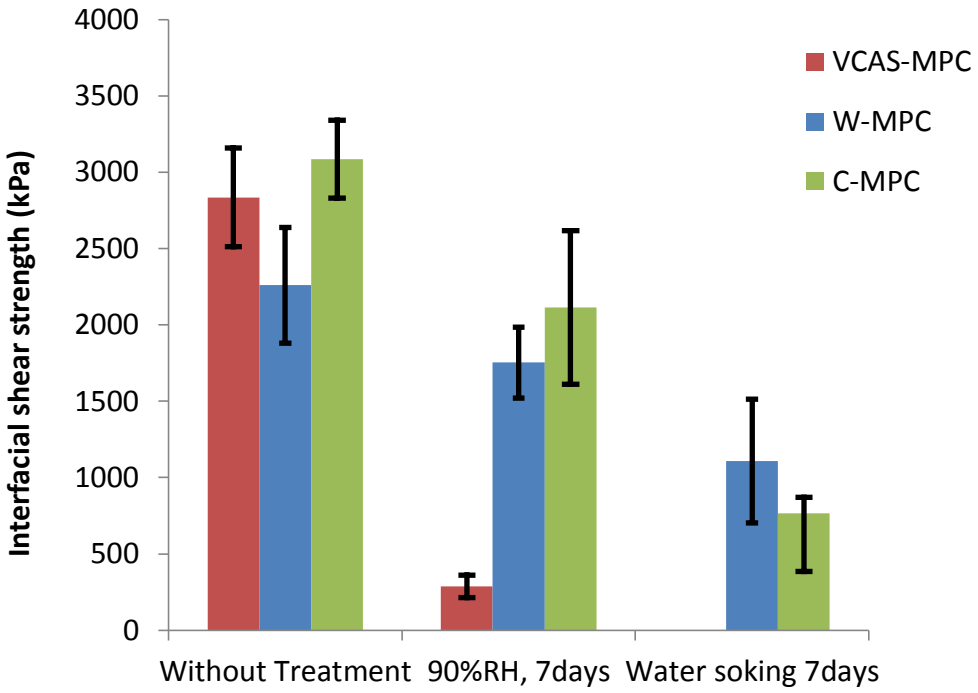


Fig 3.3 Interfacial shear strength of MPC/maple pull-out specimens without treatment and 90%RH and water immersion for 7days

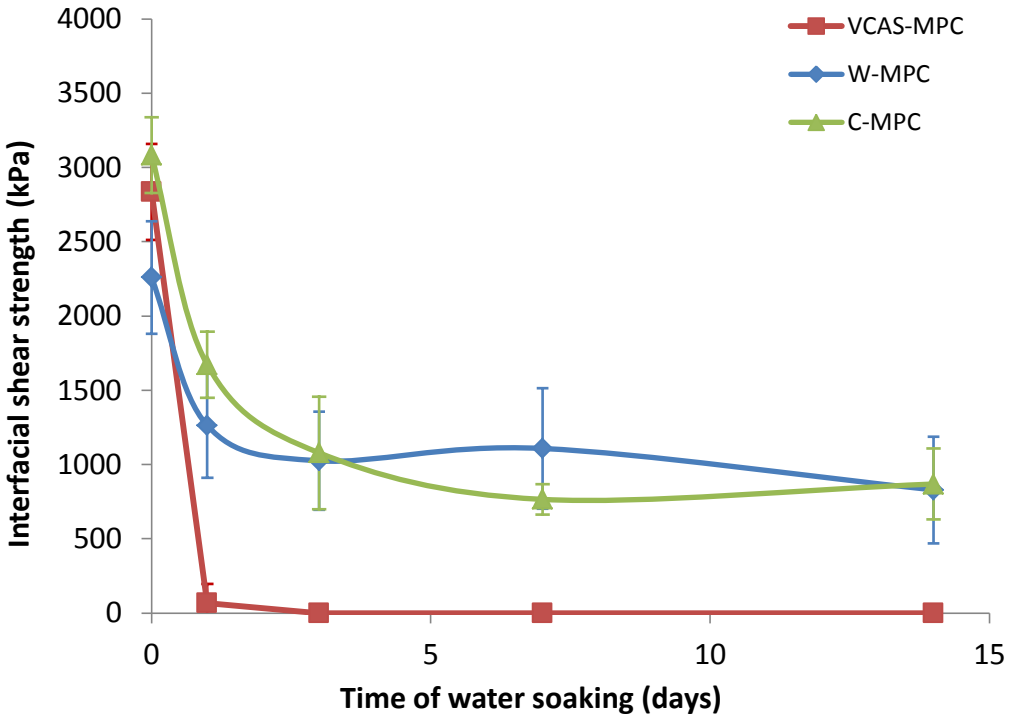


Fig 3.4 Failure strength of MPC/maple pull-out specimens with different water soaking treatments

3.4.3 Fracture of the MPC/maple pull-out specimens

The fracture type of all exposed VCAS-MPC/maple specimens is MPC split failure, but an interfacial failure was predominate for W-MPC/maple and C-MPC/maple specimens. Fig 3.5 shows the appearance of some VCAS- MPC/maple pull-out specimens before and after exposure. The surfaces of unexposed VCAS- MPC/maple specimens are smooth; after 7-day conditioning at 90% RH, the surfaces are quite rough; and after 14-day water immersion, cracks can be observed on the surfaces.

Unlike the VCAS-MPC, there was little fracture or roughness was observed MPC on the surfaces of treated W- MPC/maple or C-MPC/maple specimens. However, some small clear crystal-like structures were observed on the surfaces of W- MPC/maple or C-MPC/maple specimens after the 14-day water soaking treatment in Fig 3.6.

Recrystallization of phosphate salt [7] is a possible to explanation to this crystal formation.

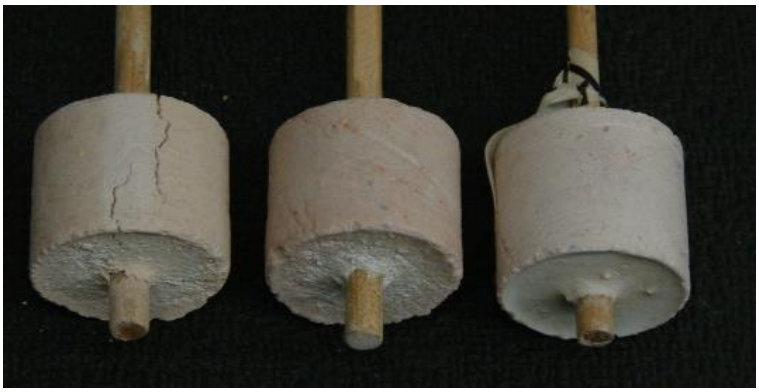
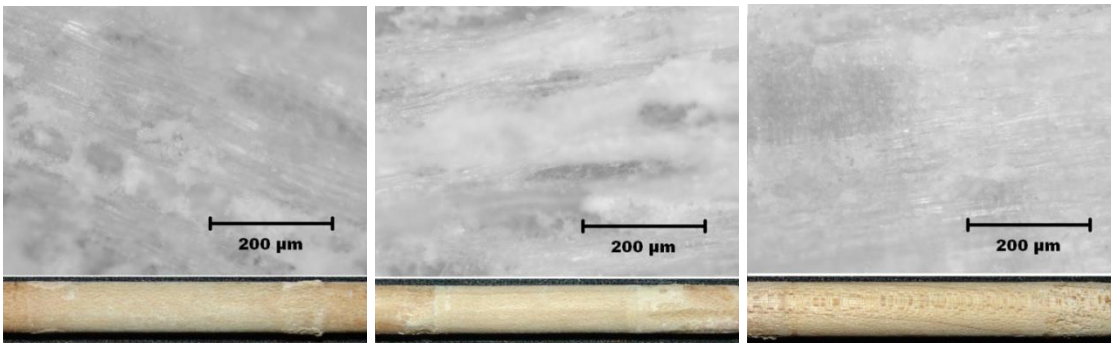


Fig 3.5 Untested VCAS- MPC/maple pull-out specimens with different treatment after conditioning (From left to right: Water soaking, 14d; 90% RH, 7d; Without Treatment)

Fig 3.6 Untested C- MPC/maple pull-out specimens with different treatment after conditioning (From left to right: Water soaking, 14d; 90% RH, 7d; Without Treatment)

Fig 3.7 shows a photographic and microscopic image of the fractured surfaces of the MPC/maple pull-out specimens with 14-day water soaking treatment. A few MPC fragments can be observed on the wooden rod surface shown in Fig 3.7 for the VCAS and W-MPCs likely due to the deterioration of the MPC structure itself, especially with the VCAS-based MPC.



(a) (b) (c)

Fig 3.7 Fracture surfaces of MPC/maple pull-out specimens with 14 day water soaking treatment: (a) VCAS-MPC, (b) W-MPC, and (c) C-MPC

3.5 Conclusion

In this research, the interfacial bond durability when exposed to moisture environments was evaluated for VCAS, wollastonite, and Portland cement based aggregate MPC/maple composites. These treatment methods included exposure to 90% RH conditioning and water immersion. Weight gain was seen in both the specimens containing the wooden rod and the MPCs without any wood. The weight gain was especially prevalent for the VCAS-MPC indicating that the VCAS itself absorbs more water than the other aggregates or it develops voids or fissures within the MPC structure where moisture can be collected via capillary action. The pull-out test results indicate that moisture can influence the VCAS-MPC block and the interfacial bonding of VCAS-MPC/maple strongly. The interfacial bonding strengths of W-MPC/maple and C-MPC/maple are also decreased by these treatments, but at a lesser degree than with the VCAS-MPC. After 14-day water soaking, cracks were observed on the surface of VCAS-MPC/maple pull-out specimens; also, some colorless crystal structures were observed on the surface of W-MPC/maple and C-MPC/maple pull-out specimens. These are closely related with the split fracture of VCAS-MPC/maple specimens. Photographs

also show the split fracture of VCAS-MPC/maple specimens and the interfacial fracture of W-MPC/maple and C-MPC/maple specimens. From these results, VCAS-MPC has proved to be an inferior aggregate to the Portland cement and wollastanite-based MPCs, but C-MPC/maple and W-MPC/maple have the potential to be utilized with high moisture exposure.

References

1 Donahue, P. K., & Aro, M. D. (2006). Durable Phosphate-Bonded Natural Fiber Composite Products. *10th International Inorganic-Bonded Fiber Composites Conference*, (pp. 79-88). São Paulo – Brazil.

2 Forest Products Laboratory (US). (1987). *Wood handbook: wood as an engineering material (No. 72).* United States Government Printing.

3 Horsakulthai, V., Phiuvanna, S., & Kaenbud, W. (2011). Investigation on the corrosion resistance of bagasse-rice husk-wood ash blended cement concrete by impressed voltage. *Construction and Building Materials, 25(1)*, 54-60.

4 John, V. M., Cincotto, M. A., Sjöström, C., Agopyan, V., & Oliveira, C. T. (2005). Durability of slag mortar reinforced with coconut fibre. *Cement and Concrete Composites, 27(5)*, 565-574.

5 Mittal, M., Prakash, S., & Nath, S. K. (2012). Recrystallization of Amorphous Phases via Post-Coating Heat-Treatment of Plasma-Sprayed Hydroxyapatite Coatings. *Materials and Manufacturing Processes, 27(9)*, 1001-1006.

6 Papadopoulos, A. N. (2009). Physical-mechanical properties and durability against basidiomycetes of particleboards made from cement and Carpinus betulus L. wood particles. *Wood Research (Bratislava), 54(2)*, 95-100 .

7 Soroushian, P., Elzafraney, M., Nossoni, A., & Chowdhury, H. (2006). Evaluation of normal-weight and light-weight fillers in extruded cellulose fiber cement products. *Cement and Concrete Composites, 28(1)*, 69-76.

8 Uysal, M., & Akyuncu, V. (2012). Durability performance of concrete incorporating Class F and Class C fly ashes. *Construction and Building Materials, 34*, 170-178.

9 Woraohot, P., Abideng, H., & Thaniya, K. (2011). Feasibility study of cement composites with para wood particle wastes: strength and durability. *Global NEST Journal, 13 (2)*, 182 -191.

CHAPTER FOUR
CONCLUSIONS

4.1 Conclusions

As a typical type of chemical bonded phosphate ceramics, magnesium phosphate ceramic (MPC) was bonded with sugar maple in this research. The interfacial properties of MPC and sugar maple were evaluated with various MPCs formulation designing and various moisture treatments.

Interfacial bond test methods, pH measurements and water contents of MPC were studied to establish the foundation of MPC/maple research. A pull-out test method was utilized to assess the interfacial shear stress between the MPC and a wooden dowel rod. The pH values of MPC slurries is related with interfacial shear strength of MPC/maple by utilizing a test method of dispersing 10 g solid samples into 100 g water and measured by using pH meter. A linear assumption for calculating the water content of various MPC formulations was established for keeping MPC slurries in similar workability and fluidity. The water content coefficients of the MPC components are: 0.35 for vitrified calcium aluminio-silicate (VCAS), 0.22 for Portland cement, 0.39 for wollastonite and 0.27 for MPC binder.

The interfacial strengths of sugar maple and MPCs with various MKP/MgO ratios were evaluated in this study. The results show that a 3:1 weight ratio of MKP and MgO has the best binder performance. The difference between the average failure stress values and average initial crack stress values decreased with the increasing of MKP/MgO ratio. The starting pH value of MPC slurries decreased slightly with the increasing of

MKP/MgO ratio due to the weak acidity of MKP. The fracture type of these specimens is interfacial failure. For evaluating the MPC/maple interfacial shear properties with different MPC binder, Portland cement, wollastonite and VCAS levels by using pull-out test method, a design of experiment was generated by an Optimal-IV mixture design for special cubic model. The test results indicates that MPC binder level is the primary factor which influences the interfacial properties, wollastonite and VCAS can mutually promote the interfacial property , but the bond strength is decreased when Portland cement is mixed with the wollastonite and VCAS.

The starting pH values of the MPC slurries are closely related with the interfacial strength, the interfacial strength are generally increased with the decreasing of pH value. This relationship is potentially because of the dissolution rate and ability of MgO, where a more acidic solution provides a higher dissolution rate of MgO. The fracture type analyses shows that there are two types of fracture usually observed on the fracture surfaces, MPC block split failure usually observed in low MPC binder level specimens and MPC/maple interfacial bond failure usually observed in high MPC binder level specimens.

VCAS-MPC, W-MPC and C-MPC were reinforced by 0 wt.%, 0.5 wt.% and 1 wt.% polyvinyl alcohol (PVA) fiber and prepared for pull-out test. The test results indicate that these PVA fibers decreased the MPC/maple interfacial pull-out strength of VCAS-MPC and C-MPC, but increased interfacial strength of W-MPC. The interfacial failure mechanism of PVA reinforced MPCs is similar than non-reinforced MPCs.

To measure the moisture performance of the MPC/wood interface, pull-out specimens were exposed to 90% RH conditioning and water immersion. After exposure to these treatments, VCAS-MPC absorbed more moisture and water than W-MPC and C-MPC. Water and moisture was found to influence the VCAS-MPC block and the interfacial bonding of VCAS-MPC/maple strongly. The pull-out test results indicate that the interfacial bonding strengths of VCAS-MPC/maple, W-MPC/maple and C-MPC/maple are decreased by these treatments. After 14-day water soaking, some significantly cracks were observed on the surface of VCAS-MPC/maple pull-out specimens; also, crystals were observed on the surface of W-MPC/maple and C-MPC/maple pull-out specimens. Microscopic images also indicate the split fracture of VCAS-MPC/maple specimens and the interfacial fracture of W-MPC/maple and C-MPC/maple specimens. VCAS-MPC was found to have a much lower durability than W-MPC and C-MPC under the influence of moisture, this likely caused the low interfacial strength of VCAS-MPC/maple after conditioning.

4.2 Future studies

Following points are valuable to be studied in future:

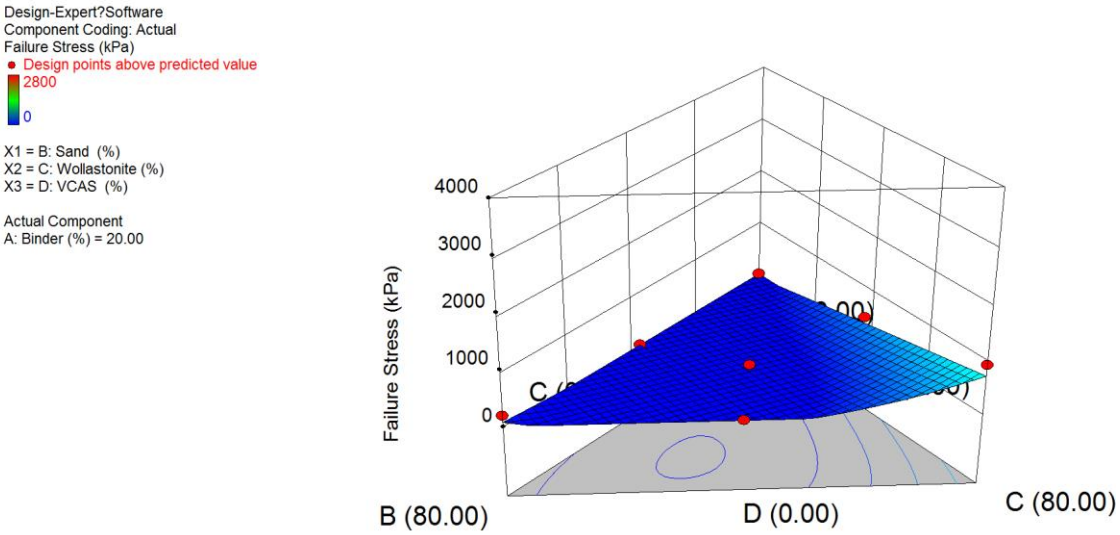
- Studies on more test methods to evaluate the interfacial properties of CBPC/wood
- More accurate theory to explain the relationship among workability, fluidity, water content and CBPC formulas
- The mechanism of the CBPC/wood interfacial fracture
- The influences of more types of aggregates fillers and additives in CBPC on interfacial properties of CBPC/wood

- The influences of more reinforcement fibers in CBPC on interfacial properties of CBPC/wood
- The interfacial microstructure of CBPC/wood
- The environmental durability of more types of CBPC
- The mechanism of the cracks in VCAS-MPC blocks and the crystals on the MPC surfaces under moisture treatment

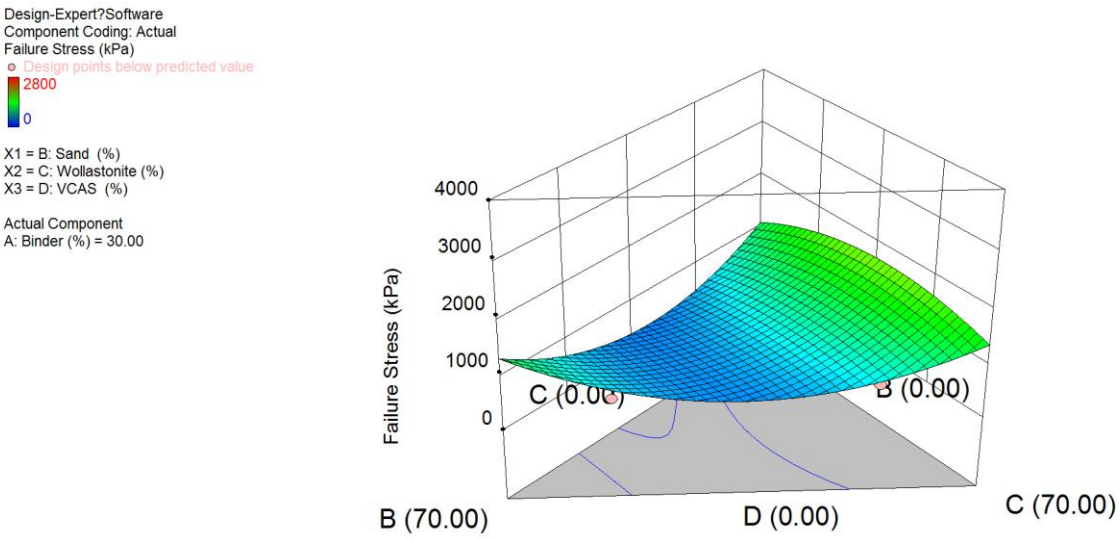
APPENDIX A

The cubic model fitting of the average specimen failure stresses with different binder and aggregates levels

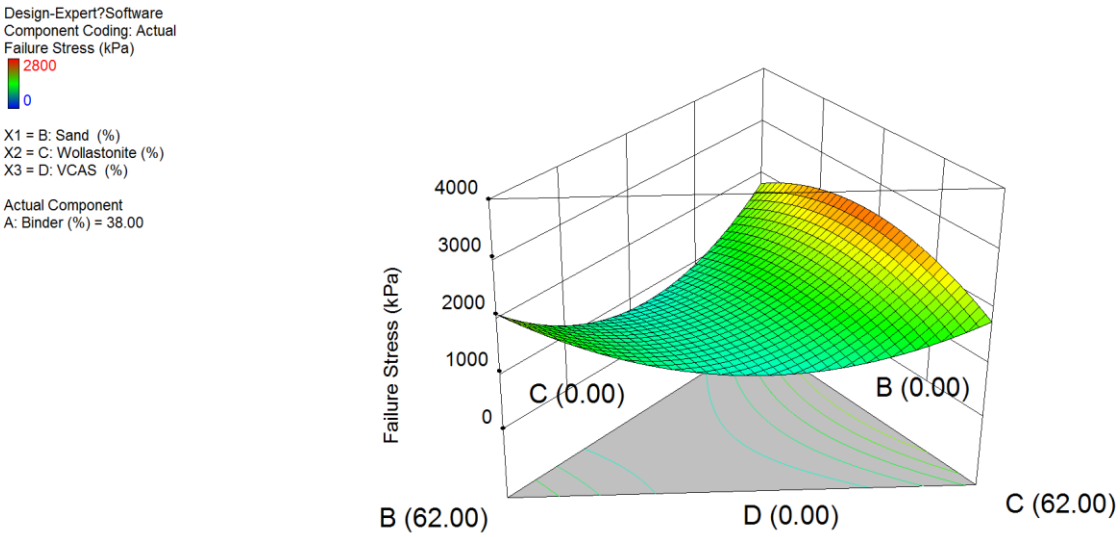
(a) binder level = 20%, (b) binder level = 30%, (c) binder level = 38%,(d) binder level = 46.67%, (e) binder level = 60%, (f) binder level = 70% and (g) binder level = 90%,



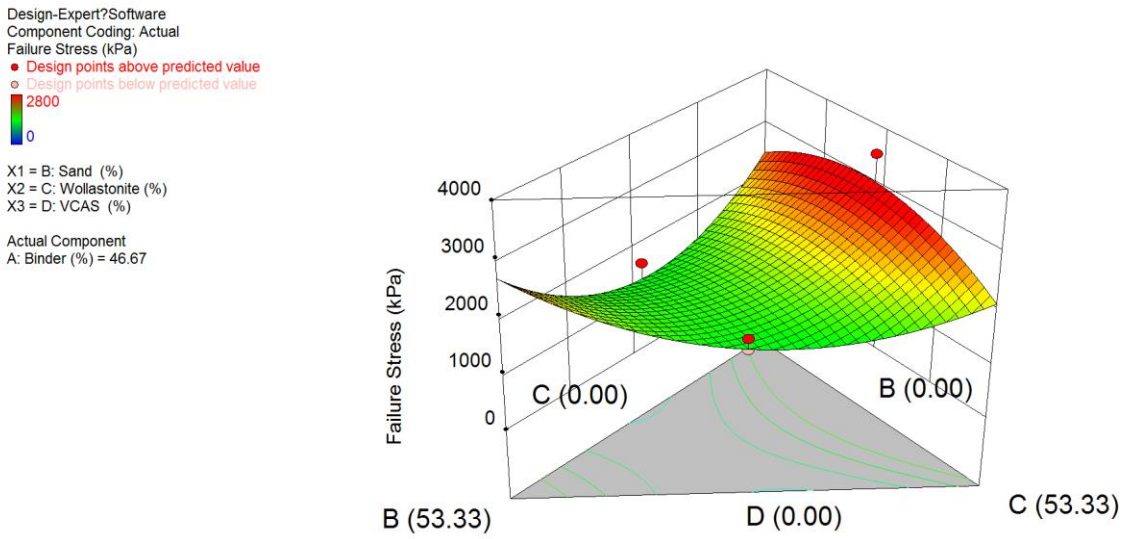
(a)


Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
Design points below predicted value
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 30.00
Failure Stress (kPa)
4000
3000
2000
1000
0
C (0.00)
B (0.00)
B (70.00)
D (0.00)
C (70.00)

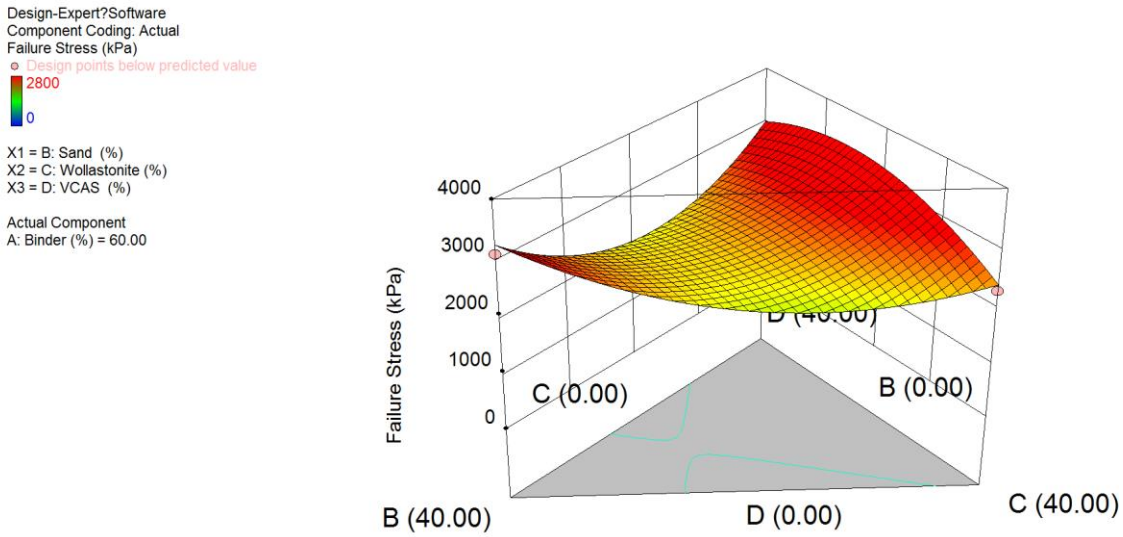
(b)


Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 38.00
Failure Stress (kPa)
4000
3000
2000
1000
0
C (0.00)
B (0.00)
B (62.00)
D (0.00)
C (62.00)

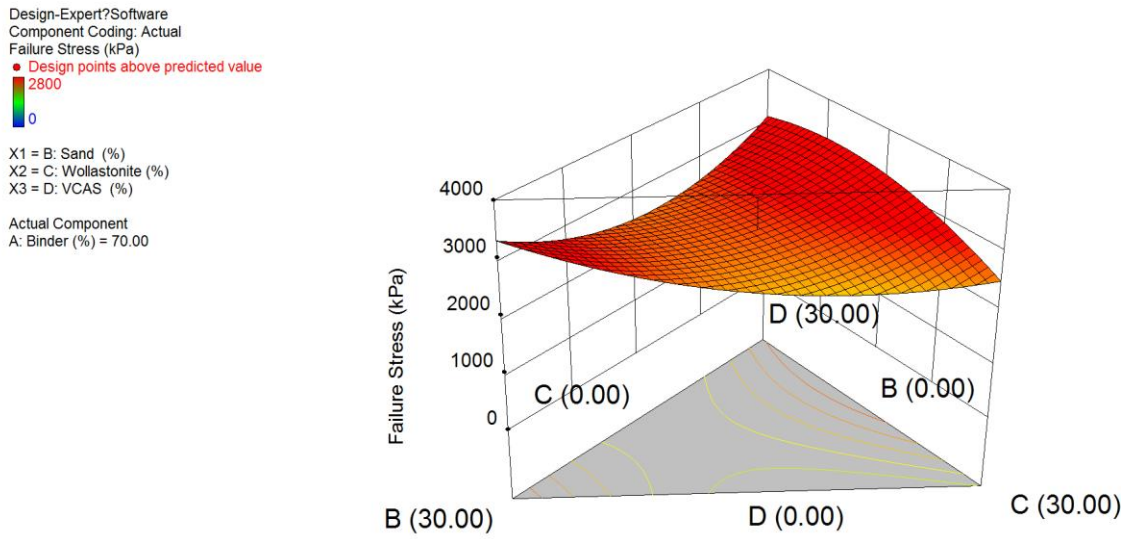
(c)


Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
Design points above predicted value
Design points below predicted value
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 46.67
Failure Stress (kPa)
4000
3000
2000
1000
0
C (0.00)
B (0.00)
B (53.33)
D (0.00)
C (53.33)

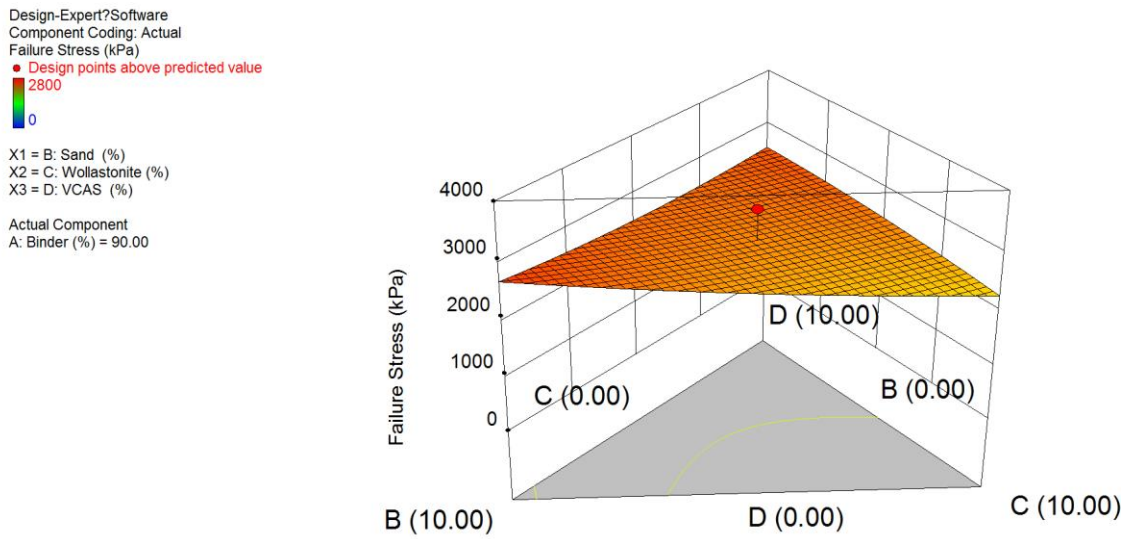
(d)


Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
Design points below predicted value
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 60.00
Failure Stress (kPa)
4000
3000
2000
1000
0
C (0.00)
B (0.00)
B (40.00)
D (0.00)
C (40.00)

(e)


Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
Design points above predicted value
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 70.00
Failure Stress (kPa)
4000
3000
2000
1000
0
D (30.00)
C (0.00)
B (0.00)
B (30.00)
D (0.00)
C (30.00)

(f)

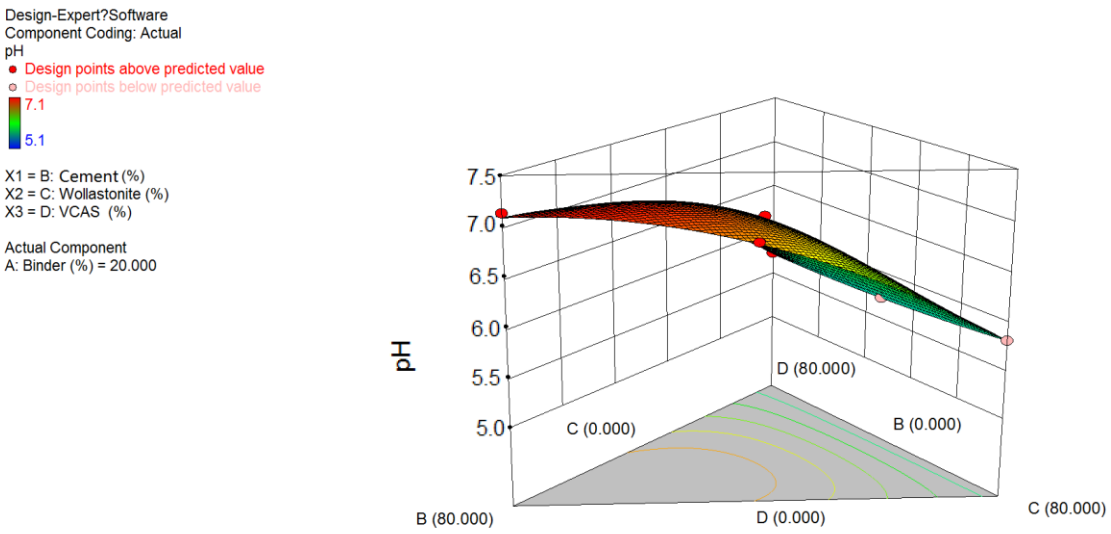

Design-Expert?Software
Component Coding: Actual
Failure Stress (kPa)
Design points above predicted value
2800
0
X1 = B: Sand (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 90.00
Failure Stress (kPa)
4000
3000
2000
1000
0
D (10.00)
C (0.00)
B (0.00)
B (10.00)
D (0.00)
C (10.00)

(g)

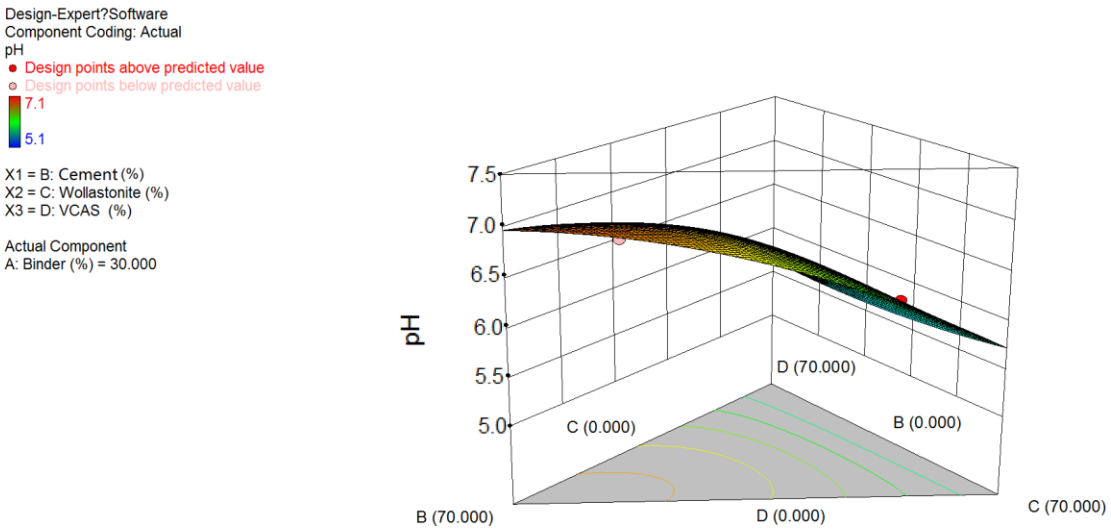
APPENDIX B

The cubic model fitting of the MPC slurries starting pH value with different binder and aggregates levels

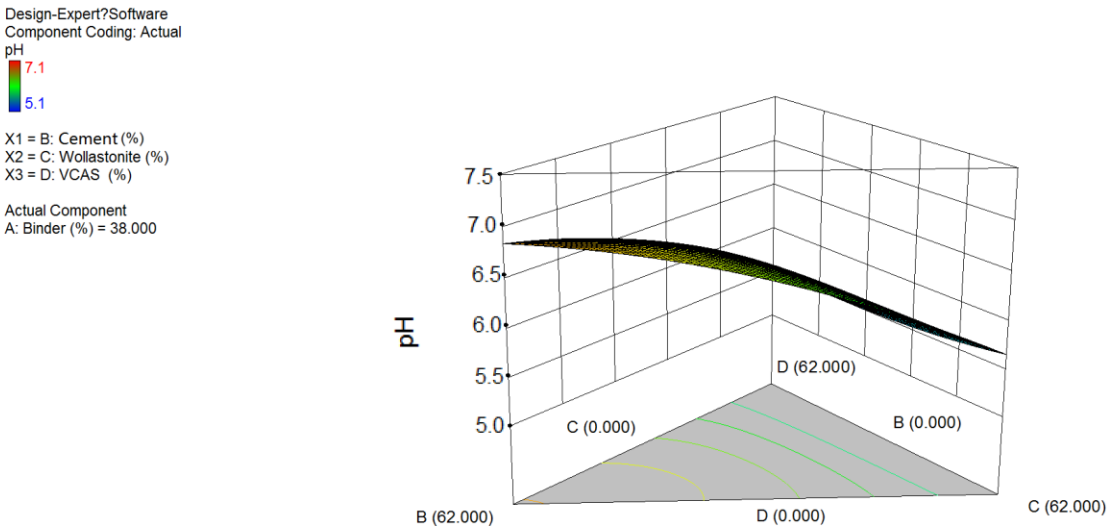
(a) binder level = 20%, (b) binder level = 30%, (c) binder level = 38%,(d) binder level = 46.67%, (e) binder level = 60%, (f) binder level = 70% and (g) binder level = 90%,



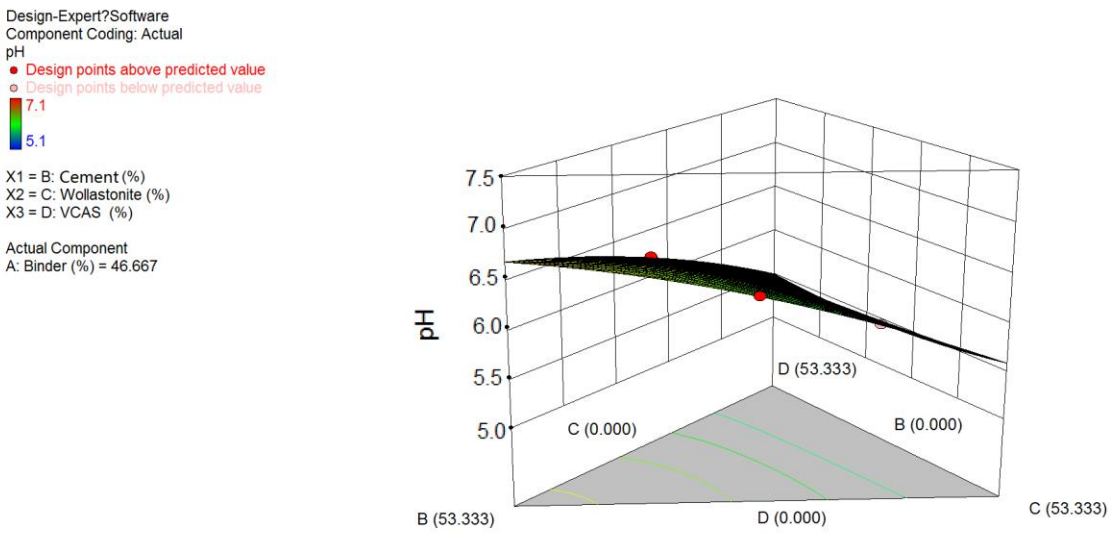
(a)


Design-Expert?Software
Component Coding: Actual
pH
Design points above predicted value
Design points below predicted value
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 30.000
pH
7.5
7.0
6.5
6.0
5.5
5.0
D (70.000)
C (0.000)
B (0.000)
B (70.000)
D (0.000)
C (70.000)

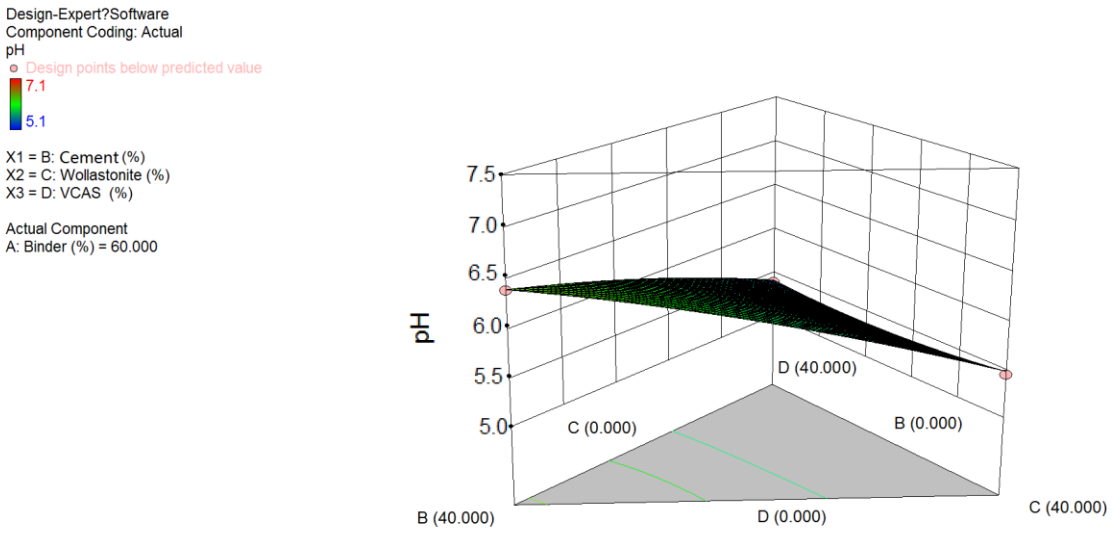
(b)


Design-Expert?Software
Component Coding: Actual
pH
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 38.000
pH
7.5
7.0
6.5
6.0
5.5
5.0
D (62.000)
C (0.000)
B (0.000)
B (62.000)
D (0.000)
C (62.000)

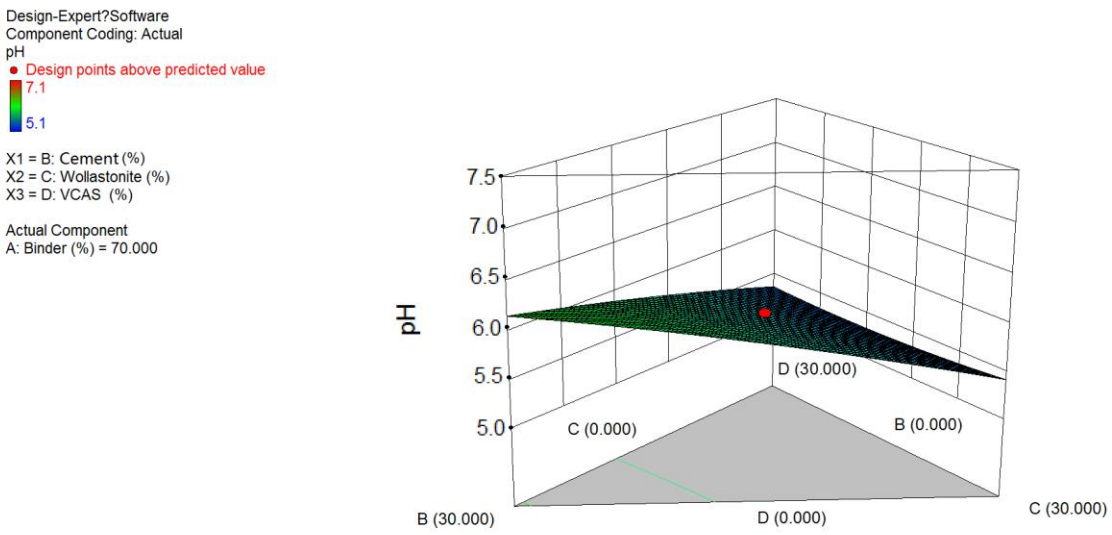
(c)


Design-Expert?Software
Component Coding: Actual
pH
Design points above predicted value
Design points below predicted value
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 46.667
pH
7.5
7.0
6.5
6.0
5.5
5.0
D (53.333)
C (0.000)
B (0.000)
B (53.333)
D (0.000)
C (53.333)

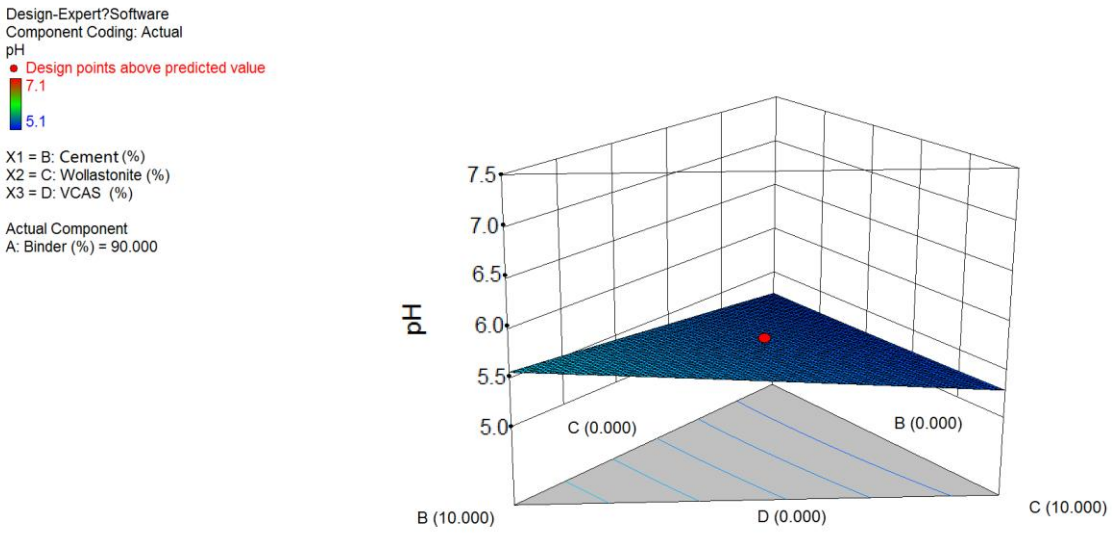
(d)


Design-Expert?Software
Component Coding: Actual
pH
Design points below predicted value
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 60.000
pH
7.5
7.0
6.5
6.0
5.5
5.0
D (40.000)
C (0.000)
B (0.000)
B (40.000)
D (0.000)
C (40.000)

(e)


Design-Expert?Software
Component Coding: Actual
pH
Design points above predicted value
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 70.000
pH
7.5
7.0
6.5
6.0
5.5
5.0
D (30.000)
C (0.000)
B (0.000)
B (30.000)
D (0.000)
C (30.000)

(f)

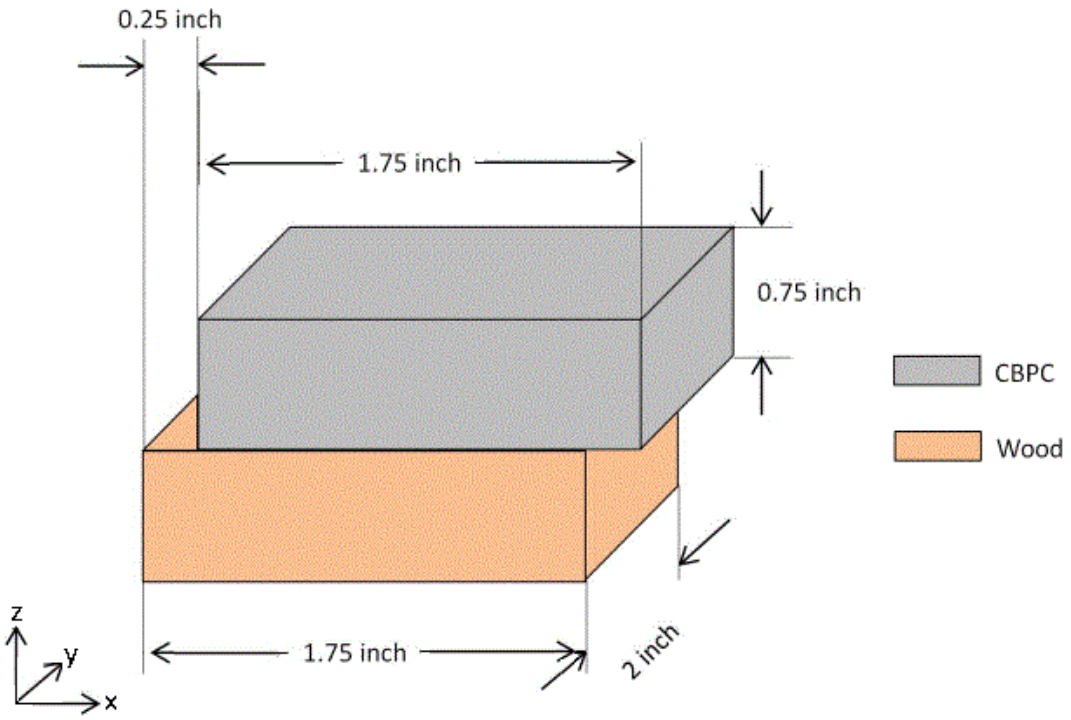

Design-Expert?Software
Component Coding: Actual
pH
Design points above predicted value
7.1
5.1
X1 = B: Cement (%)
X2 = C: Wollastonite (%)
X3 = D: VCAS (%)
Actual Component
A: Binder (%) = 90.000
pH
7.5
7.0
6.5
6.0
5.5
5.0
C (0.000)
B (0.000)
B (10.000)
D (0.000)
C (10.000)

(g)

APPENDIX C

Shear block test for MPC/sugar maple specimens

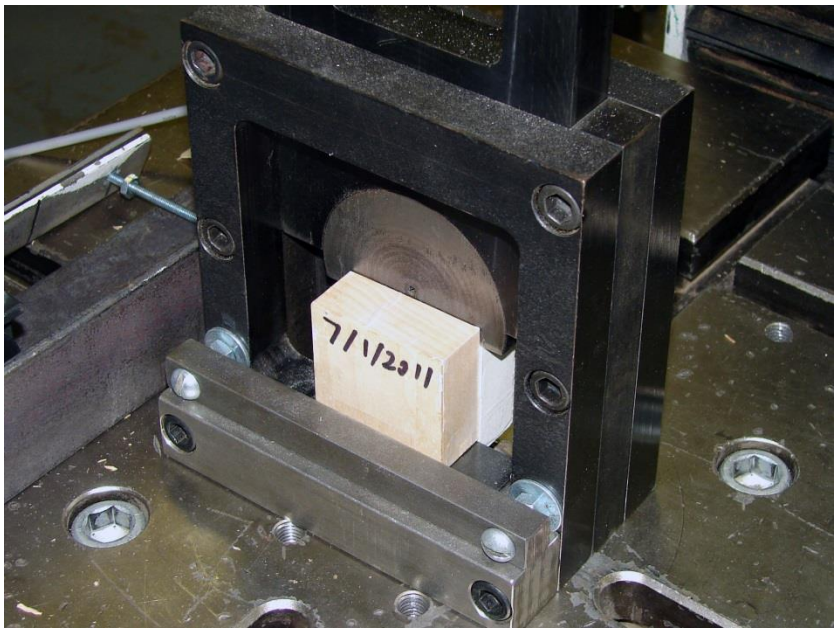
By following ASTM D905-08 standard (ASTM D905-08), the structure, shape and size of shear-block test specimens for evaluating interfacial shear strength of MPCs and sugar maple are shown in Figure below. The specimens are combined with a CBPC block and a wood block. The size of both of these blocks is 44.5 mm × 50.8mm × 19.1 mm (1.75 inch × 2 inch × 0.75 inch). X-axis is the longitudinal direction of wood block, y-axis is the tangential direction, and z-axis is the radial direction.



Structure, shape and size of shear-block specimens

The shear-block specimens are prepared by casting the MPC in a mold on the surface of the wood block.

The maple wood blocks were cut into right size and conditioned at 64% RH, 22 ℃ for at least 7 days. After the conditioning, the bonding wood surface were cleaned and prepared by using 200 mesh sand paper. The wood surfaces that are not going to bond with CBPCs were coated with plastic tape. The molds were assembled and the wood blocks were put into the molds. The dry solid raw materials of the MPC were weighed and dry mixed in a polyethylene plastic bowl. Water was then added to the dry ingredients and mixed for an additional 10 minutes. The slurry was filled into the molds and vibrated on a vibration table for 10 minutes. Once the MPC solidified (24 hrs), the specimens were cured at 64% RH, 22 ℃ for at least 7 days prior to any testing.



Mechanical test of a shear-block MPC/wood specimen

The mechanical test of shear-block specimen was implemented by installing a shear-block specimen on a shearing tool which described in ASTM D905-08. Figure above shows the mechanical testing set-up of a shear-block MPC/wood specimen. The

specimens were compressed with a 1.27 mm (0.05 inch) per minute compression rate until failure with a load-displacement data collection rate of 25Hz.

With the data gained from the mechanical test, the interfacial shear strength can be calculated,

$$T = \frac{F}{A}$$

Where,

T, interfacial shear strength

F, debonding force, the max load on the load-displacement curve

A, interfacial bond area.

Specimens formulas design of shear-block feasibility test

Formula code	MPCs formula	Water content in slurry	Number of replicates	Average shear strength (kPa)	Coeff. of variation (kPa)
A	35.7 wt.% MKP, 14.3 wt.% MgO, 25 wt.% VCAS, 25% wt.% Wollastonite	25 wt.%	3	1821	626
B	35.7 wt.% MKP, 14.3 wt.% MgO, 25 wt.% VCAS, 25% wt.% Wollastonite	32 wt.%	3	649	172

To verify the feasibility of the test method, some shear-block specimens have been prepared and tested. The interfacial failure for these 6 specimens was interfacial failure. The load-displacement curves show that all the interfacial failure is brittle fracture, which is observed in the instantaneous drop in load after achieving the maximum load.

Reference

ASTM D905-08. *Standard Test Method for Strength Properties of Adhesive Bonds in Shear by Compression Loading*.