

EXPLORE ACCELERATED PCC PAVEMENT REPAIRS USING METAKAOLIN-BASED  
GEOPOLYMER CONCRETE

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**Title**

Explore Accelerated PCC Pavement Repairs Using Metakaolin-based  
Geopolymer Concrete

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The Supervisory Committee certifies that this *disquisition* complies with North Dakota  
State University's regulations and meets the accepted standards for the degree of

**MASTER OF SCIENCE**

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## ABSTRACT

In order to adopt geopolymer concrete as a pavement repair material due to its better durability, splitting and slant shear tests are performed. Effect of curing time, degradation of the pavement concrete under different acid conditions on the bond strength of geopolymer with conventional concrete, and comparison of the metakaolin geopolymer with other pavement repair materials are analyzed. It was found curing time affects the interface bond strength greatly and the interface bond strength degrades quickly in an acid environment. Effect of molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ , calcium aluminate cement, and slag on early strength of the geopolymer have been studied. It was found molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  of 1.0 gave the highest early strength in 24 hours. Also, freeze-thaw durability of geopolymer concrete are investigated by exposing the specimens to rapid freeze-thaw cycles. Based on these research results, adopting metakaolin geopolymer in accelerated PCC pavement repairs is a feasible option.

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## CHAPTER 1. INTRODUCTION

### 1.1. Introduction

Portland cement concrete (PCC) pavement and structures need to be repaired due to different reasons such as deterioration, poor riding quality, and structural failures. It is widely known that the most repair materials for concrete repair applications today are polymer-modified cement, consisting of Portland cement with additional of polymer. Portland cement is the world's most used construction binder material (Fernandez-Jimenez, et al, 2006). However, cement production emits large amounts of CO<sub>2</sub> that pollutes the atmosphere (Aleem and Arumairaj, 2012), and consumes significant amount of energy (required temperature up to 1400-1500°C). Production of one ton of Portland cement releases one ton of CO<sub>2</sub> into the atmosphere (Hardjito et al, 2004a). Cement production (Madeleine, 2012) contributes 5%-7% of all global greenhouse emissions in total. Figure 1 shows the emission of CO<sub>2</sub> during Portland cement production. It is a common viewpoint that finding an alternative material to the Portland cement is imminent.



**Figure 1.** Emission of CO<sub>2</sub> during Portland cement production (Van Chanh et al, 2008)

On the other hand, geopolymer is a new construction material which could be produced by the chemical action of inorganic molecules, without using any Portland cement. The geopolymer binder could be produced through chemical reaction between aluminosilicate materials such as fly ash or metakaolin that are rich in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and alkaline solutions such as sodium hydroxide or sodium silicate. Fly ash is a by-product of burnt coal that could be obtained from the thermal power plant, and it is readily available worldwide (Hardjito et al, 2004b). Metakaolin is produced by heating kaolin (a natural clay) at  $750^\circ\text{C}$  and could be produced in a large quantity with homogeneous properties (Rovnaník, 2010). Even though other types of alumina-silicate exist, the metakaolin is used in this study due to its large quantity and homogeneous properties. Geopolymer binder production releases 80-90% less  $\text{CO}_2$  than Portland cement does, which makes it a green material. The geopolymer concrete can also be manufactured and implemented using the same equipment and practices used for Portland cement concrete. So the best alternative to Portland cement in the earth is geopolymer (Kim, et al, 2006).

Davidovits found the geopolymer after the reaction between polymer and geological origin source material in 1970's (Davidovits, 1988). Shortly after Davidovits's finding, the geopolymer binder was quickly researched as the main binder to replace Portland cement (Duxson et al, 2007; Gourley, 2003). Typically, synthesis of geopolymer consists of three steps. The first step is to dissolve alumino-silicate under strong alkali solution; then the free ions re-orientate into clusters in the solution, and the last step is polycondensation. The geopolymer forms very rapidly, consequently the three steps occur almost simultaneously, which makes the kinetics in the chemical reaction inter-dependent (Kamarudin et al, 2011).

To use the geopolymer as a repair material, the bond strength between the substrate concrete and the repair material (Geissert et al, 1999; Momayez et al, 2005) is critical. The properties of geopolymer concrete (Hardjito et al, 2004c; Hardjito et al, 2005) such as the modulus of elasticity, Poisson's ratio, and the tensile strength are similar to those of Portland cement concrete, which shows the compatibility between the geopolymer concrete and Portland cement concrete. In addition, durability and rapid curing of geopolymer concrete need to be considered before using it as a new repair material. However, there is no specific publications regarding to use geopolymer mortar as a pavement repair material, and no specific publications are available concerning the freeze-thaw resistance of metakaolin-based geopolymer concrete. This thesis will take the initiative and discuss the use of geopolymer mortar as a pavement repair material and characterize the freeze-thaw resistance of geopolymer concrete.

## **1.2. Research objectives**

The objectives of this research are to experimentally assess the possibility of using metakaolin-based geopolymer mortar as a pavement repair material and characterize the durability of metakaolin-based geopolymer concrete against freeze and thaw. The research includes the effect of aggressive environments on the bond strength between geopolymer mortar and existing concrete and the effect of rapid freeze-thaw on metakaolin-based geopolymer concrete. The bond strength of geopolymer mortar to existing concrete was evaluated by splitting tensile test and slant shear test with line interface at 30° and 45°. Also, the durability of geopolymer concrete was evaluated by means of destructive and un-destructive tests, where the compressive strength and relative dynamic modulus of elasticity of geopolymer concrete with different mix ratios was tested and compared.

In summary, the research objectives are:

- I. To investigate the feasibility of using metakaolin-based geopolymer mortar as a repair material under various aggressive environments.
- II. To systematically characterize the bond strength between geopolymer mortar and concrete substrate under different aggressive environments and compare it with current repair materials in market.
- III. To study the effect of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  ratio, aluminum calcium cement, and slag on the early strength of the geopolymer mortar, for the purpose to find a rapid curing binder.
- IV. To evaluate the durability of metakaolin-based geopolymer concrete.

### **1.3. Scope of the research**

In this thesis, most of work was conducted through experiments. The main scope of the experimental work is to evaluate the bond strength and durability of the suggested metakaolin-based geopolymer with conventional concrete substrate. Materials used in this research are metakaolin, which can be obtained by heating kaolin (a natural clay) at  $750^\circ\text{C}$ , and alkaline solution such as sodium silicate solution ( $\text{Na}_2\text{Si}_3\text{O}_7$ ) and sodium hydroxide solution ( $\text{NaOH}$ ).

### **1.4. Thesis organization**

This thesis is organized into six chapters. Chapter one shows the effect of using Portland cement concrete on the environment and the motivation for developing metakaolin-based geopolymer concrete as an alternative to Portland cement concrete. Chapter two provides a literature review of previous researches on geopolymer. It includes the historical background of developing alkali activated binder systems, the chemistry of geopolymer, the reaction mechanism of geopolymer, and the advantages and disadvantages of using geopolymer in lieu of

Portland cement. Chapter three reports the experimental results of splitting tensile test of composite materials and slant shear test with line interface at 30° and 45° which are carried out to find the bond strength of geopolymer mortar to existing concrete at normal and acid environments. Chapter four experimentally discusses the effect of the ratio of SiO<sub>2</sub> to Na<sub>2</sub>O, adding aluminum calcium cement, and slag on the early strength of the geopolymer mortar. Chapter five reports the resistance of geopolymer concrete to rapid freezing and thawing cycles. The relative dynamic modulus of elasticity and compressive strength of geopolymer concrete are determined after they are subjected to certain cycles of freeze-thaw following ASTM-C666, for resistance of concrete to rapid freezing and thawing. Chapter six provides the conclusions and recommendations for future work.

### **1.5. Team effort**

Dalu Zhang assisted me to prepare and test the specimens. Especially, Dalu Zhang helped me test the freeze-thaw durability and compressive strength of geopolymer concrete.

## CHAPTER 2. LITERATURE REVIEW

### 2.1. Introduction

An extensive review about geopolymer is presented in this chapter. The literature review includes the historical background, terminology, chemistry, applications, and properties of geopolymer. Also, current progress on geopolymer and its application in pavement repairs are discussed in this chapter.

### 2.2. Historical background

A historical background about some important events on development of alkali-activated binders is chronologically presented in this section. The beginning was with Feret's work which is considered related to the development of alkali-activated binders by blending slag with ordinary Portland cement without using alkali activator (Feret, 1939; Roy, 1999). But the major contribution in the field of alkali-activated binders was led by the work of Purdon in the 1940s (Purdon, 1940). Purdon used sodium hydroxide to activate the blast furnace slag. According to Purdon, alkali hydroxide acted as catalysts.

In 1959, the ancient Roman and Egyptian constructions were first examined to find out the composition of the binders used to build ancient Roman and Egyptian constructions (Glukhovsky, 1959). The compositions of the binders were aluminosilicate calcium hydrates and crystalline phases of analcite. Aluminosilicate calcium hydrates is like the ones in the Portland cement and crystalline phases of analcite is a natural rock that would explain the durability of ancient Roman and Egyptian constructions. Based on the result of this investigation, new binders named "*soil-cement*" were developed by Glukhovsky. Ground aluminosilicate mixed with rich alkali industrial wastes were the main components of "*soil-cement*".



Ancient constructions repaired with Portland cement were also investigated in (Malinowsky, 1979; Longton et al, 1984; Roy et al, 1989). Malinowsky concluded that the repairing material decayed only after 10 years and had low durability compare to ancient construction. In addition, the ancient binders were studied to find out why ancient constructions have high durability, and the reason was due to its high level of amorphous zeolitic compounds according to (Campbell et al, 1991). It had been also reported that ancient constructions were stable and durable due to the presence of zeolitic compounds in ancient binders (Longton et al, 1984; Roy et al, 1989; Granizo, 1998).

The term “geopolymer” was named in 1978 by Davidovits (Davidovits, 1979), which was later used as patented binders obtained from the alkali-activator of metakaolin (Davidovits and Sawyer, 1985). Davidovits assumed that the pyramids were made by man-made binders not natural stone. Moreover, the “F-cement” in Finland (Forss, 1983) and “geocements” in the Ukraine were assigned under this category (Glukhovsky, 1994; Krivenko, 1997). For the basic compositions of alkali-activated binders, Krevenko suggested that the binding systems could separate into two different categories:  $\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  and  $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ , even though they are overlapped on some of the compositions (Glukhovsky, 1994; Krivenko, 1997; Talling et al, 1989).

Most of the investigations on alkali-activated binders used blast furnace slag with the alkali solution known as “*Alkali-slag cement*” or “*Alkali-activated slag cement*” (Forss, 1983; Talling et al, 1989; Malolepszy et al, 1986; Malek et al, 1986; Deja et al, 1989; Majumbar et al, 1989; Roy et al, 1991; Roy et al, 1993; Wang et al 1995; Jiang et al, 1997; Clarke, 1997). Blast furnace slag is a by-product of iron production. Blast furnace slag has high content of calcium because the calcium carbonate is used in the calcination process. C-S-H,  $(\text{C,M})_4\text{AH}_{13}$ , or

hydrotalcite and minor amounts of  $C_2ASH_8$  are the main reaction products of alkali-activated slag cements. However, other aluminosilicate binders of natural and waste products were also investigated as binders to be activated under strong alkali solution.

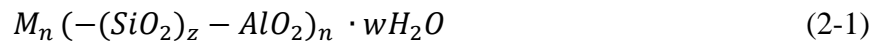
### **2.3. Terminology**

Geopolymer is an inorganic alumino-silicate polymer with a chemical composition similar to zeolites but with an amorphous microstructure. Davidovits proposed the term 'Poly(sialate)' to use for the chemical designation of geopolymers based on silico-aluminate where sialate is an abbreviation for Silicon-oxo-Aluminate (Davidovits, 1988). In addition, Davidovits also discussed in details the chemistry and terminology of inorganic polymers (Davidovits, 1988). The geopolymerization process involves dissolution of alumino-silicate under strong alkali solution, yielding polymeric Si-O-Al-O bonds in amorphous form.

Alumina silicate binders that are rich in alumina and silica are also named alkaline cements or alkali-activated cements, but this name makes civil engineers confused because of alkali-aggregate reaction which is also harmful for Portland concrete. Calling these new binders as alkali cement is not very accurate due to the ability of Portland cement to harden in alkaline solution. As known in Portland concrete, the alkali-aggregate reaction is one of the concerns in the Portland concrete, since most of aggregate has high silica that could chemically react with alkali in Portland cement and cause failure of Portland concrete. The failure could occur when the reaction between silica in aggregate and alkali in cement take place and form gel to swell. As a result of swelling, the gel can induce enough pressure to damage the concrete. On the other hand, geopolymer concrete does not show any sign of alkali-aggregate reaction and does not suffer from alkali-aggregate reaction even in the presence of high alkalinity (Davidovits, 1999).

## 2.4. Geopolymer chemistry

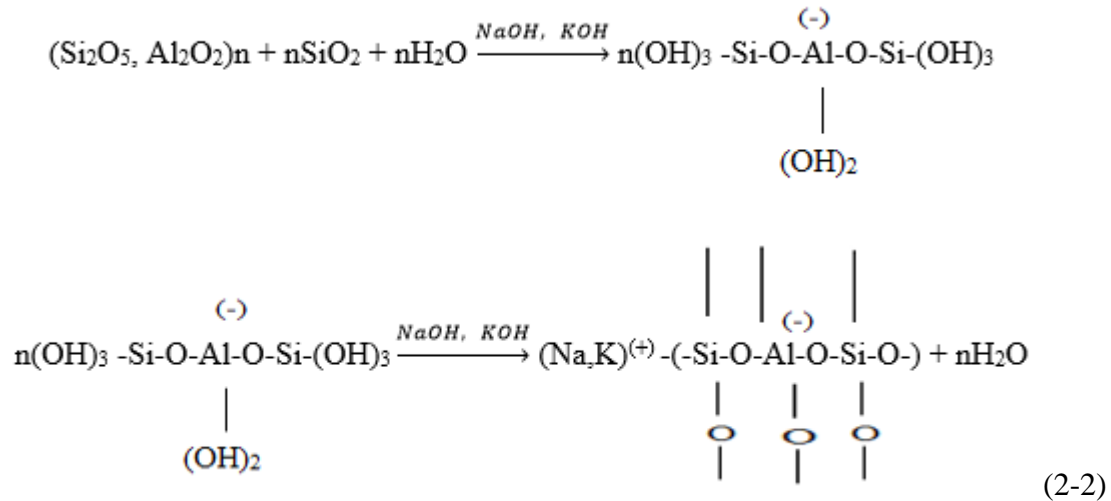
As mentioned in terminology, Davidovits used the term “Geopolymer” to name the alumino-silicate binders that have chemical composition similar to that found in zeolites, but with an amorphous microstructure, and formed in alkaline environment. Davidovits also used another term “Poly(sialate)”, which sialate known as an abbreviation form for silicon-oxo-aluminate, to describe the chemical designation or molecular structure of geopolymers based on silico-aluminates (Davidovits, 1988a; Davidovits, 1988b; Davidovits, 1991; Van Jaarsveld et al, 2002). Polysialates are defined as chain and ring polymers with  $Si^{4+}$  and  $Al^{3+}$  in IV-fold coordination with oxygen and range from amorphous to semi-crystalline. Equation 2-1 presents the empirical formula of Polysialates:



Where M refers to alkali cation such as potassium or sodium, “n” refers to the degree of polycondensation, and “z” is either 1, 2, or 3 or higher up to 32 (Davidovits, 1988b; Davidovits, 1984; Davidovits, 1994; Davidovits, 1999). In addition, Davidovits differentiated three types of polysialates as shown below (Davidovits, 1999):

- Poly (sialate), which has [-Si-O-Al-O-] as the repeating unit.
- Poly (sialate-siloxo), which has [-Si-O-Al-O-Si-O-] as the repeating unit.
- Poly (sialate-disiloxo), which has [-Si-O-Al-O-Si-O-Si-O-] as the repeating unit.

Geopolymer can be produced by a chemical reaction between alumino-silicate binders and high alkaline solution, yielding a polymeric Si-O-Al-O bonds. The chemical reaction process between alumino-silicate binders and high alkali solution is called geopolymerization. Equation 2-2 presents the schematic formation of geopolymer and an example of polycondensation by alkali into polysialate-siloxo (Wallah et al, 2006).



The second part of equation 2-2 was discussed in details by (Rangan, 2008), and reported below:

“The last term in Equation 2-2 reveals that water is released during the chemical reaction that occurs in the formation of geopolymers. This water, expelled from the geopolymer matrix during the curing and further drying periods, leaves behind discontinuous nanopores in the matrix, which provide benefits to the performance of geopolymers. The water in a geopolymer mixture, therefore, plays no role in the chemical reaction that takes place; it merely provides the workability to the mixture during handling. This is in contrast to the chemical reaction of water in a Portland cement concrete mixture during the hydration process”.

Portland cement hardens through the hydration process and forms calcium-silicate-hydrates (C-S-H) gel for matrix formation and strength, whereas geopolymer hardens through the geopolymerization process and forms 3D frameworks using the polycondensation of alumino-silicate precursors and the alkali activator to attain structural strength. Anyway, geopolymerization process has not been fully understood yet. Recently, another model or theory for geopolymerization has been developed based on the model that proposed by (Glukhovskiy, 1959). Also, the conceptual model for geopolymerization is presented in (Duxson et al, 2007).

## **2.5. Constituents of geopolymer**

The constituents of geopolymer concrete are:

- Alumino-silicate binders
- Alkaline activator

Alumino-silicate materials used to produce geopolymer are the ones that rich in silica and alumina such as fly ash and metakaolin. While the most common alkaline activator used to produce geopolymer is a combination of sodium silicate solution (water glass) and sodium hydroxide (NaOH).

### ***2.5.1. Alumino-silicate materials***

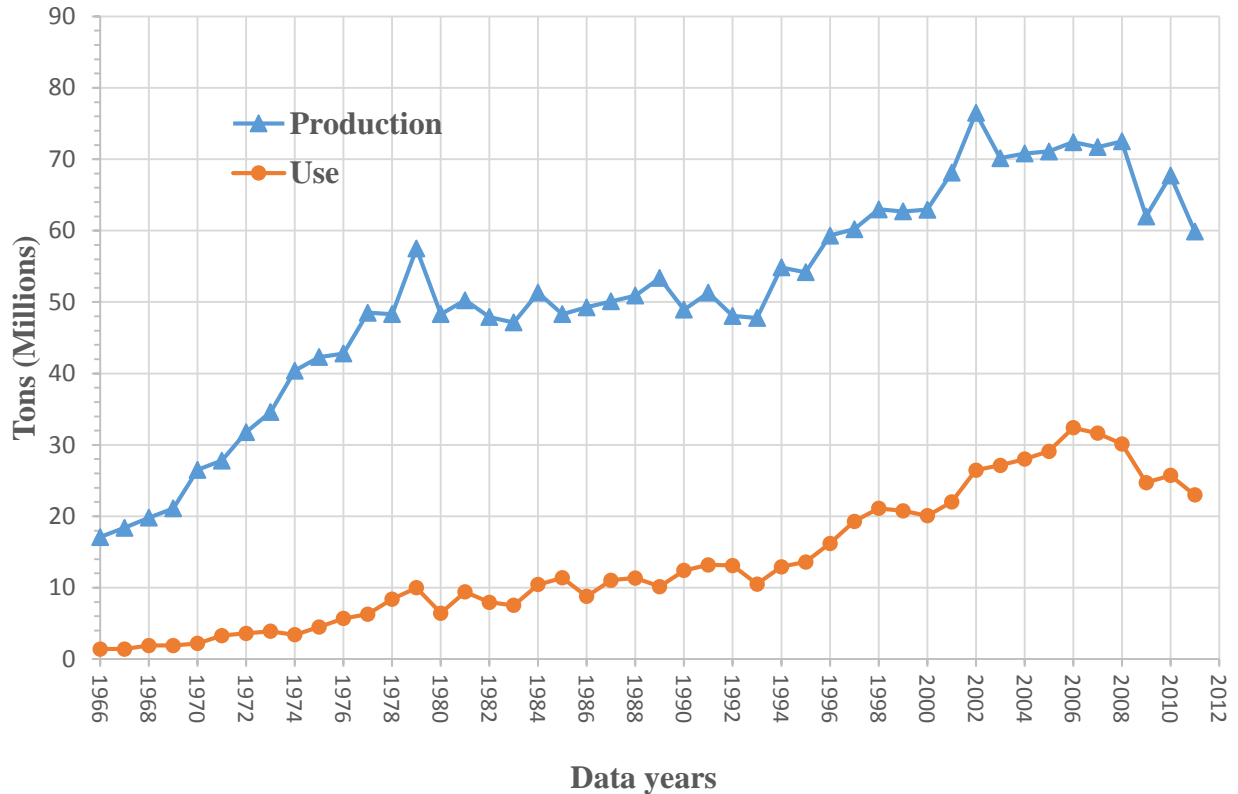
Any material that is rich in silicon and aluminum can be used as geopolymer. There are several alumino-silicate materials that have been used to produce geopolymer. However, the most common alumino-silicate materials are low calcium fly ash Class F and metakaolin. Silicon and aluminum are the primary reactants in the geopolymerization process.

Fly ash is defined by the American Concrete Institute, ACI 116R, as “the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gases from the combustion zone to the particle removal system” (ACI Committee 232 2004). Fly ash is one of the most available materials in the World, and fly ash will be available in the future for many years. The utilization of fly ash is still limited so far. The main components of fly ash are aluminum, silicon, calcium, magnesium, and iron. The typical particles of fly ash are spherical in shape and the diameters vary from 1  $\mu\text{m}$  to 150  $\mu\text{m}$  (Nawy, 2008).

ASTM C618 divided fly ash into two classes, low-calcium fly ash (Class F) and high-calcium fly ash (Class C). They are different in chemical composition and physical properties.

Low-calcium (ASTM Class F) fly ash can be obtained by burning anthracite or bituminous coal, where high-calcium (ASTM Class C) fly ash can be obtained by burning lignite or subbituminous coal. The percentage of unburned material in low-calcium fly ash should be less than 5%,  $\text{Fe}_2\text{O}_3$  content should be less than 10%, reactive silica content should range between 40-50%, 80-90% particles of low-calcium fly ash should be smaller than 45  $\mu\text{m}$ , and has low CaO content (Fernández-Jiménez et al, 2003). The high quantity of calcium in the high-calcium fly is not recommended because it can change the microstructure of geopolymer, so low-calcium fly ash is preferable (Gourley, 2003). On the contrary, high-calcium fly ash can develop higher compressive strength in the early age due to the formation of calcium-silicate-hydrate gel and other calcium compounds (Van Jaarsveld et al, 2003), but the formation of calcium-silicate-hydrate gel would reduce the corrosion resistance.

The largest fly ash producer in the World is China with 70 million tons per year (Fu, 2010), then the United States with 68 million tons per year (Ramme et al, 2004). Figure 2 shows a comparison between the production and use of coal ash from 1966 to 2011 (ACAA, <http://www.aaa-usa.org/>). Figure 2 shows a huge gap between the production and use of coal ash.



**Figure 2.** Comparison between production and use of coal ash from 1966 to 2011

Metakaolin is defined as a dehydroxylated pozzolanic material that obtained by firing raw kaolin at high temperature. Metakaolin is produced by heating kaolin (a natural clay) at 750°C for 6 hours and could be produced in a large quantity with homogeneous properties (Rovnaník, 2010). The raw material used to manufacture metakaolin is kaolin or kaolinite  $[Al_2Si_2O_5(OH)_4]$ . Kaolin is a fine, white, and natural clay, and kaolin has been utilized in the porcelain industry. The main components of metakaolin are similar to the main components of high-calcium fly ash. Metakaolin has been become the preferred alumino-silicate material among researchers (Barbosa et al, 2003; Duxson et al, 2007; Fernández-Jiménez et al, 2008) due to its high rate of dissolution in the reactant solution, ability to manufacture with same homogenous properties, easy to control over Si/Al ratio, and its colour (Gourley, 2003). However, using fly ash to produce geopolymer is cheaper than using metakaolin due to the use of the calcination in producing metakaolin.

### **2.5.2. Alkaline activator**

The most used alkaline activator to activate the aluminosilicate materials is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate. An addition of sodium hydroxide (NaOH) solution to sodium silicate solution (water glass) has become the most used alkaline activator due to its enhancement on the reaction between the aluminosilicate material and the solution (Xu et al, 2000). In addition, Single alkaline activator can be used to activate the aluminosilicate materials (Palomo et al, 1999; Teixeira-Pinto et al, 2002). The alkaline activator has been reported to play an important role in the geopolymerization process (Palomo et al, 1999).

## **2.6. Advantages and disadvantages of geopolymer concrete**

### **2.6.1. Advantages**

The main reason for the continued investigation on geopolymer concrete is its higher mechanical properties of geopolymer concrete compared to those of Portland cement concrete. Compare with Portland cement concrete, geopolymer concrete has many advantages over Portland cement concrete. From environmental aspect, geopolymer concrete would bring a lot of environmental benefits and reduce environmental concerns in producing concrete. Producing one ton of Portland cement requires 2.8 tons of raw materials (Khale et al, 2007), and emits one ton of CO<sub>2</sub> into the atmosphere (Hardjito et al, 2004a). Moreover, alumina silicate binders that are rich in alumina and silica such as fly ash is worldwide available, and fly ash will be disposed in the landfill if it is not used. As a result, disposing these materials into landfill would create a risk through leaching metal elements into ground water.



Economically, production of geopolymer binders would bring lots of benefits for the economy over Portland cement. The price of Portland cement production is high due to high amounts of energy that are required to produce Portland cement. Portland cement production requires temperature between (1400-1500 °C) which makes it energy-intensive process and costly (Fernández-Jiménez et al, 2005). On the other hand, binders that are used to produce geopolymer are readily available such as fly ash and blast furnace slag, and therefore it is inexpensive to obtain them. It has been reported that 60-70% of fly ash is disposed in the landfill which could potentially pollute the inland and marine waters (Sumajouw et al, 2006). The cost of geopolymer concrete is about 10 to 30% cheaper than the cost of Portland cement concrete (Lloyd et al, 2010; Rangan, 2008). Taking into account the properties of geopolymer concrete such as very little drying shrinkage, excellent resistance to acid, rapid strength gain will add more economic benefits when geopolymer concrete is used in infrastructure applications.

It has been reported that geopolymer possesses excellent resistance to acids. Geopolymer shows superior resistance to acid attack due to lower calcium content of the source material and geopolymer does not show any gypsum or ettringite formation during acid attack (Škvára et al, 2007), while Portland cement deteriorates very badly when it is attacked by acids due to expansive gypsum and ettringite formation which causes cracking and spalling in the concrete. In addition, metakaolin-based geopolymer mortar when immersed in seawater, sodium sulfate, and sulfuric acid, did not show any sign of deterioration in microstructure and reduction in strength (Khale et al, 2007). X-ray diffraction analysis was used to find out if geopolymer specimens would have expansive hydration products after immersed for a period of 1.5 years in solutions of sodium chloride (NaCl) and MgSO<sub>4</sub> (McDonald et al, 2006), but it failed to find any presence of expansive hydration products in geopolymer specimens. Concrete sample fails to be considered

durable if it expands more than 0.5% of its geometric dimensions after exposed to sulfate attack. Geopolymer specimens only had less than 0.02% change in length after exposed to sulfate attack for a period of 24 weeks (Khale et al, 2007). In addition, geopolymer specimens only lost 3 % of its mass when they are immersed in sulfuric acid, while Portland cement samples were totally destroyed (Khale et al, 2007; Škvára et al, 2007). The visual appearances of geopolymer concrete specimens after and before immersed in sodium sulfate solution and tap water for a period of one year are shown in (Wallah et al, 2006). The geopolymer specimens after exposures to different sodium sulfate solutions did not show any sign of cracking and surface erosion on the specimens.

Geopolymer mortar performs much better at high temperature than Portland cement mortar does. Based on (Fernández-Jiménez et al, 2008), Portland cement showed high bending and compressive strength at room temperature, but the bending strength of Portland cement significantly decreases at 400 °C due to the loss of the  $\text{Ca}(\text{OH})_2$  content. Also the compressive strength of Portland cement sharply decreases beyond 600 °C. On the other hand, the bending strength of fly ash-based geopolymer barely changed with temperature, and its compressive strength sharply increased over 400 °C as reported in (Fernández-Jiménez et al, 2008). The fracture toughness of Portland cement and fly ash geopolymer was also investigated in (Fernández-Jiménez et al, 2008). Both materials have almost the same toughness at ambient temperature, but beyond 400 °C, the toughness of Portland cement slightly goes down till the half of initial values at 600 °C, while that of fly ash geopolymer does not change to a temperature of 600 °C. To illustrate the effect of exposure to high temperature on Portland cement and fly ash mortars, the variation in the residual values for bending ( $\sigma_{FR}$ ) and compressive strength ( $\sigma_{CR}$ ), standardized to the respective bending ( $\sigma_{FO}$ ) and compressive strength ( $\sigma_{CO}$ ) values at ambient temperature are reported in (Fernández-Jiménez et al, 2008).

Less shrinkage is an advantage of geopolymer concrete. Geopolymer mortar did not show any shrinkage when the reaction occurred and the dimensional characteristics of the fresh paste did not change (Škvára et al, 2007). The drying shrinkage strain of fly ash-based geopolymer concrete at different days was investigated in (Wallah and Rangan, 2006). The geopolymer concrete specimens were first cured at 60 °C for 24 hours, then let the specimens to cure at ambient temperature and steam, respectively. The drying shrinkage strain of geopolymer concrete slightly fluctuated and was only 100 micro strains during a one-year period. In addition, there is insignificant variations of drying shrinkage strains between both cured specimens. However, the difference between the drying shrinkage strain of heat-cured and ambient was studied in (Wallah and Rangan, 2006). The drying shrinkage strains of geopolymer concrete specimens that cured in ambient temperature are much larger than those heat-cured due to water that evaporated during geopolymerization process.

### ***2.6.2. Disadvantages***

Little variations in the chemical composition of geopolymer binders greatly affect the resulting properties. The physical properties and the kinetic degree get significantly affected by the amount of calcium in the raw materials. In addition, the workability of geopolymer concrete is less than that of Portland cement concrete. Adding 2% or more of superplasticizers increases the workability of geopolymer concrete and slightly decreases the compressive strength of geopolymer concrete. Moreover, the cost of geopolymer concrete could be cheaper or more expensive than that of Portland cement concrete. The reasons the cost of geopolymer concrete can be higher or cheaper than that of Portland cement concrete are the location of the raw materials, the energy source, and transportation (McLellan et al, 2011). Geopolymer concrete

needs a very good control to be used on site. One of the drawbacks of geopolymer concrete is the health and safety issues associated with high corrosive activator solutions.

## **2.7. Geopolymer application**

Geopolymer has many great properties such as less CO<sub>2</sub> emission, low energy consuming, low production cost, and high early strength. All these properties make geopolymer materials possible to be widely used in different industrial fields such as civil engineering, automobile and aerospace, plastic industries, waste management, art and decoration, and retrofit of buildings (Abdullah et al, 2011; Li et al, 2004). For example, geopolymer mold and tooling has been utilized to develop the fighter plane “Rafle” by the French aeronautical company. In addition, geopolymer has efficiently been used to immobilize hazardous wastes (Comrie et al, 1988). Geopolymer also can be used to not only for heavy metals, but also for many different elements, ions, and compounds (Provis and Van Deventer, 2009). Fly ash-based geopolymer concrete can be adopted where Portland cement concrete is usually used (Ryu et al, 2013). The applications of geopolymer materials can be classified based on the molar ratio of Si to Al (Wallah and Rangan, 2006). Numerous different applications of geopolymer materials are mentioned in (Edouard, 2011). However, there is only a very little application of geopolymer concrete in the construction industry so far.

## **2.8. Ethics of geopolymer concrete**

Based on the code of ethics in the National Society of Professional Engineers “Engineers shall at all times strive to serve the public interest and are encouraged to adhere to the principles of sustainable development in order to protect the environment for future generations (NSPE Code of Ethics for Engineers).” Geopolymer concrete can be called an ethical solution, since fly

ash is known as a highly toxic material and carcinogen in its raw form, by chemically transferring the harmful effects into useful materials. Using fly ash in geopolymer will reduce the amount of fly ash that ends up in landfill. This is considered a huge contribution that confirms geopolymer concrete is an ethical technology. In addition, the definition of sustainable development as stated by National Society of Professional Engineers is “the challenge of meeting human needs for natural resources, industrial products, energy, food, transportation, shelter, and effective waste management while conserving and protecting environmental quality and the natural resources essential for future development. According to the definition of sustainable development, geopolymer concrete is a sustainable technology.

The section in the ASCE code of ethics states that “Engineers [will] uphold and advance the integrity, honor and dignity of the engineering profession by using their knowledge and skill for the enhancement of human welfare and the environment (Code of Ethics. *American Society of Civil Engineers.*)” Currently, Portland cement is used to produce concrete. As mentioned before, production of one ton of Portland cement emits one ton of CO<sub>2</sub> into the atmosphere and consumes huge quantity of energy. On the other hand, using geopolymer concrete instead of Portland cement concrete will release 80-90% less of CO<sub>2</sub> into the atmosphere.

## **CHAPTER 3. BOND STRENGTH OF PCC PAVEMENT REPAIRS USING METAKAOLIN-BASED GEOPOLYMER MORTAR**

### **3.1. Introduction**

There are more than 4 million miles of roadways in the U.S. Most of them degrades rapidly and requires frequently maintenance and rehabilitation that would need a large portion of federal and state investment. In addition, delays for road users are considered as an indirect cost that doubles the financial burdens. Portland cement concrete pavement is a common pavement type of these roadways that premature fails and requires early repair (Lee et al, 2005). The aim of repairing the Portland cement concrete pavement is to restore the load carrying capacity of roadways and to enhance its function and durability for an extra period of time. For these reasons, searching for a durable and reliable pavement repair material is one of the challenges in Civil Engineering field. In this chapter, metakaolin-based geopolymer mortar will be developed and used as a new pavement repair material that has high performance and cost-effective.

To use geopolymer as a pavement repair material (Geissert et al, 1999; Momayez et al, 2005), the bond strength between the substrate concrete and the repair material is critical. The properties of geopolymer concrete (Hardjito et al, 2004c; Hardjito et al, 2005) such as the modulus of elasticity, Poisson's ratio, and the tensile strength are similar to those of Portland cement concrete, which shows the compatibility between the geopolymer concrete and Portland cement concrete. Furthermore, the geopolymer concrete degrades significantly less than the Portland cement concrete does when they are soaked in an acid solution (Bakharev et al, 2003; Rangan et al, 2005). Geopolymers also present low permeability and excellent anticorrosion, and effective bonding with cement paste and mortar (Zhang et al, 2010). Moreover, geopolymers can be implemented using the same equipment and practices used for Portland cement concrete to

repair deteriorated infrastructures such as manholes, pipes and chambers (Montes et al, 2012). All these merits make geopolymer an excellent candidate for pavement repair; however the durability of these applications has not been evaluated in literatures. Therefore, in this chapter, the possibility of using the geopolymer as a repair material under various aggressive environments will be studied. Since one of the most critical factors impacting repair durability is the bond strength between geopolymer and existing concrete, a splitting tensile and slant shear test will be employed, and their results will be compared with these of repair materials in market.

### **3.2. Experimental study**

Evaluation of the bond strength of the metakaolin-based geopolymer mortar to concrete substrate will be performed using split tensile and slant shear test with line interface at 30° and 45°. In order to reduce the number of influence factors and minimize the surface heterogeneity and focus on the bond strength of geopolymer and conventional concrete, the effect of coarse aggregates is excluded temporarily.

Since all concrete pavement will subject to degradation at some level during their usage life and hydration products decompose in acid environment, an experiment to submerge the concrete substrate into a 0.5 N HCl solution for different duration is chosen to represent different stage of concrete pavement degradation. 0.5 N HCl solution corresponds to a pH = 0.3 strong acid environment. Consider the linear chemical reaction in the acid-alkaline reaction process, this solution concentration could be extrapolated to different pH level environments with different durations. For example, degradation in a pH=0.3 solution for 5 days will be equivalent to degradation in a pH = 3.0 environment for 7 years. In order to assess the feasibility of using geopolymer mortar for degraded concrete pavement repairs, bond strength of geopolymer mortar and degraded conventional concrete substrate is characterized.

### 3.2.1. Materials

The metakaolin was supplied by Fishstone Studio Inc. Elgin, IL. The sodium silicate solution (water glass) was supplied by The Science Company, Denver, CO. The chemical composition of the metakaolin is presented in Table 1 which is obtained from the supplier's data sheet. The chemical composition of sodium silicate solution consists of 9.2% Na<sub>2</sub>O, 28.67% SiO<sub>2</sub>, and 63.39% H<sub>2</sub>O with SiO<sub>2</sub>/ Na<sub>2</sub>O ratio of 3.21. Then, the sodium hydroxide (NaOH) in flakes of 98% purity was supplied by Alfa Aesar, Ward Hill, MA. Type I cement and river sand were used to prepare the concrete substrate. Alkaline silicate solution was prepared 24 hours prior to use by dissolving sodium hydroxide pellets (Flake, 98.0%) in sodium silicate (water glass).

**Table 1.** Chemical composition of metakaolin

<b>Component (%)</b>	<b>Metakaolin</b>
Al <sub>2</sub> O <sub>3</sub>	40.94
SiO <sub>2</sub>	55.01
K <sub>2</sub> O	0.6
Na <sub>2</sub> O	0.09
CaO	0.14
MgO	0.34
Fe <sub>2</sub> O <sub>3</sub>	0.55
TiO <sub>2</sub>	0.55
LOI	1.54

### 3.2.2. Specimen preparation

The specimen of splitting tensile test is prepared by casting a 50x100 mm (2x4 inch) cylinder for bond strength testing. The cylinder is longitudinally divided in half. One half contained cement mortar with mix ratio of 1(cement):3(river sand) at water/cement ratio of 0.5, and cure for 28 days. The cement mortar portion has the same mix design for all specimens. The cured cement mortar results in a compressive strength of 35.0 MPa. The other half contained the



geopolymer mortar, will be added after 28 days cure period. Also, the bond strength will be determined by slant shear test with interface line at 30° and 45°. The geopolymer portion is casted to the cement mortar substrate specimens on a slant plane inclined angle of 30° and 45° to form a 75x150 mm (3x6 inch) composite cylinder specimens and 50x50x50 mm (2x2x2 inch) composite cubic specimens, respectively. In addition, twelve cubes of size 50x50x50 mm (2x2x2 inch) will be prepared for compressive strength test of geopolymer mortar.

For the degradation experiments, the cement mortar is submerged in a plastic bucket filled with 0.5 N HCl solution through a clipper, taken out after the designated duration, and dried for one day before bonding with geopolymer mortar.

Geopolymer portion is prepared by mechanically mixing metakaolin and sand for 3 min, then adding the activator solution to the mixture and mixing it for 5 min with additional 65 ml water in order to improve workability of the mortar. The ratio of water to solid is 0.201. The water components are the water from sodium silicate and extra water, and the solid components are the solid from metakaolin and sand. The geopolymer mortar portion is composed of 300 g river sand, 100 g metakaolin, 82 g alkaline silicate solution, and 29 ml water. All specimens are cured at room temperature and have the same mix ratio. Please note the mix ratio used to prepare the geopolymer cubes for the compressive strength testing is the same as the mix ratio used to prepare the geopolymer mortar portion for the bond strength testing. In all the geopolymer samples prepared, the SiO<sub>2</sub> to Na<sub>2</sub>O ratio is kept at 1.4.

### ***3.2.3. Compressive strength test***

Compressive strength of the geopolymer mortars is measured using the compression machine (ASTM C109/109M standard). The compressive strength of metakaolin-based geopolymer concrete after 24 hours, 3 days, 7 days, and 28 days of curing at ambient

temperature is measured. The fresh geopolymer mortar are mechanically mixed then poured in 50 mm standard steel cubic mold. According to ASTM C109/109M, the samples are compacted by tampers in two layers. The samples are first cured in molds for 3 days and then at room temperature.

#### ***3.2.4. Bond strength test (Split tensile test)***

The splitting strength of the composite cylinder is used to measure the bond strength between the substrate concrete and the repair material (Momayez et al, 2005, Geissert et al, 1999). Split tensile test (ASTM C496 / C496M – 11) is a standard test method of split tensile strength of homogeneous cylindrical specimen. This test can also be used for composite cylinders, made of half substrate concrete and half repair material as shown in Figure 3.



**Figure 3.** Cylindrical split tensile test

#### ***3.2.5. Bond strength test (Slant shear test)***

Another accepted test to investigate the bond strength among the researchers is the slant shear test in which the interface is under combined state of shear and compression stresses. It has

been adopted by several international codes (ASTM C882 / C882M – 13a) as a standard test to investigate the bond strength of repair materials. The slant shear test represents more closely the real stress situation in the construction site due to the shear component (Neshvadian Bakhsh, 2010).

### ***3.2.6. Interface image analysis and porosity***

Interface properties after acid immersion, such as roughness of interface surface and porosity of the cement mortar, are also checked to analyze the durability of geopolymer mortar and conventional concrete bonding.

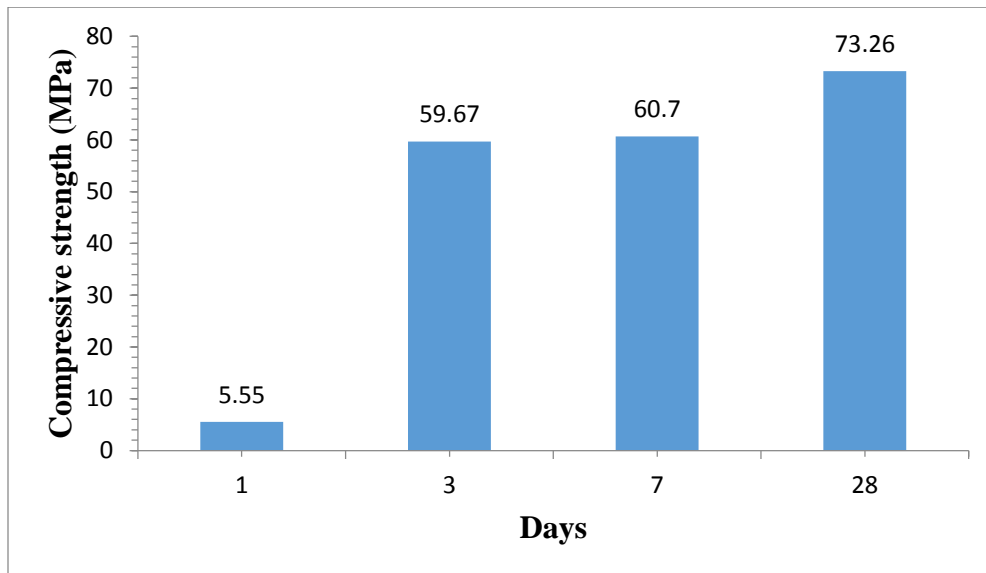
## **3.3. Results and discussion**

### ***3.3.1. Compressive strength***

Compressive strength of the geopolymer mortars is measured using ASTM C109/C109M. Table 2 and Figure 4 show the results of the compressive strength of the geopolymer mortar which cures at room temperature and tests at different curing times. The compressive strength is calculated as the average value of three repeated samples. The results in Table 2 indicate that the geopolymer concrete that cures at room temperature would have lower compressive strength at 24 hours of curing time. However, the compressive strength of geopolymer after three days of curing reaches 80% of its final strength, which is mainly due to the increase in curing time and the increase of reaction completion rate between the metakaolin and alkaline solution.

**Table 2.** Compressive strength of geopolymer mortar

days cured	Average compressive strength of 3 cubic samples (MPa)	Standard deviation	Coefficient of variation
1	5.55	1.292	0.233
3	59.67	1.392	0.023
7	60.7	2.309	0.038
28	73.26	1.618	0.022



**Figure 4.** Compressive strength of the metakaolin-based geopolymer mortar

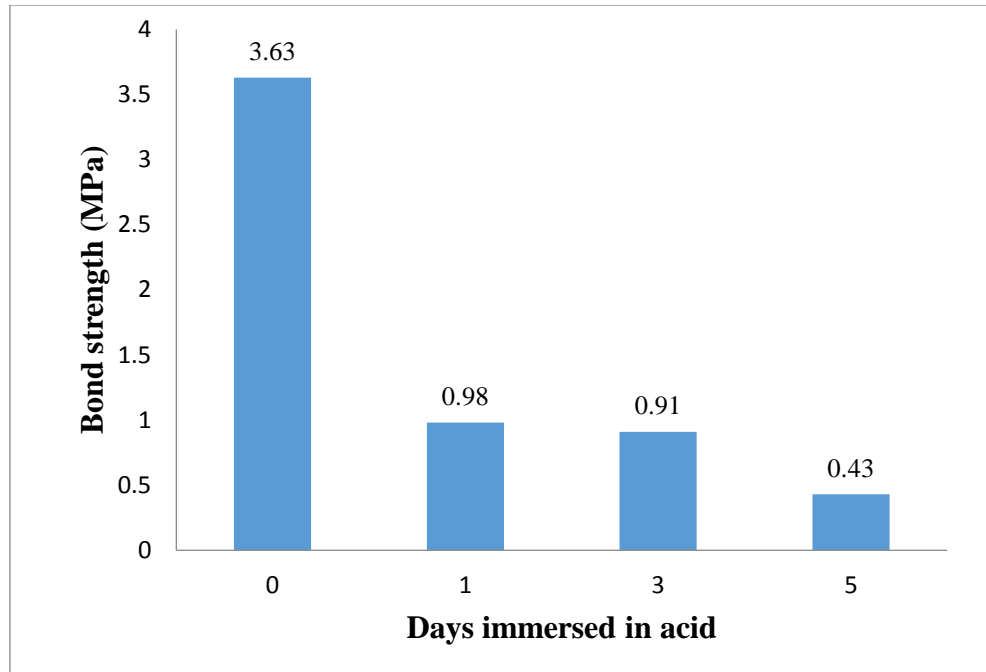
### **3.3.2. Bond strength (Split tensile test)**

The split tensile test of the manufactured cylindrical composite material shows the bond strength between geopolymer and concrete substrate. Twenty-four cement portion specimens are first cured at room temperature for 28 days, then 18 cement mortar specimens are soaked in 0.5 N HCl for different durations. Six half-specimens of fresh cement mortar without soaking in acid and the 18 soaked ones are repositioned to the mold and the other empty half of the mold is filled

with geopolymer mortar. After 3 days of curing, the specimens are demoulded and tested under splitting test. Table 3 and Figure 5 show the results of the splitting test. The bond strength is calculated by the equation  $\sigma = 2P/\pi A$  based on references (Momayez et al, 2005, Geissert et al, 1999). One of the typical failure modes occurred at the interface is shown in Figure 6. It is observed that all the failure modes are always an adhesion failure at the interface. Based on reference (Springkel and Ozyildirim, 2000), bond strength test results may be classified based on strength quality defined in Table 4.

**Table 3.** Results of splitting tests

Spec. No.	Cured days	Cross section area (mm <sup>2</sup> )	Bond strength (MPa)
Geopolymer mortar with cement mortar without immersion			
1	3	5161	4.2
2	3	5161	3.4
3	3	5161	3.3
Geopolymer mortar with deteriorated cement mortar by immersed in 0.5 N HCl for One day			
1	3	5161	0.94
2	3	5161	1
3	3	5161	1
Geopolymer mortar with deteriorated cement mortar by immersed in 0.5 N HCl for Three days			
1	3	5161	0.89
2	3	5161	0.94
3	3	5161	0.92
Geopolymer mortar with deteriorated cement mortar by immersed in 0.5 N HCl for Five days			
1	3	5161	0.35
2	3	5161	0.38
3	3	5161	0.58



**Figure 5.** The bond strength between geopolymer mortar and cement mortar with different deterioration time

**Table 4.** Bond strength quality

<b>Bond strength (MPa)</b>	<b>Quality</b>
2.1	Excellent
1.7 to 2.1	Very good
1.4 to 1.7	Good
0.7 to 1.4	Fair
0 to 0.7	poor

Based on Table 4, the bond strength between geopolymer and concrete substrate without soaking in acid is excellent. And the bond strength between geopolymer and concrete substrate that is soaked in acid for 24 hours and three days show fair bond strength, while the bond strength between geopolymer and concrete substrate that is soaked in acid for five days is poor. For these conditions, a full depth replacement is recommended.



**Figure 6.** Failure mode between metakaolin-based geopolymer mortar and conventional concrete

Table 5 presents a comparison of the bond strength based on splitting test of the current results with other repair materials obtained from literatures (Momayez et al, 2005, Tayeh et al, 2013). The first four repair materials consist of sand–cement mortars containing 0%, 5%, 7%, or 10% of silica fume. The fifth and sixth repair materials are modified cement-based. One of the modified cementitious mortars is made by replacing 10% of the cement content with a polymer concrete adhesive K100. The other modified cementitious mortar is made by replacing 20% of the cement content with styrene butadiene resin (SBR) (Momayez et al, 2005). The seventh repair material is ultra-high performance fiber concrete(UHPFC) which contained Type-I ordinary Portland cement, densified silica fume, well graded sieved and dried mining sand, very high strength micro-steel fiber, and polycarboxylate ether based (PCE) superplasticizer (Tayeh et al, 2013). The last material is the metakaolin-based geopolymer mortar suggested in this thesis. The comparison between the seven repair materials is shown in Figure 7. In the table, different roughness of the interface surface is also included for the literature materials. However for the current study, effect of roughness will be explored in the next phase.

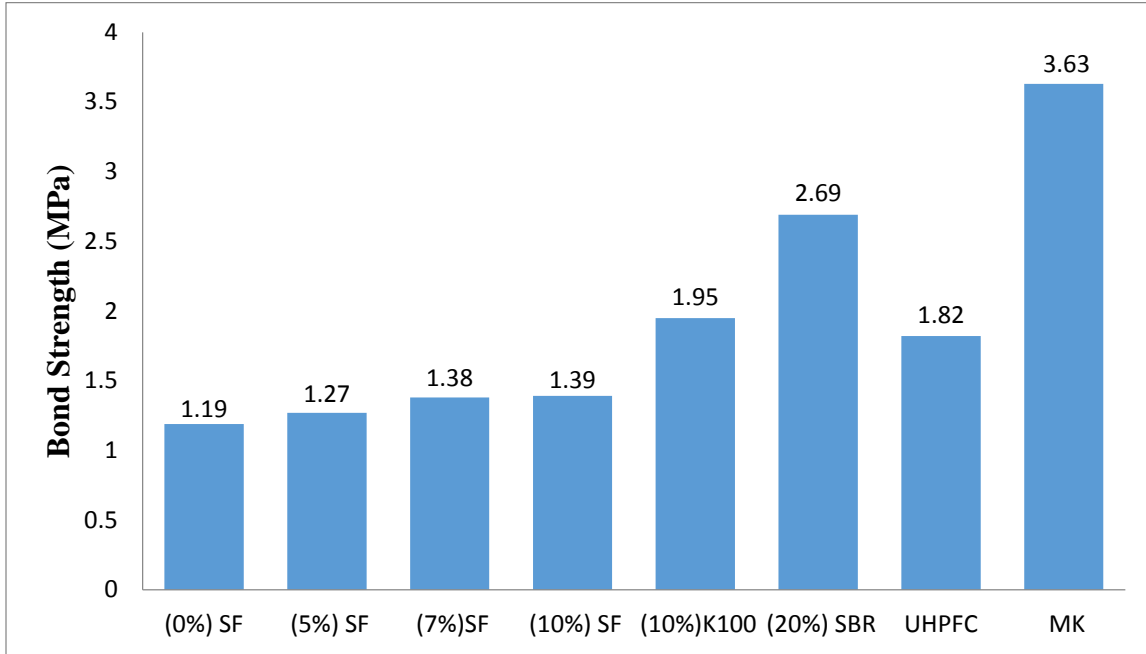
**Table 5.** Bond strength of different repair materials by split test

<b>Specimen group</b>	<b>Repair material</b>	<b>Curing days</b>	<b>Compressive strength (MPa)</b>	<b>Roughness</b>	<b>Bond strength (MPa)</b>
RL	0% SF	28	36	L	1.19
RH				H	1.36
5L	5% SF	28	37	L	1.27
5H				H	1.44
7L	7% SF	28	41	L	1.38
7H				H	1.62
10L	10% SF	28	43	L	1.39
10H				H	1.64
KL	Modified by K100	28	35	L	1.95
KH				H	2.14
SL	Modified by SBR	28	38	L	2.69
SH				H	2.9
UHPFC	Ultra-high performance fiber concrete	28	170	-	1.82
MK	Metakaolin	28	73.26	-	3.63

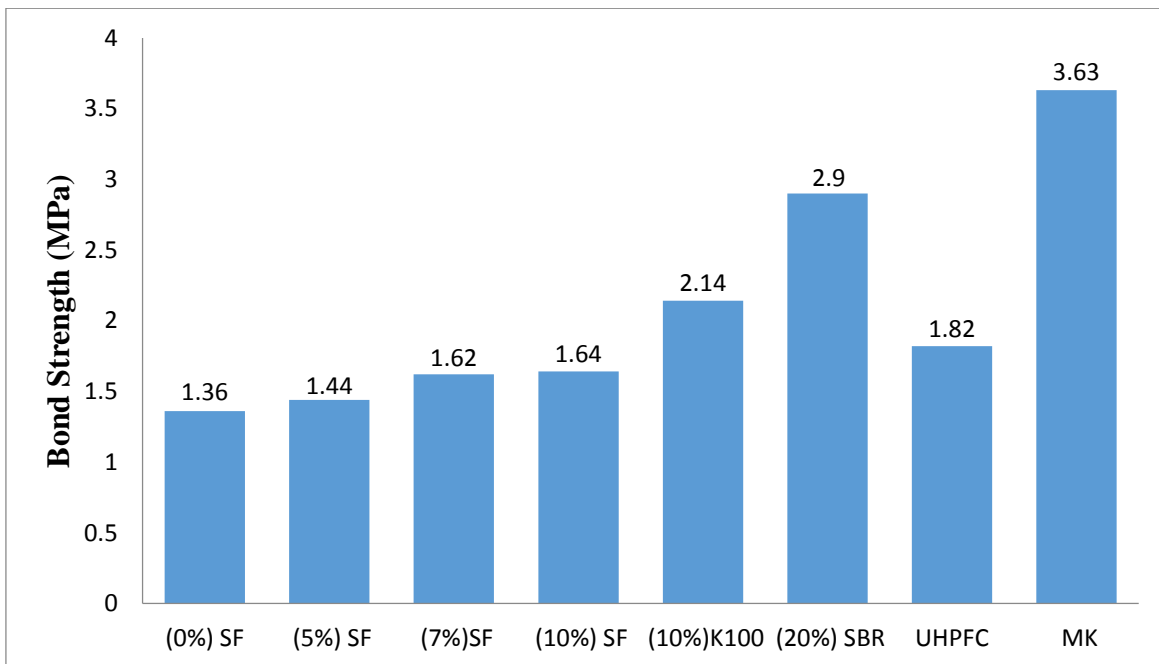
L= low roughness, H = high roughness



(a) Low roughness



(b) High roughness



**Figure 7.** Bond strength of different repair materials by split test: (a) low roughness and (b) high roughness

From Figure 7, it can be seen that the suggested metakaolin geopolymer shows much higher bonded strength compared to several repair materials in the market. It needs to point out that the curing conditions for the materials in literature are different from the geopolymer material. For all the cementitious sand–cement mortars containing 0%, 5%, 7%, or 10% of silica fume, and the two polymer modified cements, they are moisture cured at 20°C for the first 7 days, following with 50% humidity at the same temperature for 14 days, and tested after 1 day dry. For the UHPFC material, the composite specimens were steam cured for 48 hours at a temperature of 90°C and submerged in a water tank for another 14 days before the experimental strength test.

### ***3.3.3. Bond strength (Slant shear test)***

The bond strength between cement mortar substrate and geopolymer mortar is also investigated by the slant shear test. The geopolymer mortar is bonded to cement mortar substrate after 28 days of curing with an angle of 30° and 45° as shown in Figure 8. The interface surface during loading is subjected to the combination of shear stress and compression stresses.



**Figure 8.** Slant shear test with line interface of 30° and 45°

The bond strength is calculated by dividing the maximum load on bond area following ASTM C882 / C882M – 13a. After three days of curing, the specimens are demoulded, then tested under slant shear tests. The average bond strength of the three samples with line interface at 30° is 15.6 MPa with standard deviation of 0.99 MPa and coefficient of variation is 6.33 %. On the other hand, the average bond strength of the three samples with line interface at 45° is 42.2 MPa with standard deviation of 1.4 MPa and coefficient of variation of 3.35 %. Based on (Chynoweth et al, 1996), the acceptable bond strength of slant shear test of repair materials should fall between 6.9~12 MPa and 13.8~20.7 MPa at test ages 7 and 28 days, respectively. The bond strength between geopolymer mortar and cement mortar substrate at test age 3 days is higher than the ACI requirement at test age 7 days and falls in the ranges of the ACI requirement at test age 28 days. Failure modes of the slant shear test with line interface at 30° occurs in the substrate mortar as shown in Figure 9, which indicates a split failure in the cement mortar portion due to the superior bond of the interface between geopolymer and the cement mortar than that between the cement mortars themselves. On the other hand, most failure modes for the slant shear test with line interface at 45° follow the interface surface with small particle disintegration as shown in Figure 10, due to decreased compressive stress along the interface. And the failure is a shear failure with three times load capacity comparing to that of the specimen with 30° slant interface, partially due to the decreased compressive stress normal to the interface reduces the opportunity for the split failure in cement mortar.



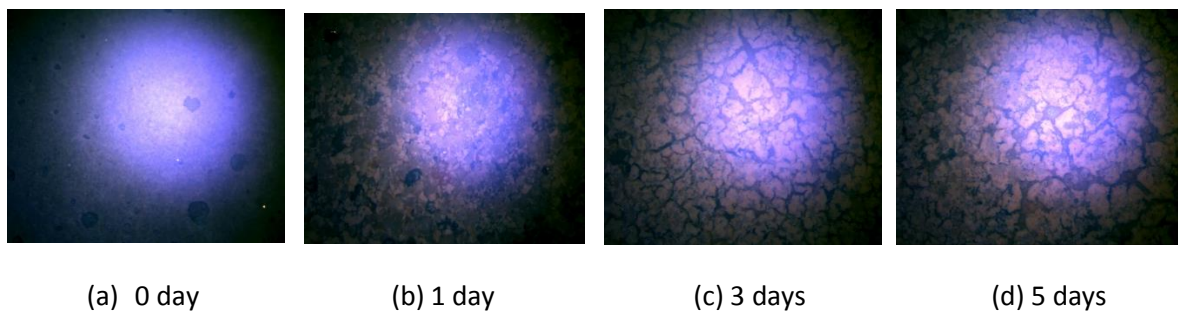
**Figure 9.** Failure mode of slant shear test with line interface at  $30^\circ$  between metakaolin-based geopolymer mortar and conventional mortar



**Figure 10.** Failure mode of slant shear test with line interface at  $45^\circ$  between metakaolin-based geopolymer mortar and conventional mortar

### 3.3.4. Interface roughness and porosity after acid immersion

Convention cement mortar with the mixture ratio defined above is submerged into the 0.5 N HCl solution for different durations. The interface surface after 1 day, 3 days, and 5 days submersion are compared with the fresh cured cement mortar interface. It is found that cement mortar crazing becomes more and more apparent due to acid erosion, as shown in Figure 11. It is obvious that the interface of cement mortar has been weakened tremendously. The degradation of cement mortar in acid could also be observed from the porosity increase due to its weight loss in acid as shown in Table 6. The acid immersion reduces the stiffness of cement mortar interface and degrades the bonding of Geopolymer with it.



**Figure 11.** Surface image of cement mortar after different time of immersion in acid

**Table 6.** Weight loss of cement mortar after different days of immersion in acid

Numbers of days of immersion in acid	Weight loss (%)
0	0
1	3.57
3	3.77
5	4.52

### **3.4. Summary**

In this chapter, metakaolin-based geopolymer mortar was developed to be used as a new pavement repair material at normal and aggressive environments. The bond strength between cement mortar and geopolymer mortar was investigated through splitting tensile test and slant shear test with line interface at 30° and 45°. The experimental results indicated that the curing duration exhibits a significant effect on the compressive strength of the geopolymer mortar and the bond strength decreases as the cement mortar deteriorates. In addition, the comparison between the suggested geopolymer mortar with other pavement repair materials in the market shows the superior bond strength of the suggested metakaolin-based geopolymer to substrate mortar.

## CHAPTER 4. IMPROVING EARLY STRENGTH OF GEOPOLYMER MORTAR THROUGH MIXTURE TUNING AND ADDITIVES

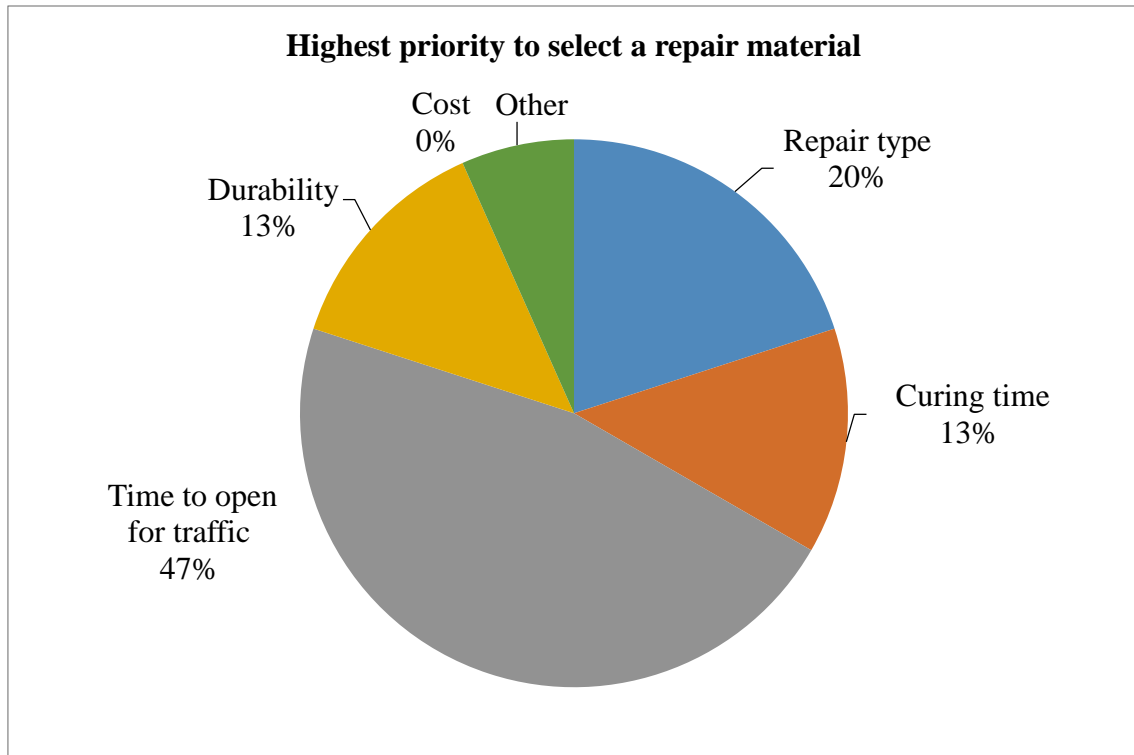
### 4.1. Introduction

Traffic volume has increased rapidly in the urban areas for the last decades (Dam et al, 2005; Buch et al, 2008). Delays due to pavement repair have become less and less tolerable. “Early-opening-to-traffic” (EOT) rehabilitation strategies have been used by most departments of transportations (DOTs) to reduce delays during pavement rehabilitation (Buch et al, 2008). In EOT rehabilitation strategies, a material should be able to harden and open for the traffic at the same day, and the repair work is only allowed at night or during periods of low traffic. Portland cement concrete with accelerating admixture that can gain enough strength to carry traffic load in less than 24 hours and occasionally within 4 hours, is usually used in this application. Yet, high early strength Portland cement concrete has been reported to suffer from lack of durability (Dam et al, 2005; Buch et al, 2008). The minimum compressive strength required to be open to traffic is usually around 20.7 MPa. Based on a survey over 20 states with similar climate as North Dakota (Yang et al, 2013), it is found that 73.7% of states use accelerated pavement repair for Portland cement concrete. In addition, more than 40% of states use the time to open for traffic as the most important factor to select a repair material. Table 7 and Figure 12 present the factors that state agencies use to select a repair material. For illustration, time to open for traffic in Table 7 was chosen as the highest priority by seven states for selecting a repair material, and the second priority for two agencies.

**Table 7.** The factors that agencies use to select a repair material

Options	1	2	3	4	5	6
Repair type	3	3	1	1	2	1
Curing time	2	3	2	2	2	0
Time to open for traffic (criteria for time to open for traffic, such as strength gain)	7	2	1	0	1	0
Durability	2	1	5	3	0	0
Cost	0	1	3	3	4	0
Others	1	0	0	0	0	1

\*Note: The number in the table is the number of states selecting the individual factor at the different priority to determine the repair material.



**Figure 12.** Highest priority to select a repair material



In chapter 3, metakaolin geopolymer mortar has shown superior bond strength comparing to other repair materials in the market. In this chapter, several factors that affect the mechanical properties and accelerate the geopolymerization process of geopolymer mortar will be studied in order to meet the requirements of early opening to traffic. The effect of  $\text{SiO}_2/\text{Na}_2\text{O}$  at five different ratios will be investigated in order to accelerate the geopolymerization process. Also, investigation of adding slag and calcium aluminate cement by weight on the strength of metakaolin geopolymer mortar will be performed. The study in this chapter focuses on the effect of these parameters on the compressive strength of metakaolin geopolymer mortar, since the compressive strength is the most used criteria by agencies to open to traffic. Based on a survey over 20 states with similar climate as North Dakota (Yang et al, 2013), 84.62% of states use compressive strength criteria to determine the time to open for traffic. Table 8 summarizes the minimum required compressive strength to open for traffic.

**Table 8.** The minimum required compressive strength to open for traffic

<b>State</b>	<b>Compressive strength</b>
Colorado	20.7 MPa
Kansas	24.2 MPa
Minnesota	20.7 MPa
Missouri	20.7 MPa
Nebraska	24.2 MPa
Oregon	17.3 MPa if "rapid set" or similar product is used. 20.7 MPa for Type I/II/III cement
Pennsylvania	20.7 MPa for all repairs except partial depth = 13.8 MPa
South Dakota	Varies depending on time to open to traffic. From 24.8 to 27.6 MPa.
Utah	27.6 MPa
Washington	17.3 MPa
Wisconsin	20.7 MPa

One way to accelerate the geopolymerization process is to let the geopolymer cure at elevated temperature which is complicated and hard to apply at the field site. However, the most common activating solution used to activate the alumino-silicate materials is a mixture of sodium hydroxide (NaOH) and water glass ( $\text{Na}_2\text{SiO}_3$ ). There is only a few researchers who investigated the effect of  $\text{SiO}_2/\text{NaO}_2$  on the properties of geopolymer concrete. But, the influence of  $\text{SiO}_2/\text{NaO}_2$  ratio on accelerating the geopolymerization process of geopolymer concrete is neglected, even though it has been reported that the  $\text{SiO}_2/\text{NaO}_2$  ratio plays an important role in its mechanical properties. In addition, the effect of adding aluminate silicate cement to metakaolin on its geopolymerization process is also investigated. Aluminate silicate cement can harden and set within 1 to 3 minutes and known to have the quickest hydration reaction of all calcium aluminate minerals (Rovnanik, 2010). Also, Blending slag with other alumino-silicate binders has shown to increase the compressive strength and enhance other properties (Deb et al, 2014). To study the effect of slag on the geopolymerization process, replacing metakaolin partially with slag is worthy to investigate. In summary, the scope of this chapter is to evaluate the effect of different ratios of  $\text{SiO}_2/\text{NaO}_2$ , aluminate silicate cement, and slag on the early strength of the geopolymer mortar, for the purpose to find a rapid curing binder. The results will be compared with the results of geopolymer mortar without adding any setting accelerator.

## **4.2. Materials and methods**

### ***4.2.1. Materials***

The chemical compositions of metakaolin, slag, and calcium aluminate cement are presented in Table 9 which are obtained from the suppliers' data sheets. Metakaolin was supplied by Fishstone Studio Inc. Elgin, IL. The contents of silica and alumina in metakaolin are about

97% of chemical composition of metakaolin. Slag or blast furnace slag is a byproduct of iron making in a blast furnace. Slag used in this research was obtained from Holcim US Inc. St. Paul, MN. The specific gravity of slag is 2.89. On the contrary to metakaolin, slag contains high content of CaO. Calcium aluminate cement was obtained from Kerneos Inc. Chesapeake, VA. Calcium aluminate cement possesses good mechanical properties and can gain high early strength when it is used as the primary binder. Its specific gravity is 3.24.

The most common used alkaline activator to prepare geopolymer is a mixture of sodium hydroxide (NaOH) and sodium silicate (water glass) ( $\text{Na}_2\text{SiO}_3$ ). The chemical composition of sodium silicate solution consists of 9.2%  $\text{Na}_2\text{O}$ , 28.67%  $\text{SiO}_2$ , and 63.39%  $\text{H}_2\text{O}$  with  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of 3.21. The sodium hydroxide (NaOH) in flakes of 98% purity was supplied by Alfa Aesar, Ward Hill, MA. River sand were used to prepare the geopolymer mortar. Alkaline silicate solution was prepared 24 hours prior to use by dissolving sodium hydroxide pellets (Flake, 98.0%) in sodium silicate (water glass).

**Table 9.** Chemical compositions of metakaolin, slag, and calcium aluminate cement

<b>Oxide</b>	<b>Mass (%)</b>		
	<b>Metakaolin</b>	<b>Slag</b>	<b>Calcium aluminate cement</b>
<b>Al<sub>2</sub>O<sub>3</sub></b>	40.94	7.34	≥ 37.0
<b>SiO<sub>2</sub></b>	55.01	37.95	≤ 6.0
<b>K<sub>2</sub>O</b>	0.6	0.36	< 0.2
<b>Na<sub>2</sub>O</b>	0.09	0.27	< 0.2
<b>CaO</b>	0.14	38.93	≤ 39.8
<b>MgO</b>	0.34	10.22	< 1.5
<b>Fe<sub>2</sub>O<sub>3</sub></b>	0.55	0.54	≤ 18.5
<b>TiO<sub>2</sub></b>	0.55	0.39	< 4.0
<b>Cl</b>	0	0.09	0
<b>Mn<sub>2</sub>O<sub>3</sub></b>	0	0.55	0
<b>SO<sub>3</sub></b>	0	2.69	< 0.4
<b>LOI</b>	1.54	1.8	-
<b>Total</b>	98.22	99.6	-

LOI: Loss on ignition

#### ***4.2.2. Specimens preparation***

The molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  of the waterglass solution used in this research is 3.21. The effect of different molar ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  of the alkaline solution is studied in order to accelerate the geopolymerization process and gain early high strength. Ratios of 0.8, 1, 1.2, 1.4, and 1.8 of  $\text{SiO}_2/\text{Na}_2\text{O}$  of alkaline solution are prepared by adding sodium hydroxide pellets to adjust the molar ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  of alkaline solution. The  $\text{SiO}_2$  content comes only from sodium silicate solution (waterglass), while  $\text{Na}_2\text{O}$  comes from waterglass and sodium hydroxide solution. By the way, the alkaline solution is prepared 24 hours prior to use. In the preparation of geopolymer mortars, metakaolin and river sand are mechanically mixed for 3 minutes, then the alkaline solution is added and mixed for another 5 minutes with additional 65 ml water to enhance the workability of geopolymer mortar. The ratio of water to solid is 0.201 for all mix ratios. The water components are the water from sodium silicate and extra water, and the solid components are the solid from metakaolin and sand. The geopolymer mortar portion is composed of 675 g river sand, 225 g metakaolin, 186 g alkaline silicate solution with five different ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$ , and 65 ml water. Then, the geopolymer mortars are molded into 50 mm cubes and cured at ambient temperature for compressive strength testing. The geopolymer mortars with five different  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratios of alkaline solution are tested at ages of 1, 2, and 3 days to find the effect of  $\text{SiO}_2/\text{Na}_2\text{O}$  on the early strength of geopolymer mortars.

After the effect of molar ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  of alkaline solution is investigated, the best  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio giving the highest early strength is found. Adding calcium aluminate cement and slag to accelerate the geopolymerization process is also performed. Calcium aluminate cement is added to geopolymer mortar at different ratios of 20% and 30% by weight at molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  of 1. On the other hand, metakaolin is partially replaced in geopolymer

mortar with slag at level of 30% by weight at molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  of 1. Metakaolin is partially replaced with 30% of slag. 30% of slag is selected based on literature which shows the best ratio to replace alumino-silicate binder by slag is 30%. Table 10 summarizes all mix ratios.

**Table 10.** Summary of mixture proportions

Mix	Metakaolin (g)	Calcium aluminate cement (g)	Slag (g)	Sand (g)	alkaline solution (g)	$\text{SiO}_2/\text{Na}_2\text{O}$	Extra water (ml)
M1	225	-	-	675	186	0.8	65
M2	225	-	-	675	186	1	65
M3	225	-	-	675	186	1.2	65
M4	225	-	-	675	186	1.4	65
M5	225	-	-	675	186	1.8	65
M6	225	45	-	675	186	1	65
M7	225	67.5	-	675	186	1	65
M8	157.5	-	67.5	675	186	1	65

#### 4.2.3. Compressive strength test

50 mm cubic specimens are used to measure the compressive strength of geopolymer mortar following ASTM C109/109M standard. The compressive strength of geopolymer mortars 1, 2, and 3 days with different parameters is found. The one day compressive strength is measured to provide the information on the geopolymer strength prior to use it in early-opening-to-traffic pavement repairs.

### 4.3. Results and discussions

#### 4.3.1. *The effect of different molar ratios of SiO<sub>2</sub>/ Na<sub>2</sub>O of the alkaline solution*

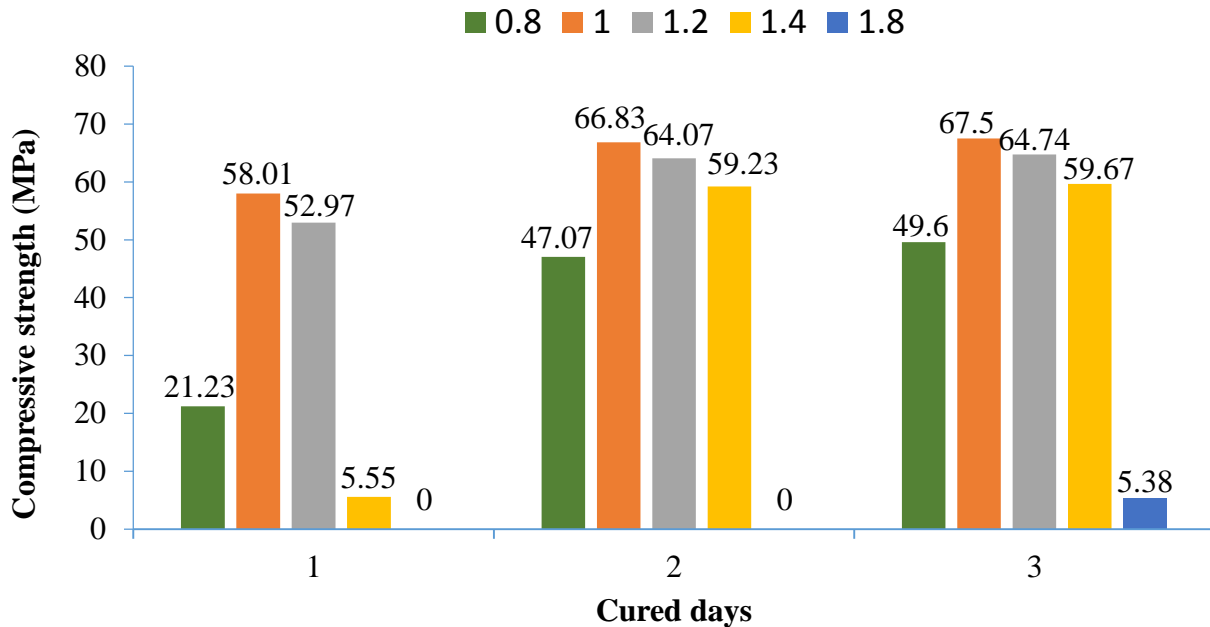
One of the most important property to describe concrete is the compressive strength due to its correlation to other concrete properties. The compressive strength of metakaolin-based geopolymer mortars with different molar ratios of SiO<sub>2</sub>/ Na<sub>2</sub>O of the alkaline solution at the ages of 1, 2, and 3 days are shown in Table 11 and Figure 13. It is observed from the results that the curing age significantly affect the compressive strength of geopolymer mortars, so that the compressive strength of geopolymer mortars increases as the curing age increases.

Five ratios of molar ratios SiO<sub>2</sub> to Na<sub>2</sub>O of alkaline solution are studied and the mix ratio of geopolymer mortar is kept constant for all five different ratios. After 1 days curing, the average compressive strength of three samples of ratios 0.8, 1, 1.2, 1.4, and 1.8 are 21.23 MPa, 58.01 MPa, 52.97 MPa, 5.55 MPa, and 0 MPa with standard deviations of 3.949 MPa, 2.65 MPa, 2.443 MPa, 1.292 MPa, and 0 MPA at coefficient of variations of 0.186%, 0.046%, 0.046%, 0.233%, and 0%, respectively. The maximum compressive strength is at ratio SiO<sub>2</sub>/Na<sub>2</sub>O =1 because the silica and alumina highly dissolved at this ratio which accelerates the geopolymerization process and improves the compressive strength. However, it is observed that the workability decreases as the SiO<sub>2</sub>/Na<sub>2</sub>O ratio decreases. In addition, the results of compressive strength show that the compressive strength of metakaolin-based geopolymer mortar increases with increase of the curing age.

**Table 11.** Compressive strength of geopolymer mortars at five different ratios of SiO<sub>2</sub>/Na<sub>2</sub>O

<b>SiO<sub>2</sub>/Na<sub>2</sub>O</b>	<b>Cured days</b>	<b>Compressive strength (MPa)</b>	<b>Standard deviation</b>	<b>Coefficient of variation</b>
<b>0.8</b>	1	21.23	3.949	0.186
	2	47.07	0.942	0.020
	3	49.6	2.049	0.041
<b>1</b>	1	58.01	2.650	0.046
	2	66.83	2.604	0.039
	3	67.5	3.315	0.048
<b>1.2</b>	1	52.97	2.443	0.046
	2	64.07	1.673	0.026
	3	64.74	0.654	0.010
<b>1.4</b>	1	5.55	1.292	0.233
	2	59.23	0.979	0.017
	3	59.67	1.392	0.023
<b>1.8</b>	1	0	0.000	0.000
	2	0	0.000	0.000
	3	5.38	0.600	0.109





**Figure 13.** Average compressive strength of geopolymer mortar with different ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  at curing ages of 1, 2, and 3 days

The maximum compressive strength of geopolymer mortars at curing age of one day is 58.01 MPa at molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O} = 1$ . It is observed from the results that the compressive strength increases when the molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  increases from 0.8 to 1. On the other hand, the compressive strength significantly decreases when the molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$  increases from 1 to 1.8.

The results give an opportunity to control the compressive strength and the workability of geopolymer mortar by adjusting the molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ . The decrease in the  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio is a result of increasing NaOH in the alkaline solution. Based on (Škvára et al, 2006), sodium plays an important role for the formation of geopolymer since it works as charge balancing ions. However, adding more sodium silicate would result in decreasing the compressive strength because excess sodium silicate prevents water from evaporation and structural formation.

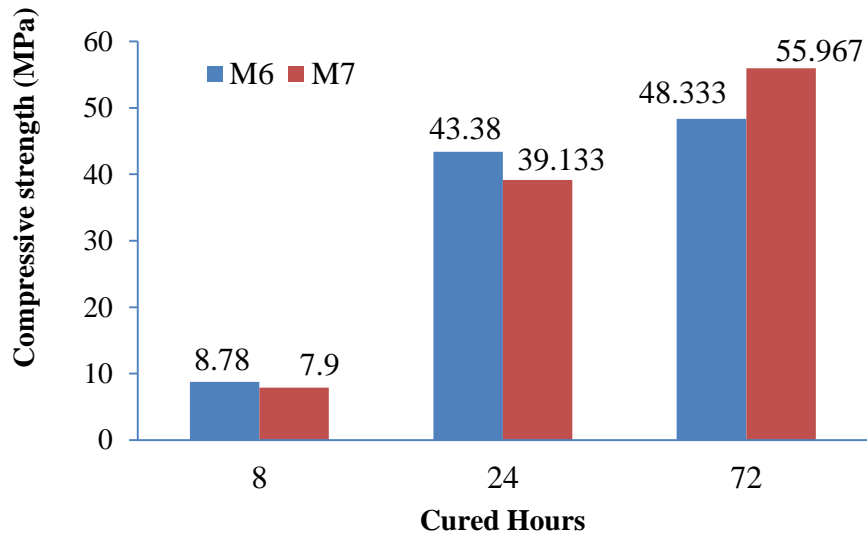
The investigation of using different molar ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  in the alkaline solution leads successfully to accelerate the geopolymerization process and gain early strength of geopolymer mortar.  $\text{SiO}_2/\text{Na}_2\text{O}$  ratios of 0.8, 1, and 1.2 achieve the required strength that determined by DOTs to open to traffic within 24 hours. However, molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O} = 1$  gives the highest compressive strength, which is selected to be investigated further with adding other accelerated setting material in order to shorten the time to open for traffic.

#### ***4.3.2. The effect of adding calcium aluminate cement to metakaolin***

Reaching high early strength within 8 hours increases the opportunity of geopolymer to be used in concrete pavement repairs with priority on early opening to traffic. Calcium aluminate cement is added to geopolymer mortar to shorten the setting time, with ratio of 20% and 30% to metakaolin by weight. The compressive strength of adding calcium aluminate cement to metakaolin is shown in Table 12 and Figure 14.

**Table 12.** The effect of calcium aluminate cement on compressive strength of geopolymer

<b>Mix</b>	<b>Cured hours</b>	<b>Compressive strength (MPa)</b>	<b>Standard deviation (MPa)</b>	<b>Coefficient of variation (%)</b>
<b>M6</b>	8	8.780	0.630	0.072
	24	43.380	0.430	0.010
	72	48.333	1.544	0.032
<b>M7</b>	8	7.900	0.284	0.036
	24	39.133	0.962	0.025
	72	55.967	1.730	0.031



**Figure 14.** Average compressive strength of geopolymer mortar with adding calcium aluminate cement in different weight at curing ages of 8, 24, and 72 hours

Calcium aluminate cement is added to reduce the setting time. It is observed that it reduces the setting time and decreases the compressive strength at 24 hours compared to the result of compressive strength at  $\text{SiO}_2/\text{Na}_2\text{O} = 1$  without adding any accelerator. In addition, waterglass works as retarder on the hydration of calcium aluminate cement. There are no significantly differences in compressive strength when calcium aluminate cement is added in ratios of 20% and 30% of metakaolin weight, but the workability is so low at the ratio of 30%.

#### ***4.3.3. The effect of partially replacing metakaolin with slag***

Blending slag with metakaolin has been investigated to reduce the setting time. Metakaolin is partially replaced with slag at a ratio of 30% to metakaolin by weight at  $\text{SiO}_2/\text{Na}_2\text{O} = 1$ . Table 13 summarizes the effect of slag replacement to metakaolin on the compressive strength of geopolymer mortar.

**Table 13.** The effect of slag replacement to metakaolin on the compressive strength of geopolymer mortar

Mix	Cured hours	Compressive strength (MPa)	Standard deviation (MPa)	Coefficient of variation (%)
M8	8	0.000	0.000	0.000
	24	13.48	0.903	0.067
	72	44.57	0.967	0.022

Although slag has been reported to enhance the compressive strength and reduce the setting time due to calcium content in slag, the results here show that slag negatively affects the compressive strength and increase the setting time. The specimens after only 8 hours were still in liquid stage, so the compressive strength was zero. However, slag has proved to increase the workability of geopolymer mortar.

#### 4.4. Summary

The influence of  $\text{SiO}_2/\text{Na}_2\text{O}$  at five different ratios, adding calcium aluminate cement, and adding slag in the early strength of metakaolin-based geopolymer mortar are discussed in this chapter. The purpose of this chapter is to accelerate the geopolymerization process to make geopolymer gains high early strength in order to be used in EOT since geopolymer mortar has shown high bond strength in Chapter 3. It was found that  $\text{SiO}_2/\text{Na}_2\text{O} = 1$  gives higher strength at 24 hours of curing at ambient temperature and meet the requirements to open early to traffic. In addition, adding 20% of calcium aluminate cement is more effective in term of accelerating the geopolymerization process. Also, replacing partially metakaolin with slag negatively affects the early strength of geopolymer mortar.

## CHAPTER 5. FREEZE-THAW DURABILITY OF GEOPOLYMER CONCRETE

### 5.1. Introduction

Previous studies in chapter 3 and 4 have reported that geopolymer mortar can be used as a pavement repair material and can be used in EOT technique since geopolymer mortar shows higher bond strength than the repair materials in the market and high strength within 24 hours at ambient temperature, respectively. However, geopolymer concrete has better durability than Portland cement concrete (Ariffin et al, 2013; Reddy et al, 2012; Sanni et al, 2012), but there is no specific study discussing the freeze-thaw durability of metakaolin-based geopolymer concrete, which is a very important property for a material to be successfully applied as a repair material. The most important consideration for concrete that is used in northern parts of the world and other places that have freezing and thawing problems is its freeze-thaw performance. In this chapter, the durability of metakaolin-based geopolymer concrete will be investigated by subjecting the geopolymer concrete to rapid freeze-thaw cycles. In addition, the freeze-thaw durability of geopolymer concrete at different ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  with adding calcium aluminate cement and slag will be investigated.

ACI defines the durability of concrete as the ability of concrete to resist weathering conditions, chemical attack, abrasion, or any other process of deterioration while maintaining its desired engineering properties. ACI also defines the cold weather as the period where more than three continuous days have mean daily temperature less than  $40^\circ\text{F}$  ( $4.44^\circ\text{C}$ ). The attack of cyclic freezing and thawing can lead to pavement deterioration by cracking and spalling of the concrete surfaces as shown in Figure 15. The deterioration due to freeze-thaw requires considerable repair or even replacement of any structure before it reaches its expected life. The freeze-thaw durability of concrete can be determined by using ASTM C-666. Durability of concrete is the

percent ratio of the dynamic modulus of elasticity after a number of freeze and thaw cycles to the initial value before the freeze and thaw cycles (Hamoush et al, 2011). However, several researchers have proposed different theories to explain the concrete damage due to freeze and thaw cycles. For instance, critical saturation theory is based on the expansion of water in pores when it freezes to ice it occupies 9% more than the volume of that water. If there is no enough space for the expansion, it will create stress in concrete and cause cracks.



**Figure 15.** Pavement damage due to freeze-thaw cycles (civildigital.com)

## **5.2. Experimental procedures**

### ***5.2.1. Materials and mix proportions***

The materials that are used to prepare metakaolin-based geopolymer concrete samples are metakaolin as alumino-silicate binder, calcium aluminate cement and slag as setting accelerators, fine sand, coarse aggregate, combination of sodium hydroxide and sodium silicate solution as alkaline liquid activator, and water. In the preparation of geopolymer concrete, metakaolin, fine sand, and coarse aggregate are mixed in a rotating drum mixer with fixed blades for three minutes as shown in Figure 16, then the alkaline solution is added and mixed for another five minutes with additional water to enhance the workability of geopolymer concrete.



**Figure 16.** Mixer used for manufacturing geopolymer concrete

Five geopolymer concrete mixtures are prepared which are designated as Mix-1, Mix-2, Mix-3, Mix-4, and Mix-5. Table 14 summarizes the mix ratios proportions of geopolymer concrete. The fresh geopolymer concrete is poured immediately after mixing into 3x4x16-in. (75x100x405-mm) steel mold, in case of rectangular beam specimens, and into 3x6-in. (75x150-mm) disposable plastic mold to form cylindrical specimens as shown in Figure 17.

**Table 14.** Mix proportions of geopolymer concrete

<b>Ingredient</b>	<b>Mix-1</b>	<b>Mix-2</b>	<b>Mix-3</b>	<b>Mix-4</b>	<b>Mix-5</b>
<b>Metakaolin (g)</b>	450	360	450	360	360
<b>Slag (g)</b>	0	90	0	90	90
<b>Aluminate silicate cement (g)</b>	0	0	0	0	90
<b>Fine sand (g)</b>	675	675	675	675	675
<b>Coarse aggregate (g)</b>	1350	1350	1350	1350	1350
<b>Alkaline solution (g)</b>	562	562	562	562	562
<b>Water/solid</b>	0.148	0.148	0.148	0.148	0.148
<b>Water/Metakaolin</b>	0.813	0.813	0.813	0.813	0.813
<b>SiO<sub>2</sub>/Na<sub>2</sub>O</b>	1.4	1.4	1	1	1.4
<b>Curing temperature</b>	Room	Room	Room	Room	Room



**Figure 17.** Fresh geopolymer concrete specimens (Mix-5)

### ***5.2.2. Freeze-thaw testing***

Freeze-thaw resistance of concrete is determined using ASTM C 666 (Procedure A). All geopolymer concrete specimens are first cured 14 days at ambient temperature prior to testing. The specimens are subjected to multiple rapid freeze-thaw cycles in the freeze-thaw chamber while the specimens are fully saturated as shown in Figure 18. The dynamic modulus of elasticity, weight loss, and compressive strength of geopolymer concrete specimens will be recorded at 0, 30, 60, 90, 120, 150, 180, 210, 240, 270, and 300 freeze-thaw cycles. The sonometer as seen in Figure 19 is used to find the transverse frequency to calculate the dynamic modulus of elasticity. The relative dynamic modulus of elasticity (RDME) is the ratio of the dynamic modulus of elasticity after a specific number of freeze-thaw cycles to the initial value of the dynamic modulus of elasticity before subjected to freeze-thaw cycles. According to ASTM C 666 (Procedure A), the specimen is considered not to be durable if the RDME drops to 60% or its weight loss exceeds 5%. A thermistor sensor is embedded in the center of the concrete sample to control the temperature of the concrete samples. In a single cycle, the temperature in the center



of concrete sample drops from 40°F (4.44°C) to 0°F (-17.8°C) for 1.5 hour, followed by a hold at 0°F (-17.8°C) for 0.5 hour, then rises from 0°F (-17.8°C) to 40°F (4.44°C) for 1.5 hour, followed by a hold at 40°F (4.44°C) for 0.5 hour. One complete cycle takes around 4 hours to complete. The RDME is calculated at every 30 freeze-thaw cycles.



**Figure 18.** Freeze-thaw test chamber



**Figure 19.** Sonometer used in determining dynamic modulus of freeze-thaw test specimens

### 5.3. Results and discussions

After 30 freeze-thaw cycles in accordance with ASTM C666, the weight loss data of all five mix ratios are listed in Table 15, together with the RDME. The Mix-1 (Only metakaolin with 1.4 molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ ) specimens experienced the highest weight loss, which was four times higher than the Mix-3 (Only metakaolin with 1 molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ ) specimens. Both the Mix-2 (Metakaolin with slag at 1.4 molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ ) and Mix-4 (Metakaolin with slag at 1 molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ ) specimens underwent less weight loss comparing to other specimens with same molar ratio of alkaline but without adding slag. From the results, it can be concluded that geopolymer concrete with higher water content is less frost resistance than geopolymer concrete with lower water content. In addition, the freeze-thaw cycles has significant effect on the durability of the geopolymer concrete. The drop in the dynamic modulus of elasticity of geopolymer concrete samples with freeze-thaw cycles means the loss of the stiffness. According to the ASTM C 666 Standard Test (Procedure A), Mix-3 and Mix-4 are giving the best durability compared to other mixtures since they lost less than 5% of their weight. The weight loss observed is mainly due to the spalling of concrete surface with freeze-thaw cycles. However, results indicate a significant loss of weight and RDME after only 30 cycles. Figure 20 and Figure 21 present the effect of freeze-thaw cycles on geopolymer concrete.

**Table 15.** RDME and Weight loss after 30 freeze-thaw cycles

<b>Mix No.</b>	<b>Mix-1</b>	<b>Mix-2</b>	<b>Mix-3</b>	<b>Mix-4</b>	<b>Mix-5</b>
<b>Weight loss (%)</b>	6.86	5.82	1.88	1.29	6.31
<b>RDME (%)</b>	-	-	46.21	37.72	37.88



**Figure 20.** Surface of geopolymer concrete specimens after 30 cycles of freeze-thaw



**Figure 21.** Effect of 30 cycles of freeze-thaw on cylindrical geopolymer concrete specimens

#### **5.4. Summary**

In this chapter, the freeze-thaw resistance of metakaolin-based geopolymer concrete was investigated through laboratory experiments by subjecting the geopolymer concrete to rapid freeze-thaw cycles. The freeze-thaw durability of five different mix ratios of geopolymer concrete was explored. The effect of rapid freeze-thaw cycles on geopolymer concrete were studied by recording the dynamic modulus of elasticity, weight loss, and compressive strength of geopolymer concrete specimens at certain numbers of cycles.

## CHAPTER 6. CONCLUSIONS AND RECOMMENDATIONS

### 6.1. Conclusions

This thesis experimentally evaluates the possibility of using metakaolin-based geopolymer mortar/concrete as a pavement repair material and characterizes the durability of metakaolin-based geopolymer concrete against freeze and thaw. The research includes the effect of aggressive environments on the bond strength between geopolymer mortar and existing concrete and the effect of rapid freeze-thaw on metakaolin-based geopolymer concrete. The bond strength of geopolymer mortar to existing concrete was evaluated by splitting tensile test and slant shear test with line interface at 30° and 45°. Also, the durability of geopolymer concrete was evaluated by means of destructive and non-destructive tests, where the compressive strength and relative dynamic modulus of elasticity of geopolymer concrete with different mix ratios were tested and compared.

In chapter 3, a new cementless metakaolin geopolymer pavement repair material is developed that cures at room temperature. The developed geopolymer concrete can obtain 80% of its final strength within three days, although the geopolymer concrete shows lower strength at 24 hours, which indicates the curing duration exhibits a significant effect on the compressive strength of the geopolymer concrete. Furthermore, this research pilot tested the geopolymer concrete as a new pavement repair material. Through the splitting test conducted, the experimental results indicated that the bond strength decreases as the cement mortar deteriorates. The majority of the failure modes in the samples tested by splitting tests are always an adhesion failure at the interface. The comparison between the suggested geopolymer concrete with other pavement repair materials in the market shows the superior bond strength of the suggested metakaolin-based geopolymer to substrate concrete. The bond strength between the cement

mortar and the geopolymer mortar through the slant shear test is also conducted. It is found that the failure started at the mortar substrate and most of failure modes occur through cement mortar substrate, which indicates an excellent bond interface formed by geopolymer mortar with cement substrate.

In chapter 4, experimental works have been carried out to investigate the effect of the molar ratios of  $\text{SiO}_2/\text{Na}_2\text{O}$  of the alkaline solution, adding calcium aluminate cement to metakaolin, and replacing partially metakaolin with slag on the early compressive strength of the geopolymer mortars. All parameters are found to tremendously influence the early compressive strength of the geopolymer mortars. By investigation of the effect  $\text{SiO}_2/\text{Na}_2\text{O}$  on geopolymer mortar,  $\text{SiO}_2/\text{Na}_2\text{O} = 1$  is found to be the optimum ratio which accelerates the geopolymerization process and enhances the compressive strength. In addition, calcium aluminate cement has been found to be used an accelerator for geopolymer, and the best adding ratio of calcium aluminate cement to metakaolin is 20% by weight. Calcium aluminate cement plays a significant role to accelerate the geopolymerization process and results in faster strength gain and higher compressive strength. Slag blended with metakaolin has less compressive strength than that of metakaolin when it is used alone. Following the superior bond strength of geopolymer to concrete substrate found in chapter 3, geopolymer has proven to be a good candidate for pavement repairs and can be used for repairs specified for opening early to traffic.

In chapter 5, freeze-thaw resistance of metakaolin-based geopolymer concrete were investigated. Five different mix ratios of geopolymer concrete were exposed to standard rapid freeze-thaw test. From test results, it can be concluded that the mix with the  $\text{SiO}_2/\text{Na}_2\text{O}$  molar ratio equal to 1 gives higher durability than the mix with the  $\text{SiO}_2/\text{Na}_2$  molar ratio equal to 1.4, the geopolymer concrete mix ratio with adding slag shows less weight loss than the others. However,

all five mix ratios failed to be durable since their RDME dropped to less than 60% of its original dynamic modulus of elasticity and Mix-1, Mix-2, and Mix-5 lost more than 5% of its original weight.

## **6.2. Recommendations and future work**

Even though the results obtained in this thesis would increase the body of knowledge on using metakaolin-based geopolymer concrete as a pavement repair material, extensive research is needed on using geopolymer in lieu of Portland cement. For the future work, the freeze-thaw durability of geopolymer concrete is worthy to be more investigated, especially for pavement repairs in northern US regions. Another area for future work is to develop a non-alkali activator and geopolymerization accelerators, which will greatly enhance work safety and broaden the application fields of geopolymer concrete.

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