Influence of mix design and tailoring on thermal performance of geopolymers

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INFLUENCE OF MIX DESIGN AND TAILORING ON THERMAL PERFORMANCE OF GEOPOLYMERS

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SUMMARY

Geopolymer is a novel material that has wide-ranging applications. While geopolymer could serve as structural material for fire resistance applications, the existing knowledge about influence of mix design factors and tailoring on its high temperature performance needs exploration. This thesis brings to light that by proper tailoring of geopolymer mix design, promising thermal performance could be realized. It enhances the understanding of high temperature response of geopolymers by establishing the relationship between mix design factors and thermal stability of the material at macro-, meso- and micro-scales. The influence of mix design factors on strength endurance, volume stability and chemical stability subject to high temperature exposure for metakaolin-based geopolymer and fly ash-based geopolymer is investigated in depth. Suitable selection of mix design factors and alkali-cation type led to development of fly ash-based geopolymers with promising thermal stability. Moreover, it was found that even using sodium as an alkali cation, not only stable but even enhanced thermal performance could be attained.

Significance of this research also lies in discovering the underlying mechanisms governing the thermal performance of geopolymers through application of various experimental techniques such as observation of cracking damage using photography, microstructure using scanning electron microscopy and mercury intrusion porosimetry, deformation using dilatometry and chemical structure using Fourier transform infrared spectroscopy and x-ray diffractometry. Through the understanding gained in this research, it is possible to design geopolymers with good thermal resistance. This systematic study brings us a step forward towards application of geopolymers as a fire-resistant construction material for structural applications.

LIST OF PUBLICATIONS

Refereed International Journal papers

1. Lahoti, M., P. Narang, K. H. Tan and E.-H. Yang (2017) "Mix design factors and strength prediction of metakaolin-based geopolymer." Ceramics International **43**(14): 11433-11441.
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Chapter 1

INTRODUCTION

1.1 Background

Fire damage can be critical in structures and in all cases the protection of people and property is essential. Despite of all the technological advancements and measures for fire prevention, there remains a threat of fire breakout always. The fire caused in 9/11 attack on the World Trade Centre, the Windsor tower fire (**Figure 1.1**), the fire in Mont Blanc (**Figure 1.2**) and the Channel tunnels, for example, have caused both heavy loss of life and loss of human assets. Protection of structures from fire is of extreme importance since it would surely contribute to reduced loss in all respects. Therefore, research in matter of fire safety is of utmost importance.

Figure 1.1: A severe fire resulting in major structural collapse of the Windsor tower, a high rise building in Madrid, Spain in 2005 (Driverlayer , Photobucket)

Figure 1.2: Damage caused by fire in Mont Blanc Tunnel, 1999 (Tunneltalk 2001)

Concrete and steel are the most used construction materials (Mindess, F. et al. 2003). Concrete has intrinsic fire resistance. It is non-combustible and has a relatively low thermal conductivity. Cracking, spalling and loss in mechanical strength of concrete after exposure to fire (**Figure 1.3**), however, are key concerns especially with high strength concrete (Khoury 1992, Ulm, Coussy et al. 1999, Chan, Luo et al. 2000, Khoury 2000, Vydra, Vodak et al. 2001, Komonen and Penttala 2003, Odelson, Kerr et al. 2007, Khoury 2008, Zhao, Zheng et al. 2017). Although concrete provides satisfactory fire endurance, for certain structures such as concrete liner of tunnels, the performance cannot suffice. There has been experience of severe dramatic tunnel fires in the past few decades. The **Table 1.1** (Sakkas, Nomikos et al. 2013) summarizes the life and property losses due to those fires. In case of a tunnel fire, there is a rapid increase in air temperature within first few minutes of fire. This results in considerable spalling of concrete and thus the tunnel lining suffers damage. This leads to safety issues both for the tunnel users and the fire rescuers. As can be seen from the table, there are direct economic losses from repair activities and indirect losses related to tunnel closure. To address the tunnel fire issues, fire resistance tests on concrete elements are required in most tunneling projects. Temperature versus time curves such

as the ISO standard fire curve, RWS curve, hydrocarbon fire curve have been adopted in various tunnel fire testing regulations. All these highlight that fire safety of any concrete structure, not just tunnels, is a serious concern.

Figure 1.3: Performance of Reinforced Concrete under fire. Image shows spalling (Driverlayer)

Table 1.1: Damage caused by tunnel fires in past two decades
(Sakkas, Nomikos et al. 2013)

Year	Tunnel	Number of victims	Repairing Cost (M€)	Loss of Revenue (M€)
1996	Eurotunnel Channel	2 injured	49	203
1999	Mont Blanc	41 deaths	189	203
1999	Tauern	12 deaths	8.5	20

2001	St. Gothard	11 deaths	Not available	Not available
2005	Frejus	2 deaths	2	3
2006	Viamala	9 deaths	Not available	Not available

The use of polypropylene (PP) fibers in concrete is generally undertaken to reduce the danger of spalling of concrete in event of a fire (Cree, Pliya et al. 2017, Maluk, Bisby et al. 2017, Yermak, Pliya et al. 2017, Khaliq and Kodur 2018). Two major causes for spalling are- rise in pore pressure and development of thermal stresses. Although, PP fibers have been shown to reduce the spalling caused by pore pressure rise, they have not been very effective in reducing the thermal stresses. This is one of the drawbacks with using PP fibers as a measure to prevent concrete from fire damage. Use of thermal barriers is another solution undertaken for concrete fire protection. However, this solution is available at a high cost. Moreover, it has been shown that the OPC hydration products namely calcium silicate hydrate, calcium hydroxide and calcium carbonate degrade when OPC concrete is subject to high temperature. And it is very difficult to avoid this deterioration of concrete micro-structure (Harmathy 1970, Harmathy 1993).

Moreover, steel, both as reinforcement in concrete and for structural applications, is much more sensitive to high temperatures as compared to concrete. Thus, fire protection is more indispensable and critical for steel structures. For steel members, in many applications, it is very important to provide insulation to prevent softening of steel at high temperatures. The insulation is also required for structures like tunnels and caverns. The common types of passive fire protection materials are listed as follows:

- Traditional materials (concrete, plaster, bricks): These are readily available and no special skills are needed for implementation. These materials are weather resistant but are slow to apply on site. The thick casing takes up the floor space and the self-weight is high.

- Board materials: Pre-fabricated non-combustible boards made by gypsum and reinforced with inert fibers. The pre-fabricated insulation boards can be applied to existing structures as a method for fire refurbishment. However, this is an expensive method and requires long installation time.
- Spray-applied fire resistive material (SFRM): This is the most common used passive fire protection material for steel structure. It is also used in reinforced concrete structures to prevent explosive spalling. SFRM usually consists of cement matrix or gypsum plaster containing vermiculite, shredded polystyrene or mineral fibers. They can be sprayed either in the form of dry-mix (sprayed mineral fiber SFRM) or wet-mix (sprayed cementitious SFRM). They have relatively low cost and can be applied to existing structures as well. However, application of SFRM makes the appearance of the structural element bulky. The adhesion or bonding to the surface of structural element is important. Missing fireproofing due to poor adhesion to steel and brittleness of SFRM has been observed. One major reason of the collapse of the World Trade Center (WTC) towers in 2001, for example, was suggested to be the dislodging of SFRM from structural members due to aircraft impact, which resulted in rapid heating of unprotected structural steel. In reinforced concrete structures, heat-induced spalling can result in severe loss of integrity and collapse of structures.
- Intumescent coating: Specially formulated *paint-like* coating can be applied onto steel surface. The coating swells upon heating. This approach is most aesthetically pleasing and most used in architecturally exposed structural steel. However, the material is much more expensive than SFRM. Intumescent coating commonly provides fire rating of 1-2 h. Generally, intumescent coating needs to be applied on site. Application of intumescent coating is fast and it does not take up space or adds to weight. Concern with it is the high cost.

Overall, it has been reported that for many applications including fire protection of tunnels, underground structures, high rise buildings, strategic objects, metallic

structures such as I-beams, thermal insulation of furnace, chimneys, boilers or as a composite material for ships, automobiles and aircrafts, there is necessity to develop new materials which have superior fire and mechanical performance to conventional concrete and other construction materials (Provis and van Deventer 2009).

Geopolymer is a novel construction material which can be an alternative binder to ordinary Portland cement (OPC). It has also been referred to in literature as ‘inorganic polymer glass’, ‘alkali-activated cement’, ‘mineral polymer’, and ‘alkali-bonded ceramic’ (Provis and van Deventer 2009). The term ‘Geopolymer’ was coined by Joseph Davidovits in 1978 (Davidovits and Davidovics 1991). It refers to a solid material formed by the reaction of aluminosilicate source with an alkaline solution (Xu and Van Deventer 2000). Metakaolin, fly ash and blast furnace slag are commonly used aluminosilicate sources. Geopolymer is greener than OPC and can provide a route to reduce the carbon foot print caused by intense usage of OPC (Duxson, Fernández-Jiménez et al. 2007, Weil, Jeske et al. 2007, Akan, Dhavale et al. 2017, Huseien, Mirza et al. 2017, Robayo-Salazar, Mejia-Arcila et al. 2017, Messina, Ferone et al. 2018).

The mechanism by which OPC hardens and gains strength is markedly different from geopolymer. Hence, there is a clear difference between the nano-structure of the two materials. While C-S-H (one of the major component in hydrated OPC) consists of a layered structure, geopolymer consists of a three dimensional network structure of silicon and aluminum linked by oxygen atoms (**Figure 1.4**). Geopolymers possess excellent mechanical properties and their compressive strength can be greater than 60MPa. They have excellent potential for fire, alkali-silica reaction (ASR) and acid resistance. They have inorganic framework and do not burn like organic polymers do. They are non-smoking and non-toxic too and have low processing temperature as compared to ceramic composites (Davidovits 1991). **Figure 1.5** shows an example of geopolymer concrete construction. Geopolymer can serve as a green construction material with immense potential for sustainable development and fire resistance.

Figure 1.4: Comparison of nano-structure of geopolymer and C-S-H

Figure 1.5: University of Queensland (Geopolymer concrete construction)

1.2 Research motivation

In the background of this research, the need of a green construction material for structural applications and with admirable fire and mechanical performance is realized. It can be anticipated that geopolymer has capacity to fit the bill. However, for possible application of this material towards enhancing structural fire resistance, following knowledge gaps need to be addressed:

- Metakaolin-based geopolymers are considered as 'model' system to understand geopolymer characteristics and behavior. Unfortunately, there is no systematic investigation on assessing the importance of factors governing their compressive strength. Unlike OPC system, where water-to-cement ratio is the chief factor governing compressive strength, geopolymer mix design involves higher number of factors such as Si/Al, water/solids, Al/Na and H₂O/Na₂O ratios. Geopolymer is a newer and different binder system than OPC and it is important to clearly understand factors affecting its compressive strength prior to studying its high temperature performance.
- Thermal properties of metakaolin-based geopolymers at micro-scale (such as phase stability) subject to high temperature have been reported in literature. However, very limited studies report the thermal stability in terms of strength endurance, macro-cracking, and deformation resistance of the bulk geopolymer material. Moreover, the fundamental mechanisms linking the mix design with the thermal stability at macro-, meso- and micro-scales are not clearly understood. Such knowledge is essential for any potential application of the material for structural purposes.
- Fly ash-based geopolymers are environmental friendly and have more economical benefits and high temperature endurance as compared to their metakaolin counterparts. Since, fly ash properties significantly vary among

different thermal power stations, it is essential to estimate reactive content in the fly ash. This helps to determine the values of mix design factors which in their turn affect the high temperature performance of geopolymers. It is therefore important to estimate the total reactive content in the locally available fly ash.

- The choice of alkali cation is important in determining the performance of geopolymers at elevated temperature. Importance of alkali cation for metakaolin-based geopolymers has been investigated in previous research. However, such studies in relation to fly ash-based geopolymers are very limited. Moreover, these studies have not shown promising results for structural applications because of large changes in compressive strength and deformation after high temperature exposure. Research on this topic is thus necessary.
- Since not all geopolymer formulations possess good thermal resistance and the performance greatly depends on mix design factors, tailoring of these factors to achieve sound high temperature performance is essential. This knowledge is more important especially when sodium is used as alkali cation since sodium-based alkali activators provide economical advantage for commercial applications as compared to potassium-based. To the best of author's knowledge, such understanding on tailoring of geopolymer mix design is lacking in the previous research.

Addressing these research gaps would help to tailor the properties of geopolymers for structural fire resistance applications.

1.3 Research goal and objectives

The overall goal of current research is to enhance structural fire resistance. Specific objectives to achieve this goal are associated with the study of geopolymer binder to develop it as an innovative material for enhancing structural fire resistance by addressing the above mentioned research gaps. Three specific objectives are defined in this thesis:

1. To study the influence of mix design factor on the mechanical and thermal performance of geopolymers at elevated temperature;
2. To reveal the underlying mechanisms that governs the mechanical and thermal performance of geopolymers at elevated temperature; and
3. To develop structural geopolymers with enhanced mechanical and thermal performance.

1.4 Methodology

Figure 1.6 shows the research methodology applied in this research. The idea originates from the fact that in order to ensure good structural performance of geopolymers subject to high temperature heating, geopolymer must be chemically, volumetrically and strength-wise stable. A number of previous studies focus on chemical stability of geopolymers. However, to facilitate structural application of geopolymers, it needs to be ascertained that the material performs well at micro-scale (i.e. stability of chemical structure), at meso-scale (i.e. resistant to deformation) and macro-scale (i.e. strength endurance). With this purpose, the focus in current study was placed on investigating the influence of mix design factors on thermal performance of geopolymers at multi-scales. The performances at different scales are interrelated. The research methodology and research tasks were accordingly planned and have been presented below.

Figure 1.6: Research methodology

1.5 Research tasks

Figure 1.7 shows the framework of this proposed research. The framework shows that the influence of mix design factors on thermal performance of geopolymers will be investigated. Mix design factors include the precursor type (whether metakaolin or fly ash), alkali cation type (whether sodium, potassium or mixed-alkali) and factors such as Si/Al ratio, Al/Na ratio and water/solids ratio. The thermal performance of geopolymer mixes will be evaluated in terms of their strength endurance, volume stability and chemical stability. By following this roadmap, it would be possible to realize a structural geopolymer for fire resistance. Detailed research tasks are as follows:

1. Assessing mix design factors governing the compressive strength of metakaolin-based geopolymers; A combination of techniques involving experiments, statistical analysis and microstructure analysis were used to assess the significance of mix design parameters for metakaolin-based geopolymers. In addition, machine learning based classifiers were used to predict the compressive strength of geopolymers.
2. Investigating strength endurance and volume stability of metakaolin-based geopolymers subject to elevated temperature
A series of metakaolin-based geopolymers were prepared and their thermal performances were investigated subject to high temperature heating. The performance was described by measuring the residual compressive strengths, by analyzing the cracking damage and by evaluating the thermal deformation. Material characterization such as Scanning electron microscopy (SEM), X-ray diffraction (XRD and Fourier transform infrared spectroscopy (FTIR) were carried out to discover the underlying mechanisms.
3. Evaluating the potential reactivity of fly ash for geopolymerization;

Experiments were conducted on the locally available fly ash to study its potential reactive content for geopolymerization and to estimate the reactive Si/Al molar ratio. A procedure involving dissolution of fly ash in sodium hydroxide (NaOH) solution followed by a hydrochloric acid (HCl) attack was applied. ICP-OES (Inductive coupled plasma optical emission spectrometer) analysis was used to find out the reactive Si/Al ratio. The reactive Si/Al ratio was also estimated using a combination of quantitative XRD and X-ray fluorescence (XRF) techniques.

4. Designing fly ash-based geopolymers with promising thermal performance using different alkali cations;

The effect of using mixed alkali cations on thermal performance of fly ash-based geopolymers was investigated in detail. Compressive strengths after high temperature exposure (500°C and 900°C) were measured. SEM micrographs and dilatometry results were used as primary tools to explain the thermal performance. XRD and FTIR analyses were employed to study the chemical stability of geopolymers subject to elevated temperature exposure. How to attain good thermal performance by proper mix design was demonstrated in this work.

5. Tailoring mix design factors to attain sound high temperature performance for fly ash-based geopolymers using sodium as alkali cation;

Mix design factors for the fly ash geopolymer mix were varied and high temperature response of geopolymers was assessed. Detailed investigation using image analysis (to observe cracking damage and microstructure), dilatometry (to measure the thermal deformation) and XRD and FTIR (to observe the changes in chemical structure of the geopolymers were undertaken). Underlying mechanisms controlling the variegated thermal performance were studied. The influence of mix design selection (Si/Al

ratio, water content and alkali content) on thermal performance of fly ash-based geopolymers was thus evaluated.

1.6 Layout of the thesis

This thesis consists of eight chapters. Chapter 1 describes the background, knowledge gaps, motivation, goals and objectives of this research. It also presents the research methodology and research tasks carried out in this study. Chapter 2 covers details on the state-of-the-art about performance of geopolymers subject to high temperature heating. Knowledge gaps are also identified in this Chapter.

Chapters 3 and 4 discuss the performance of metakaolin based-geopolymers at ambient temperature and subject to high temperature exposure. In Chapter 3, an effort has been made to answer the important question regarding what controls the compressive strength of geopolymers using a combination of techniques, namely, experimental program, statistics and micro-structure study (Task 1). In Chapter 4, performance of metakaolin-based geopolymers subject to elevated temperature has been investigated (Task 2).

Chapter 5, 6 and 7 are related to fly ash-based geopolymers. Chapter 5 discusses how to estimate the total available reactive content in the locally available fly ash (Task 3). In Chapter 6, the effect of alkali cation has been investigated to a good depth (Task 4). In Chapter 7, the effect of mix design parameters on thermal performance of fly ash-based geopolymers using sodium as alkali cation has been investigated (Task 5).

Main conclusions from this study are summarized in Chapter 8, and future works worthy of further investigations are delineated.

Figure 1.7: Research framework

Chapter 2

LITERATURE REVIEW

This chapter gives an insight into some key aspects of geopolymer technology based on the previous research related to current topic. In particular, the properties of geopolymer, especially metakaolin-based and fly ash-based geopolymers, at ambient conditions and on high temperature exposure have been discussed. For performance at ambient, an introduction to geopolymers, the geopolymer reaction mechanism, way to find out the potential reactivity of a geopolymer precursor and factors affecting the geopolymer mechanical performance have been discussed to a good length. For performance subject to elevated temperatures, important properties of geopolymers such as phase transformations, microstructure and pore structure changes, thermal deformations, residual strengths and spalling resistance have been presented. After describing these properties, the current application of geopolymers for heat and fire resistance has been briefly explained followed by a conclusion of the literature review, identification of important research gaps related to the thesis topic. Research methodology and research framework have also been presented.

2.1 Geopolymer science

2.1.1 Geopolymer: general introduction to the novel material

Concrete is the most used man-made material in the world. Ordinary Portland cement (OPC) is conventionally used as the precursor to produce concrete. Portland cement production is one of the principal causes of greenhouse gas emission (Kumar 2001, Scrivener and Kirkpatrick 2007). Thus there has been an ongoing search for alternate

building and construction materials with reduced carbon footprint (Kajaste and Hurme 2016, Lim, Raman et al. 2018).

In 1978, Davidovits (Davidovits 1991) proposed that binders could be formed by a polymeric reaction of silicon and aluminum rich source materials of geological origin such as kaolin clay or waste product from coal power plant such as fly ash, or blast furnace slag and rice husk ash with alkaline liquids. These binders were termed as geopolymers and they harden just like concrete. The main reaction product in this process is an alkaline aluminosilicate gel which is X-ray amorphous and is characterized by short-range structural order (Granizo, Alonso et al. 2002). In addition, Na-Herschelite-type zeolites and hydroxysodalite are formed as secondary reaction products particularly when fly ash is used as a precursor (Fernandez-Jimenez and Palomo 2003, Palomo, Alonso et al. 2004). Along with these reaction products, the geopolymer binder also consists of the unreacted solid precursor particles and the pore network of the gel containing the water used for mixing the precursor. This water is generally supplied through the alkaline activating solution (Provis and van Deventer 2009). The geopolymer gel is a three-dimensional network of aluminate and silicate tetrahedra. Since Al^{3+} in the aluminate tetrahedra $(\text{AlO}_4)^{-1}$ is in four-fold coordination, the excess negative charge is balanced by the alkali metal provided by the alkaline activating solution. It is important to note that the water in geopolymer binder does not form an integral part of the geopolymer chemical structure. This is in contrast to calcium silicate hydrate gel in hydrated OPC paste where water forms an integral part of C-S-H. **Figure 2.1** shows the schematic structure of geopolymer and OPC.

Figure 2.1: Schematic molecular structure of geopolymer in contrast to OPC

2.1.2 Geopolymerization: the process of geopolymer formation

Geopolymers are a complex class of materials. The process of geopolymer formation principally involves the reaction of an alkaline solution with a reactive aluminosilicate precursor. Calcinated kaolin clay (metakaolin) or by-product from coal combustion (fly ash) are commonly used precursor for geopolymers. Metakaolin has been relatively widely used for geopolymer synthesis. Its particles have a plate-like morphology and thus it has a very high water demand for geopolymer cement and concrete applications. Fly ash is a highly variable material and its properties depend on the coal from which it is produced and also the combustion and quenching process by which it is produced. The fly ash which is low in calcium content (class F fly ash) is widely used as geopolymer precursor.

Generally, the alkaline activating solutions are alkali hydroxides or silicates under high-pH conditions (Provis 2009). The use of alkali hydroxide such as sodium hydroxide (NaOH), potassium hydroxide (KOH), lithium hydroxide (LiOH) alone, without any addition of silicates, can be a simplest activating solution in geopolymer synthesis. The use of silicates generally involves sodium silicate and potassium silicate and their properties such as density and viscosity are a function of their composition.

In the conceptual model by Duxson et al. (Duxson, Fernández-Jiménez et al. 2007), the geopolymerization process is described in the following way. Dissolution of aluminosilicate source due to contact with alkaline activating solution leads to formation of individual alumina and silicate species (probably as monomers), it is the first step in geopolymerization. These monomers interact to form dimers, and further trimers, tetramers and so on are formed. The aluminosilicate gel precipitates when the solution reaches saturation. Since reactive aluminum dissolves faster than silicon (Al-O bonds are weaker than Si-O bonds), initially the precipitated gel (Gel 1) is aluminum-rich. With progress of reaction, more silicon is dissolved from the precursor and the concentration of silicon in the gel increases giving rise to Gel 2. All these stages involving dissolution, speciation, equilibrium, gelation, reorganization and polymerization and hardening go on simultaneously although they have been shown linearly in **Figure 2.2**. It requires presence of alkaline solution for the dissolution of aluminosilicate source as well as for catalysis of the condensation reaction (Xu and Van Deventer 2000).

Figure 2.2: Simplified Geopolymerization reaction process, based on (Duxson, Fernández-Jiménez et al. 2007)

2.1.3 Potential reactivity of precursors for geopolymerization

For geopolymer synthesis, initially one needs a suitable mix design. Geopolymerization involves use of an aluminosilicate source and an alkaline activating solution. When metakaolin is used as an aluminosilicate precursor for geopolymerization, generally mix design involves usage of the following ratios - Si/Al, Al/Na and H₂O/Na₂O (Barbosa and MacKenzie 2003, Barbosa and MacKenzie 2003, Duxson, Lukey et al. 2005, Duxson 2006, Davidovits 2008, Chen, Wang et al. 2016, Borges, Bhutta et al. 2017). These ratios can be easily evaluated since metakaolin is generally almost fully amorphous. The available silicon and aluminum content can be easily evaluated using the X-ray fluorescence (XRF) analysis of the metakaolin powder. While the available sodium and water can be evaluated from the known composition of the alkaline

activating solution. Hence, it is feasible to design a metakaolin-based geopolymer mix using Si/Al, Al/Na and H₂O/Na₂O ratios.

However, the scenario is not exactly the same when fly ash is used as a geopolymer precursor. Since fly ash is not being entirely amorphous and it contains significant amounts of crystalline components such as quartz and mullite, the silicon and aluminum content available for geopolymer formation cannot be determined in a straightforward way. Hence, for fly ash-based geopolymers mix design, many researchers prefer using liquid/solid ratio and sodium silicate solution/sodium hydroxide solution ratio instead of Si/Al, Al/Na and H₂O/Na₂O ratios. However, for a clearer understanding of the reaction mechanisms, it is worth estimating the reactive contents in the geopolymer precursors. Few researchers have tried to evaluate the reactive silicon and aluminum content in the fly ash using different approaches (Fernandez-Jimenez, de la Torre et al. 2006, Fernandez-Jimenez, de la Torre et al. 2006, Chen-Tan, Van Riessen et al. 2009, Rickard, Williams et al. 2011). These findings cannot be generalized since fly ash is a highly variable material and its properties depend upon the thermal power plant from where it is sourced. However, the approaches can still be applied to estimate the potential reactivity of the locally available fly ash. In Chapter 5 of this work an effort has been made to assess the total reactive content of the locally available fly ash for geopolymerization.

2.1.4 Factors affecting geopolymer compressive strength

It is known that water-to-cement ratio is the most significant factor in determining the compressive strength of OPC binders. There has been some research studying different factors (including Si/Al ratio, Al/Na ratio, H₂O/Na₂O ratio, water/solids ratio etc.) influencing the geopolymer compressive strength. Duxson et al. (Duxson, Provis et al. 2005) studied the effect of Si/Al ratio on the compressive strength and microstructure

development of metakaolin geopolymers. It was found that the compressive strength reaches its maximum value for Si/Al close to 1.90. It had been shown that as the Si/Al ratio is gradually increased from 1.15 to 2.15, due to an increase in Si-O-Si linkages (which are stronger than Si-O-Al linkages) as well as due to a simultaneous improvement in the geopolymer microstructure (microstructure becoming more homogenous and less porous), the compressive strengths would keep increasing up to Si/Al=1.90. It was also shown that a further increase in Si/Al ratio would cause an increase in the quantity of unreacted metakaolin. These unreacted metakaolin particles may in turn act as defect sites causing weakening of material and reduction in compressive strength of the material.

Kong et al. (Kong, Sanjayan et al. 2008) also observed the variation in the compressive strength of metakaolin geopolymer with Si/Al ratio. The results, however, were quite different from Duxson's findings perhaps due to Al/M ratio in these experiments not close to unity. Theoretically, one alkali cation is required to balance the negative charge on the tetrahedrally coordinated aluminum atom. Therefore, it has been suggested that Al/M ratio should be close to unity. The heat of reaction during geopolymerization which is indicative of the degree of reaction, is inherently linked to the Al/M ratio and has been observed to increase until the Al/M ratio reaches unity, beyond which no greater heat is released (Duxson 2006). Oswaldo Burciaga-Díaz et al. (Burciaga-Díaz, Escalante-García et al. 2010) studied the influence of factors (such as blast furnace slag-to-metakaolin weight ratio, activator concentration and curing time) on the development of mechanical properties in a composite system based on blast furnace slag and metakaolin using a statistical approach. However, the effect of water content on geopolymers was not studied.

According to Rahier et al. (Rahier, Simons et al. 1997), H_2O/Na_2O ratio affects the geopolymer reaction. H_2O/Na_2O ratio determines the alkalinity of the system and

affects the degree of geopolymerization. Researchers have also tried to understand the effect of water-to-solids ratio on compressive strength for fly ash based geopolymers. Most studies of fly ash-based geopolymers disregard the influence of Si/Al ratio and suggested that compressive strength of geopolymers is dependent on the water-to-solids ratio similar to that of OPC (Hardjito and Rangan 2005, Sumajouw and Rangan 2006, Wallah and Rangan 2006).

Based on the literature review about geopolymer compressive strength at ambient conditions, it can be understood that though there has been some knowledge gained regarding the factors that may affect the strength, the degree of importance of each factor is yet unclear. That is, it is still unclear that which factors are more significant and which are less and to what degree. This research gap has been addressed in Chapter 3 of this study.

2.2 Geopolymer properties subject to elevated temperatures

Elevated temperature performance of any material is significant especially when it is to be utilized as a fire-proof material for structures, as thermal insulator, a material for refractory application and so on. Geopolymeric materials have intrinsic fire resistance. They have inorganic framework and they do not burn like organic polymers do. They are non-smoking, non-toxic and have a low processing temperature as compared to traditional ceramic composites (Davidovits 1991). Of course it should be noted that the properties and performance of geopolymer subject to elevated temperature depends on its composition or mix design and the synthesis procedure as well.

In order to apply geopolymer as a fire-resistant building and construction material, its thermal performance should be examined at the micro-, meso- and macro-scale levels. Micro-scale refers to observing the phase transformations and nano-structural

transformations occurring in the geopolymer subject to high temperature. Thus it refers to the chemical stability and the performance at this scale contributes to the stability of material at higher scale levels, namely, meso and macro. The ability of material to resist volumetric deformations and thermally induced-cracks when subject to elevated temperatures is referred to here as the meso-scale thermal stability. Macro-scale stability is related to ability of material to possess strength endurance and spalling resistance subject to elevated temperature. Understanding of the performance at these three scales brings a step closer towards structural application of the material for fire-resistance purposes. Important properties dealing with the micro-scale, meso-scale and macro-scale performance of geopolymers have been reported in literature. An effort has been made herein to present the state of the art report summarizing the important properties of geopolymers subject to elevated temperature, obtained from various literatures. **Figure 2.3** shows an overview of the same.

Figure 2.3: An overview of the properties of geopolymers subjected to high temperatures.

2.2.1 Micro-scale properties

A. Phase stability

Knowledge about phase change of geopolymers can be crucial in understanding its macro-scale properties and thus the structural performance on high temperature exposure. Barbosa et al. (Barbosa and MacKenzie 2003) studied the thermal behavior of geopolymers synthesized using metakaolin and sodium silicate in a highly alkaline medium. This geopolymer, when properly cured, exhibited remarkable thermal stability retaining its amorphous structure till onset of melting at 1300°C. They also synthesized K-PS Poly (Sialate) and K-PSDS Poly (Sialate-disiloxo) geopolymers starting from metakaolin, K-silicate and KOH pellets based on specific molar ratios (Barbosa and MacKenzie 2003). K-PS geopolymer melting point was around 1400°C and was stable till this temperature. XRD and NMR analysis suggested that the stability was due to its complete re-crystallization to the feldspars leucite and kalsilite at 1000°C. K-PSDS geopolymer, though thermally stable and had high melting point, became friable and porous when heated to temperatures above 1200°C. It did not undergo complete re-crystallization and retained certain degree of amorphous character.

Krivenko et al. (Krivenko and Kovalchuk 2007) showed that a directed synthesis would help regulate the structure formation process and features of the 'geocement' (geopolymer). They varied the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the initial geocement made from metakaolin and fly ash. The following **Table 2.1** from their study shows the existence of correlation between the initial molar ratio and products of dehydration or the phase changes at 800°C.

Table 2.1: Correlation between Si/Al ratio of precursor and geopolymer dehydration product (Krivenko and Kovalchuk 2007)

Aluminosilicate component	SiO ₂ /Al ₂ O ₃ molar ratio	
	Initial geocements	Products of dehydration (corresponding phase)
Metakaolin	2	2 (nepheline)
	4	2 (nepheline)
	6	∞ (cristobalite), 2 (nepheline)
	8	∞ (cristobalite), 2 (nepheline)
Fly ash	4	2 (nepheline)
	6	6 (albite), 2 (nepheline)
	8	∞ (cristobalite), 2 (nepheline)

Kovalchuk et al. (Kovalchuk and Krivenko 2009) also reported the role of initial alkalinity. Theoretically, lower the initial alkalinity, higher the thermal resistance because the onset temperature of crystallization is found to increase when alkalinity is lowered. However, the initial alkalinity also determines the rate of alkaline activation and regulates the development of compressive strength. That is why an optimum quantity of initial alkalinity is required to have sufficient initial strength and target properties after high temperature exposure. It has also been suggested by Fernandez-Jimenez et al (Fernández-Jiménez, Pastor et al. 2010) and Krivenko et al. (Krivenko and Kovalchuk 2007) that total alkali content in the system and the degree to which it is taken up by the reaction products formed is significant in determining the high temperature properties such as onset temperature of re-crystallization and sintering temperature and the amount of viscous sintering. Hence, it is important to tailor the initial alkali content to realize a good geopolymer mix for structural fire design. This tailoring of geopolymer mix has been discussed in Chapters 6 and 7 of this thesis.

Duxson et al. (Duxson, Lukey et al. 2007) observed the formation of crystalline phases for metakaolin geopolymers subject to elevated temperature exposure. The effect of changing alkali cation was also noted. It was observed that regardless of the alkali type (Na, K or Na-K), the amounts of crystalline phases formed decreased with an increase in Si/Al ratio of the geopolymer. Heating rate of geopolymers was also noted to alter the phase composition and thermal shrinkage of geopolymers which can be important in case of a fire event.

Temuujin et al. (Temuujin, Rickard et al. 2011) found that geopolymers calcined at 1000°C for 1 hour duration showed a X-ray amorphous structure, that is, no phase change after heating. Rickard et al. (Rickard, Temuujin et al. 2012) reported that all geopolymer samples, using fly ash as precursor, exhibited strength improving microstructure changes such as improved inter-particle binding due to sintering after firing. Some samples were instable due to non-geopolymeric phases. After firing, the geopolymer remained largely amorphous, experiencing no phase transformation. Interestingly, Rickard et al. (Rickard, Vickers et al. 2013) found that metakaolin geopolymers had crystalline (nepheline) structure after elevated temperature exposure.

Perera et al. (Perera and Trautman 2005) prepared geopolymer using metakaolin, potassium silicate and potassium hydroxide and cured at 80°C for 24 h and progressively heated it from ambient to 1400°C in air to observe the phase changes. Till 800°C they found amorphous phase and Kalsilite as major phase at 1000°C and 1250-1400°C. Leucite as major phase at 1200°C and till 1400°C there was no sign of significant melting. They found open porosity of 38% at 1000°C. The material was found to be suitable for refractory applications due to presence of two refractory phases (Kalsilite and leucite) and high porosity leading to good thermal insulation properties.

Thus, the phase changes observed in the previous literature can be summarized into the **Table 2.2.**

Table 2.2: Observation on phase changes by various researchers

Researcher	Geopolymer type	Observed phase at high temperatures
Barbosa (2003)	a. Na-PSS (MK based)	Amorphous till onset of melting 1300°C
	b. K-PS	Complete re-crystallization to the feldspars (stable upto 1400°C)
	c. K-PSDS	Incomplete re-crystallization. Friable and porous > 1200°C
Parera (2005)	MK based	Amorphous till 800°C. Crystalline (Kalsilite) as major phase at 1000°C and 1250-1400°C. (Leucite) as major phase at 1200°C
Duxson (2007)	MK based	Crystalline
Krivenko (2007)	Both MK based; FA based	Crystalline after 800°C
Temuujin (2011)	MK based	Amorphous (Calcined at 1000°C for 1 h)
Rickard (2012)	FA based	Largely amorphous after firing at 1000°C Strength improving μ -structural changes
Rickard (2013)	MK based	Crystalline (Nepheline) after firing at 1000°C
Sakkas (2013)	Fe-Ni slag based	Well Crystalline solid after 1000°C

Remarkably, researchers have reported different phase changes for geopolymers subject to thermal treatment. The good thing is that geopolymers are chemically stable

and do not undergo breakdown subject to high temperature. On the contrary, OPC hydration products such as calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and calcium carbonate (CaCO_3) undergo severe deterioration on thermal exposure (Harmathy 1970, Harmathy 1993). **Figure 2.4** shows the physic-chemical processes occurring inside Portland cement concrete during heating based on the ‘thermometer’ analogy (Khoury 2008).

Figure 2.4: Physic-chemical processes occurring inside Portland cement concrete during heating

B. Microstructure and pore structure changes

Exposure of geopolymers to high temperature affects the micro-structure in many ways. The geopolymer paste morphology will change when sintering and crystallization takes place at high temperature. The removal of physically or chemically

bound water (dehydration) at high temperature would affect the pore size distribution in the geopolymers.

The initial microstructure change happens when geopolymer is heated due to the dehydration of free water (from room temperature to above 200°C). The vapor pressure generated due to heating of water inside the material would try to escape by forming pathways. This process would damage the material due to formation of cracks. The pore structure will also change. The degree of microstructure change would depend on a number of factors. Kong et. al (Kong, Sanjayan et al. 2007) found that metakaolin-based geopolymers experienced larger damage to microstructure compared to their fly ash-based counterparts. It was attributed to a much higher amount of water required to mix metakaolin-based geopolymers and also to their lower interconnectivity of the pore structure.

At temperatures around 550°C and above, sintering and densification of the geopolymer matrix would cause the change in micro-structure (Bakharev 2006, Duxson, Lukey et al. 2006, Kong, Sanjayan et al. 2008). Geopolymer paste after high temperature exposure has fewer voids and exhibits smoother texture. The viscous sintering of the paste at high temperature also leads to crack healing. It has been suggested but has not been clearly demonstrated in literature. Geopolymer concrete will have additional micro-structure changes due to the difference in coefficient of thermal expansion of geopolymer paste and aggregates.

Bakharev (Bakharev 2006) found that the average pore size and cumulative pore volume in fly ash geopolymers increased after exposure to 800°C and 1000°C. It was suggested that the increase in porosity was related to the crystallization happening in the material at high temperature. Gourley et al. (Gourley and Johnson 2005) mentioned that since geopolymer cement is effectively a glass unlike Ordinary Portland cement which is a hydrate, resistance to heat and specifically to fire is greatly improved. The

absolute volume of water contained in the pore structure is low, and the pore structure is continuous. Thus the mode of decomposition is to melt at temperatures in excess of 1000°C, rather than explosively release water or dehydrate to a powder. Geopolymer has water in pores which absorbs heat of fire for some time, thus reducing temperature of sample, and when it vaporizes and exits, it does not damage the structure much because of the permeable pore structure.

There has been only limited information in literature substantiating the suggested microstructure transformations especially in case of fly ash based geopolymers. Recently, Rickard et al. (Rickard, Kealley et al. 2015) studied the microstructure of two geopolymer mixes- one was highly reacted, high-strength geopolymer with a compact microstructure and the other mix had a higher degree of unreacted fly ash resulting in a low strength, low density geopolymer. The poor thermal performance, strength loss and dimensional instability, of initial high-strength geopolymer were attributed to dehydration damage and macro-cracking. This geopolymer was more vulnerable because of compact microstructure. However, this damage to the geopolymer matrix was not clearly demonstrated through the SEM images. Low initial strength geopolymer was found to be very less damaged by dehydration, better able to accommodate the volumetric changes and exhibited strength gains after thermal exposure due to the sintering. The following model (**Figure 2.5**) was proposed to describe the results. The fly ash geopolymers were assumed to simply have four major phases; geopolymer gel, unreacted fly ash particles, crystalline material, and voids/pores. It was thought that:

1. Due to dehydration at high temperature, geopolymer matrix would shrink,
2. At temperatures above 500°C, amorphous aluminosilicates from unreacted fly ash would flow with more viscosity and be incorporated in geopolymer matrix.
3. The crystalline material will remain inert during high temperature exposure also

4. Small portion of the geopolymer matrix would crystallize to feldspars at temperatures above 500°C.
5. At temperatures above 500°C geopolymer matrix would shrink and increase in density while pores would combine with other pores to increase their size.

Figure 2.5: Schematic depiction of the proposed micro-structural changes upon firing
(Rickard, Kealley et al. 2015)

The conceptual model is useful to get some understanding of the microstructure changes. However, these assumptions need to be confirmed. Since SEM micrographs are sometimes unable to reveal the micro-structural changes completely, especially when the cracks are on a larger length scale than those observed through an SEM image, it is worth considering alternative techniques to capture the micro-structure

changes occurring inside the material subject to high temperature. An effort has been made to answer these research gaps related to the microstructure information of the geopolymers subject to elevated temperature in the current thesis in Chapter 4 (for metakaolin geopolymers) and Chapter 6 and 7 (for fly ash-based geopolymers).

2.2.2 Meso-scale properties

A. Thermal deformation

A material tends to expand or contract subject to elevated temperatures. Coefficient of thermal expansion is indicative of the degree to which material undergoes thermal deformation. It is defined as change in length per unit length of material per unit increase in temperature. It can be measured in-situ using techniques such as dilatometry and thermo-mechanical analysis (TMA) or ex-situ through dimensional measurements. Since thermal deformations during heating can cause stresses and potentially damage the material, these measurements are of specific interest while evaluating the thermal performance of geopolymers for high temperature applications. Dilatometry (ASTM Committee E37 2011), **Figure 2.6** is a traditional method used to precisely measure dimension changes in the material as a function of temperature. The use of a differential dilatometer makes the measurement even more precise since the sample holder expansion is eliminated. A true differential dilatometer from TA instruments (DIL 802L) was used in the current thesis.

Figure 2.6: (a) Basic set-up of dilatometer (b) Dilatometer with a differential system

Duxson et al. (Duxson, Lukey et al. 2007) and Rickard et al. (Rickard, van Riessen et al. 2010) proposed that first significant shrinkage is due to dehydration of free water (100- 300°C). Hence, the water content in material is significant and the tailoring of water content has also been discussed for metakaolin-based geopolymers (Chapter 4) and fly ash-based geopolymers (Chapter 7) respectively of this thesis.

In temperature range 300-600°C, thermal deformation can be attributed to two phenomena. One is slight shrinkage due to the physical contraction of geopolymer caused by condensation reactions of the hydroxyl groups present in geopolymers to form shorter T-O-T linkages (where 'T' is aluminum or silicon atom) (Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007, Vickers, Riessen et al. 2015). Another is due to the phase transformations occurring in the secondary phases such as quartz especially in case of fly ash geopolymers and not so much for metakaolin-based geopolymers. It has been reported that quartz, a commonly found crystalline phase in fly ash, undergoes

transformation from low to high quartz at 573°C (Deer, Howie et al. 2013) causing thermal expansion.

Between 550-900°C second major shrinkage event occurs due to the densification of geopolymer; the geopolymer gel sinters and viscous flow fills the pores (Duxson, Lukey et al. 2007, Rickard, van Riessen et al. 2010). Since crystal growth causes expansion, the degree of crystal growth in this region can also affect the magnitude of thermal deformation (Duxson, Lukey et al. 2006). Mix composition and type of impurities might also affect the deformation. Inconsistency in trend has been reported by researchers in this temperature range. Rahier et al. (Rahier, Simons et al. 1997) and Rickard et al. (Rickard, van Riessen et al. 2010) experienced some thermal expansion events along with shrinkage caused by viscous sintering in this temperature range. Duxson et al. (Duxson, Lukey et al. 2007) and Dombrowski et al. (Dombrowski, Buchwald et al. 2007) measured only shrinkage events while Barbosa et al. (Barbosa and MacKenzie 2003) experienced dimensional stability of geopolymers in this region.

Duxson et al. (Duxson, Lukey et al. 2006) reported for metakaolin-based geopolymers that the thermal shrinkage is influenced by composition of alkali activating solution (Si/Al ratio) as well as the type of alkali cation. Using potassium as alkali cation, thermal shrinkage was reduced when compared to using sodium as alkali cation. Duxson et al. (Duxson, Lukey et al. 2007) also observed that although alkali cation type does not significantly affect the onset temperature of crystallization and quantity of crystalline phases developed in geopolymers, it affects the onset temperature of densification in the order $K > Na > K > Na$. The amount of crystalline phase and gel viscosity of geopolymers were thought to be critical in determining the extent of shrinkage during densification.

Bakharev (Bakharev 2006) studied the effect of alkali cation (sodium and potassium) on thermal deformation of fly ash geopolymers. However, the effect was studied only briefly without significant tailoring of the mix design. The thermal deformation measurements were ex-situ hence less precise than the in-situ measurements. Since, for fly ash-based geopolymers there has been limited research studying the effect of alkali cation on its thermal deformation, it has been investigated and included in Chapter 6 of this thesis.

High temperature exposure causes thermal shrinkage/ expansion in geopolymers which in turn causes macro-cracking. Kong et al. (Kong, Sanjayan et al. 2007) found that metakaolin-based geopolymers required much higher amount of water as compared to fly ash-based geopolymers due to metakaolin being finer than fly ash and also due to plate-like morphology of metakaolin as compared to spherical shape particles of fly ash. Macro-cracks in the order of 0.1-0.2 mm were noticed on the surface of metakaolin geopolymer samples whereas fly ash geopolymer samples had no such cracks. Bernal et al. (Bernal, Bejarano et al. 2012) reported the macro-cracking in metakaolin-based geopolymer pastes subject to elevated temperatures could be reduced by addition of refractory aluminosilicate particles and fibers.

2.2.3 Macro-scale properties

A. Compressive strength

Changes in the compressive strength are significant in evaluating the high temperature performance of geopolymers. These changes can be affected due to structural and phase composition changes. Structural changes can include cracking, pore structure changes, densification, sintering, melting etc. Phase composition changes can be growth or destruction of crystals and transformations in geopolymer paste. The expansion of secondary phases such as in fly ash based geopolymers and the

deformation of aggregates also affect strength. Some of these changes may even enhance the mechanical properties. Densification of geopolymer causes reduction in the voids and enhances the mechanical strength (Riessen, Rickard et al. 2009). Sintering reactions cause stronger bonding between particles and thereby enhance mechanical strength. Geopolymer mix composition and presence of secondary phases would affect the temperature of densification and sintering.

Kong et al. (Kong, Sanjayan et al. 2008) studied the behavior of metakaolin-based geopolymer matrix exposed to 800°C. Si/Al ratio seemed to be a key parameter. The deterioration of compressive strength reduced with increasing Si/Al ratio. This effect was very prominent at high Si/Al ratios (>1.5) where the strength reductions observed were very small of the order of 5%. This latter observation was attributed partly to sintering of unreacted Si-rich particles in the mixtures. The effect of high temperature on compressive strength was studied in this work only for a single temperature regime of 800°C. Studying this effect over a wider range of temperatures, with proper selection of mix design parameters and to a greater depth would lead to a comprehensive understanding about the mechanical properties of metakaolin-based geopolymers subject to high temperature. This research gap has been addressed in Chapter 4 of this thesis.

Kong et al. (Kong, Sanjayan et al. 2007) compared the residual compressive strength after exposure to elevated temperatures for fly ash and metakaolin based geopolymer matrices. Fly ash geopolymers gained strength (6%) while metakaolin geopolymers lost strength (34%) after exposure to 800°C in a furnace for one hour. A large number of small pores facilitating the escape of moisture on heating and sintering of un-reacted fly ash particles were suggested to be the reasons for the strength increase in fly ash-based geopolymers. Also, since metakaolin geopolymers have higher moisture content than fly ash geopolymers, they are prone to a greater damage on exposure to high

temperatures. Water/solids ratio is thus an important factor to be considered while designing geopolymers for fire-resistance. The significance of water/solids ratio in determining the geopolymer properties at ambient conditions and on exposure to high temperature has been investigated in detail and included in Chapter 3, 4, 6 and 7 of this thesis. Further, since fly ash based-geopolymers outperform metakaolin-based geopolymers especially in high temperature performance, the Chapters 5, 6 and 7 have been dedicated to investigate the performance of geopolymers synthesized from locally available fly ash.

Kong et al. (Kong and Sanjayan 2010) also studied the behavior of geopolymer and geopolymer/aggregate composites when exposed to elevated temperatures. The strength of the fly ash-based geopolymer declined with the inclusion of aggregates i.e. geopolymer/aggregate composites caused by the differential thermal expansion between the geopolymer and aggregates. Separate dilatometry tests showed that while aggregates underwent expansion at elevated temperatures, the geopolymer matrix experienced contraction.

The importance of reactive Si/Al ratio and iron content of the fly ash on compressive strength after high temperature exposure was highlighted to a certain extent by Rickard et al. (Rickard, Williams et al. 2011, Rickard, Temuujin et al. 2012). Rickard et al. (Rickard, Kealley et al. 2015) also compared the thermally induced micro-structural changes of two fly ash mixes -one high reacted and one low reacted. In these works, fly ashes from different sources were assessed for their suitability to produce geopolymers for high temperature applications. Although the assessment of different fly ash sources is important, nonetheless, the knowhow of tailoring the geopolymer mix using a single fly ash is also very important. Not all geopolymer formulations possess good thermal resistance and the thermal performance greatly depends on mix design factors such as Si/Al ratio, Al/Na ratio and water/solids ratio other than the factors such as curing

condition, precursor type and alkali cation type. Hence, the effect of mix design factors on mechanical properties after high temperature exposure has been discussed in Chapter 4 for metakaolin-based geopolymers and in Chapter 7 for fly ash-based geopolymers.

Fernandez-Jimenez et al. (Fernández-Jiménez, Pastor et al. 2010) and Kovalchuk et al. (Kovalchuk and Krivenko 2009) suggested that the total alkali content in the geopolymer system is significant in determining the room temperature mechanical properties as well as the high temperature properties. Hence, optimum alkali content is desirable so as to attain a good geopolymer mix with sufficient initial strength and least damage after heating. Bakharev (Bakharev 2006) studied the effect of alkali cation (sodium and potassium) on thermal performance of fly ash geopolymers. It was reported that potassium based geopolymers performed better than sodium based since they underwent increase in compressive strengths after thermal exposure whereas sodium based geopolymers experienced strength reduction. However, it was reported that due to large changes in the compressive strength and deformation of the geopolymer samples on thermal exposure they were unsuitable especially for refractory applications. It is therefore important to adjust the geopolymer mix design such that stable strengths and less volume shrinkage on thermal exposure are realized. For fly ash-based geopolymers there has been limited research studying the effect of alkali cation on its thermal properties. Hence, this research gap has been addressed in 6 of this thesis.

B. Fire-induced spalling and ISO fire tests

Geopolymer based binders have shown inherently superior fire resistance as compared to Portland cement based binders (Vickers, Riessen et al. 2015). Joseph Davidovits (Davidovits 1999) observed that geopolymer cements provide excellent fire resistant properties up to 1200°C. Two complementary properties due to which this geopolymer binder was an active fire barrier are mentioned below:

- i. Nano-porosity in 3-D structure allows physically and chemically bonded water (hydroxyl groups -OH) to migrate and evaporate without damaging the hardened geopolymer. The compressive strength of hardened geopolymer was 20 MPa after 3 h at 1100°C (90 MPa at 20°C). By comparison, high-performance Portland blended cement (100 MPa at 20°C) exploded between 300°C and 400°C, because hardened Portland paste does not allow any release of vapor pressure.
- ii. The same bonded water (-OH groups) provides high endothermic properties to the substrate. Endothermic regulation is a function of Si/Al ratio. For a 10 mm thick panel exposed to a 1000°C flame, the measured back-side temperatures after 30 minutes of exposure reached 180°C, 270°C and 300°C respectively for 3 different geopolymers, namely, Na-Poly (sialate), K-Poly (sialate-siloxo) and K-Poly (sialate-disiloxo).

Zhao et al. (Zhao and Sanjayan 2011) concluded that, when compared at the same strength level, the geopolymer concrete possessed higher spalling resistance in a fire than Portland cement concrete due to its increased porosity (measured using surface exposure test and standard gas furnace fire test). Geopolymer concrete was found to have more connected pores (measure by sorptivity test), hence, it was suggested that the water vapor could escape from the geopolymer matrix quicker than in Portland cement concrete, resulting in lower internal pore pressure.

Provis et al. (Provis 2010) conducted fire testing on geopolymer concrete derived from coal fly ash and metallurgical slag, reacted with sodium silicate solution and using quartz sand and crushed granite as aggregates. Geopolymer concrete panels (4'×4'×6") were tested following the standard time-temperature curve (ISO 834-1/EN 1363-1/ASTM E119). The rate of thermal transport was found to be low and very minor degree of structural damage was observed during the 4-h fire test (**Figure 2.7**).

Figure 2.7: Geopolymer concrete panel (4'x4'x6'') after exposure to standard fire curve for duration of 4 h. No spalling observed (Provis 2010)

2.3 Fire performance of Portland cement concrete vs geopolymer concrete

It is very important and interesting to understand the differences between the performances of Portland cement concrete as compared to geopolymer concrete. The **Table 2.3** describes some of the differences. It can be observed in the table that both Portland cement concrete and geopolymer concrete are incombustible. However, the thermal conductivity for geopolymer concrete could be lower than OPC concrete. Geopolymer concrete has shown better spalling resistance compared to OPC concrete. This has been attributed to the interconnected pore structure in geopolymers as well as to the finding that water does not form part of the chemical structure in geopolymers. In case of OPC concrete, high temperature heating seriously affects the chemical structure of the hydration products such as calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) while the chemical structure of geopolymers is little affected by the dehydration reactions. Further, strength loss in geopolymers subject to high temperature heating could be prevented in geopolymers by careful selection of binder and aggregates.

Table 2.3: Fire performance of Portland cement concrete Vs geopolymer concrete

	Portland Cement Concrete	Geopolymer concrete
Combustibility	Incombustible, does not burn	Incombustible, does not burn (Davidovits 1989, Davidovits and Davidovics 1991, Lyon, Balaguru et al. 1997)
Thermal Conductivity	1–4 W/mK, at least an order of magnitude lower than that of steel (46 W/mK) (Khoury 2008).	0.2-0.4 W/mK for geopolymer binder (Davidovits 2008)
Spalling Resistance	Can experience spalling during fire.	Better spalling resistance than OPC concrete (Davidovits 2008), (Davidovits 1999), (Zhao and Sanjayan 2011), (Sarker, Kelly et al. 2014)
Microstructural damage	Other than free water loss and beginning of loss of chemically bond water close to 80°C, calcium hydroxide starts dissociating close to 300-400°C, and calcium silicate hydrate undergoes a continuous breakdown subject to elevated temperatures. Due to loss in strength of cement paste as well as aggregates, at temperatures above 600°C concrete is considered structurally not useful.	There is loss of evaporable and chemically bonded water. But as compared to Portland cement concrete, geopolymers maintain microstructural stability. The chemical bonds in geopolymers do not breakdown even though a transformation from amorphous phase to crystalline phase is often observed at temperatures close to 1000 °C.
Strength loss	Loses strength with rise in temperature. By careful selection of aggregates, strength loss can be minimized up to 600°C. At further higher temperatures there is significant strength loss (Khoury 2008).	With appropriate aggregates geopolymer concrete provide excellent fire resistant properties up to 1200°C (Davidovits 2008)

2.4 Application of geopolymers for heat and fire resistance

There have been several applications of geopolymers as cements and concretes (Gourley and Johnson 2005, Pan, Sanjayan et al. 2009, Kong and Sanjayan 2010, Zhao and Sanjayan 2011, Huiskes, Keulen et al. 2016), heat and fire resistant material (Davidovits 1991, Büchler 1999, Davidovits 1999, Liefke 1999, Barbosa and MacKenzie 2003, Cheng and Chiu 2003, Pistol, Rickard et al. 2016, Shaikh and Hosan 2016, Ali, Sanjayan et al. 2017, Galiano, Leiva et al. 2017), thermal insulator (Buchwald, Hohmann et al. 2004, Temuujin, Rickard et al. 2011, Rickard, Vickers et al. 2013, Sakkas, Nomikos et al. 2013, Rickard and van Riessen 2014, Novais, Buruberri et al. 2016) and refractory material (Perera and Trautman 2005, Kamseu, Djangang et al. 2015). It also has applications in high tech composites (Lyon, Balaguru et al. 1997, Flowerday, Ledger et al. 2006, Giancaspro, Balaguru et al. 2006) and medicine (Jämstorp 2010). Geopolymers have been used to make heat-resistant lightweight concrete and composites for making abrasive and heat-resistant industrial instruments. They might be used to make composites filled with lightweight filler (vermiculite or perlite) for heat insulation of high-temperature equipment. They have been applied to make fireproof doors of elevators and as heat-resistant adhesive to install heat-resistant aerated concrete tiles to the hot surface of a stove (Provis and van Deventer 2009). Buchler (Büchler 1999) illustrated the use of Geopolymite resins and GPMC composites in the field of air filtration at high temperatures. Liefke (Liefke 1999) demonstrated different industrial applications of foamed inorganic polymers, geopolymers, for fire protection, sound absorption and thermal insulation (TROLIT foams). Varela and Privorotskaya (Benjamin Varela 2005) explained the use of geopolymer as concrete coating for fire protection. These industrial applications of geopolymers show the potential of geopolymers to be applied as a heat and fire resistant material.

2.5 Summary

In the background of this research, the need of a green construction material for structural applications and with admirable fire and mechanical performance was realized. Based on the above literature review, it can be anticipated that geopolymer has capacity to fit the bill. However, not all geopolymer formulations perform soundly at ambient as well as on high temperature exposure. Tailoring of mix design to produce geopolymers with good thermal stability is thus essential. Consequently, the research methodology shown in **Figure 1.6** and research framework, **Figure 1.7** was crafted. Research tasks described in Chapter 1 were carried out in order to address the specific knowledge gaps and Chapters 3-7 give details of these tasks.

Chapter 3

MIX DESIGN FACTORS AND STRENGTH PREDICTION OF METAKAOLIN-BASED GEOPOLYMER

This chapter is related to performance of metakaolin-based geopolymers at ambient conditions. Geopolymer is a promising alternative binder to Portland cement. However, the importance of mix design parameters affecting the mechanical properties of geopolymer has yet to be quantitatively assessed. This work evaluates the significance of the four common mix design parameters, namely Si/Al (molar ratio), water/solids (mass ratio), Al/Na (molar ratio) and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ (molar ratio), in determining compressive strength of metakaolin-based geopolymers through experiments and statistical analyses. In addition, machine learning-based classifiers were engaged for strength predictions. Results showed that Si/Al ratio is the most significant parameter followed by Al/Na ratio. Unlike ordinary Portland cement system, water/solids ratio is not the chief factor governing strength of metakaolin-based geopolymers. Machine learning-based classifiers were able to predict the compressive strength with high precision. The strength predictions can potentially guide preliminary mix proportioning of metakaolin-based geopolymers to achieve required strength grade without going through tedious (trial and error) mix formulation.

3.1 Introduction

Geopolymer is a term coined by Joseph Davidovits in 1978 for a class of inorganic, amorphous to semi-crystalline, three-dimensional silico-aluminate materials (Davidovits 1991). Geopolymerization involves chemical reactions among various aluminosilicate oxides with silicates under highly alkaline conditions, yielding polymeric Si–O–Al–O bonds (Xu and Van Deventer 2000). The most commonly used

aluminosilicate oxide sources are metakaolin and fly ash and their dissolution in alkaline medium leads to formation of individual alumina and silicate species which then co-polymerize to form geopolymers. An alkali metal salt and hydroxide are required for the dissolution of silica and alumina to proceed, as well as for the catalysis of the condensation reaction.

It has been reported that geopolymers possess excellent mechanical properties and fire resistance (Davidovits 1989, Davidovits 2008). There has been a wide variety of research and development of geopolymers as heat-resistant materials (Büchler 1999, Davidovits 1999, Liefke 1999, Cheng and Chiu 2003), cements and concretes (Gourley and Johnson 2005, Pan, Sanjayan et al. 2009, Kong and Sanjayan 2010, Zhao and Sanjayan 2011), thermal insulation (Buchwald, Hohmann et al. 2004, Temuujin, Rickard et al. 2011, Rickard, Vickers et al. 2013, Rickard and van Riessen 2014), refractory material (Perera and Trautman 2005), high-tech composites (Lyon, Balaguru et al. 1997, Flowerday, Ledger et al. 2006, Giancaspro, Balaguru et al. 2006), and for medical applications (Jämstorp, Forsgren et al. 2010). Geopolymer cement or binder is a promising alternative to ordinary Portland cement (OPC). Portland cement production is one of the principal causes of greenhouse gas emission whereas geopolymer when used as a binder can utilize industrial by-products such as coal fly ash (Duxson, Fernández-Jiménez et al. 2007, Rickard, Williams et al. 2011) and/or ground granulated blast-furnace slag (GGBS) (Bernal, Rodríguez et al. 2011) as raw materials. In this manner, it serves as a green construction material with immense potential for sustainable development.

It is known that water-to-cement ratio is the most significant factor in determining the compressive strength of OPC binders. Unlike OPC binders, the importance of mix design parameters affecting the mechanical properties of geopolymer binder has yet to be quantitatively assessed. Previous research works on this important topic are limited

and have shortcomings. It has been suggested by Kriven et al. (Kriven, Bell et al. 2007) that the Si/Al ratio in the range between 1.75 and 2.0 produces metakaolin-based geopolymers with the highest compressive strength. Duxson et al. (Duxson, Provis et al. 2005) studied the effect of Si/Al ratio on the compressive strength and microstructure development of metakaolin-based geopolymers. He concluded that compressive strength increased with increasing Si/Al ratio in the range 1.15 to 1.90. In that series of mixes, the Al/M ('M' being the alkali cation) ratio was kept as unity and the alkalinity (H_2O/Na_2O) was maintained constant. Water-to-solids ratio, however, reduced with an increase of Si/Al ratio. Thus, it cannot be ascertained if the increase in the compressive strength of geopolymer was due to an increase of Si/Al ratio, a reduction of water-to-solids ratio, or a combination of the two.

Kong et al. (Kong, Sanjayan et al. 2008) observed that the compressive strength of metakaolin-based geopolymer varied with Si/Al ratio. Kong et al.'s results, however, were quite different from Duxson's findings since the Al/M ratio in the former set of tests was not close to unity. Theoretically, one alkali cation is required to balance the negative charge on the tetrahedrally coordinated aluminum atom. Thus, it has been suggested that Al/M ratio should be close to unity (Rahier, Simons et al. 1997, Duxson 2006). The heat of reaction during geopolymerization which is indicative of the degree of reaction is inherently linked to the Al/M ratio and has been observed to increase until the Al/M ratio reaches unity, beyond which no greater heat is released (Duxson 2006). The importance of Al/M molar ratio has been highlighted in previous research works (Rahier, Simons et al. 1997, Duxson 2006).

Yunsheng et al. (Yunsheng, Wei et al. 2010) studied the effects of three parameters, viz. Si/Al ratio, H_2O/Na_2O ratio and Al/Na ratio on the mechanical properties and microstructure of calcined kaolin-based geopolymers in accordance with orthogonal design but only for a Na-PSDS (Poly-sialate-disiloxo) type geopolymer. Thus, the

effect of Si/Al ratio was studied within a narrow range between 2.75 and 3.25 and hence the importance of Si/Al ratio could not be singled out in their test results. According to Rahier et al. (Rahier, Simons et al. 1997), the H_2O/Na_2O ratio affects the geopolymer reaction. H_2O/Na_2O ratio determines the alkalinity of the system and affects the degree of geopolymerization. Oswaldo Burciaga-Díaz et al. (Burciaga-Díaz, Escalante-García et al. 2010) studied the influence of factors (such as blast furnace slag-to-metakaolin weight ratio, activator concentration and curing time) on the development of mechanical properties in a composite system based on blast furnace slag and metakaolin using a statistical approach. However, the effect of water content on geopolymers was not studied. Lyu et al. (Lyu, Wang et al. 2013) used statistical analysis to study the factors affecting the mechanical characteristics of metakaolin-based geopolymers without considering the effect of Si/Al ratio.

For fly ash-based geopolymers, Panagiotopoulou et al. (Panagiotopoulou, Tsivilis et al. 2015) used Taguchi method for experimental design and performed analysis of variance (ANOVA) on the results so as to assess the importance of the parameters. Kazemian et al. (Kazemian, Gholizadeh Vayghan et al. 2015) used multiple linear regression technique to quantitatively assess the parameters for fly ash-based geopolymers. However, both studies did not investigate the effect of Si/Al ratio on the compressive strength of fly ash-based geopolymers. In fact, many studies of fly ash-based geopolymers ignored the influence of Si/Al ratio and suggested that compressive strength of geopolymers is dependent on the water-to-solids ratio similar to that of OPC (Hardjito and Rangan 2005, Sumajouw and Rangan 2006, Wallah and Rangan 2006).

There is a need to clearly understand the importance of mix design parameters governing the development of compressive strength of geopolymers so as to tailor its properties for desired applications. This chapter evaluates the significance of four inter-independent mix design parameters, namely Si/Al molar ratio, water/solids mass ratio,

Al/Na molar ratio and $\text{H}_2\text{O}/\text{Na}_2\text{O}$ molar ratio, in determining compressive strength of metakaolin-based geopolymers through experiments and statistical analyses. A total of 35 geopolymers (using metakaolin as precursor and sodium-based alkali as activator) with a wide range of mix design parameters were synthesized and compressive strengths were measured. Attribute evaluation by means of correlation-based feature selection (CFS) algorithm and ANOVA were engaged for data analyses to evaluate the significance of the four mix design parameters contributing to compressive strength. Morphology of the specimens was obtained by means of scanning electron microscope (SEM), which reveals the influences of four mix design parameters on microstructure of geopolymers and provides physical reasoning and interpretation to the statistics results. Multiple machine learning-based classifiers including the random forests classifier, the Naïve Bayes algorithm, and the k-nearest neighbor (k-nn) classifier were used to predict compressive strength of metakaolin-based geopolymer based on the four mix design parameters.

3.2 Methodology

3.2.1 Experimental program

A total of 35 metakaolin-based geopolymer mixes with a wide range of the four parameters were synthesized in this study as shown in **Table 3.1**. The mixes were prepared by changing the proportions of metakaolin and sodium silicate solution. The concentration of sodium silicate solution was also varied. In some cases, fine rock powder ($d_{50} = 5.7 \mu\text{m}$) was added to the geopolymer mix as filler in order to study the influence of high Si/Al molar ratio on the compressive strength. Thus, experimental parameters of **Table 3.1** were established.

Table 3.1: Mix design and compressive strength of the thirty-five (35) metakaolin-based geopolymers synthesized in this study

Mix No.	Si/Al	water/solids	Al/Na	H ₂ O/Na ₂ O	Compressive strength (MPa)
1	1.03	0.52	1.37	11.00	15.97±0.75
2	1.03	0.52	1.00	8.50	30.24±1.25
3	1.03	0.67	1.00	11.00	20.91±1.13
4	1.25	0.52	1.23	11.00	21.51±3.61
5	1.25	0.52	1.00	9.30	21.11±1.63
6	1.25	0.62	1.00	11.00	19.80±0.90
7	1.50	0.52	1.11	11.00	54.88±2.78
8	1.50	0.52	1.00	10.20	53.55±4.46
9	1.50	0.56	1.00	11.00	55.86±2.85
10	1.59	0.31	0.57	11.30	61.63±18.79
11	1.60	0.47	1.00	10.00	44.80±2.15
12	1.60	0.48	1.00	10.00	49.68±1.57
13	1.69	0.34	1.51	11.30	67.35±3.19
14	1.70	0.45	1.00	9.45	63.00±3.45
15	1.75	0.45	1.00	10.00	55.68±2.68
16	1.75	0.46	1.00	10.00	58.68±1.97
17	1.75	0.52	1.00	11.00	63.48±3.75
18	1.85	0.39	1.21	11.30	69.81±2.12
19	1.88	0.39	1.17	11.30	77.56±17.09
20	1.90	0.51	1.00	11.55	61.28±3.56
21	1.90	0.54	1.00	12.20	52.32±4.46
22	2.00	0.48	1.00	11.00	66.67±5.19
23	2.00	0.52	0.91	11.00	72.51±2.43
24	2.00	0.52	1.00	11.90	65.78±2.38
25	2.11	0.45	0.93	11.30	62.54±8.08
26	2.16	0.46	0.88	11.30	75.53±8.59
27	2.26	0.48	0.82	11.30	78.96±11.01
28	2.55	0.53	0.66	11.30	33.44±13.09
29	2.72	0.55	0.59	11.30	47.60±8.79
30	2.80	0.56	0.57	11.30	43.57±3.12
31	3.47	0.63	0.42	11.30	21.10±5.95
32	3.80	0.66	0.36	11.30	32.26±4.32
33	3.95	0.67	0.35	11.30	12.04±1.36
34	4.42	0.69	0.30	11.30	3.58±0.33
35	6.34	0.76	0.19	11.30	0.00

Metakaolin is rich in SiO_2 and Al_2O_3 and therefore is an ideal precursor for geopolymer formation. Metakaolin easily participates in geopolymerization compared to other precursors such as fly ash due to its highly amorphous nature. Thus, metakaolin geopolymer system is often used as a model system to understand geopolymer chemistry (Provis and van Deventer 2009). Metakaolin was supplied by BASF and chemical composition of the material is included in **Table 3.2**. As can be seen, metakaolin used in this study has about 97% of SiO_2 and Al_2O_3 in total. The mean particle size of metakaolin was $1.3\ \mu\text{m}$ and its XRD pattern is shown in **Figure 3.1**. In the XRD pattern, a hump could be observed in the $2\ \theta$ range between 15° and 35° . This hump represents typical amorphous nature of metakaolin. A few peaks corresponding to muscovite, a commonly found impurity in metakaolin, were also detected in the diffractogram of metakaolin.

Table 3.2: Chemical composition of Metakaolin

Chemical Composition	SiO_2	Al_2O_3	Na_2O	K_2O	TiO_2	Fe_2O_3
Weight percentage (%)	53.0	43.8	0.23	0.19	1.70	0.43
Chemical Composition	CaO	MgO	P_2O_5	SO_3	LOI	
Weight percentage (%)	0.02	0.03	0.03	0.03	0.46	

Figure 3.1: XRD pattern of metakaolin (star refers to muscovite, a commonly found impurity in metakaolin)

Sodium-based alkali was used as the activator for the synthesis of geopolymer in the current study. To prepare sodium hydroxide solution, a calculated quantity of NaOH pellets (99.8% in purity, purchased from Schedelco Pte. Ltd) was dissolved in ultrapure water from Milli-Q water filtration station. Various amounts of amorphous silica (Fumed Silica, CAB-O-SIL® M-5) were dissolved into the freshly prepared hot sodium hydroxide solution using a magnetic stirrer under room temperature to obtain desired composition of sodium silicate solution. The amorphous silica or fumed silica is a manufactured product from Cabot Cooperation, Illinois, USA. It has more than 99.8% SiO₂ in a fine powder form. The dissolution of fumed silica in sodium hydroxide solution by the magnetic stirrer was done till a clear solution was obtained. The solution was allowed to cool down and was then used the next day for geopolymer synthesis.

To prepare geopolymer specimens, metakaolin powder was mixed with sodium silicate

solution of various concentrations in a planetary mixer (Kenwood Titanium Timer Major KMM040) for ten minutes. The fresh paste was poured into 50 mm cube molds in two lifts. To ensure proper compaction and removal of entrapped air bubbles, the molds were vibrated after each lift. The molds were then covered with plastic to avoid water evaporation. The specimens were cured at ambient conditions in the temperature range of 25-30°C for 24 h. After which, the specimens were de-molded and sealed in plastic bags at ambient conditions till the testing date.

The 7-day compressive strengths were measured using a compression testing machine with a loading rate of 60 kN/min (ASTM 2016). At least three samples were tested for each mix to determine its compressive strength. The average values and the standard deviation are summarized in **Table 3.1**. A thermal field emission SEM (JSM-7600F) was used to observe the microstructure of specimens at magnification levels of 10k. Samples were taken from fractured surfaces of cubes after the compression test. Samples were first oven-dried at 105°C for 24 h to remove all evaporable water. After which, selected samples were mounted on a stub using a carbon tape and coated with a platinum layer using a JEOL sputter coater (JFC-1600 Auto fine coater) employing a 20 mA current for a duration of 30 seconds prior to SEM imaging.

3.2.2 Statistical analyses

In a geopolymer mix design, it is not possible to keep three of the four parameters (Si/Al molar ratio, water/solids mass ratio, Al/Na molar ratio and H₂O/Na₂O molar ratio) constant while varying only one parameter to study its influence. Noting the inter-dependency of the parameters, statistical analyses were engaged to evaluate the relative importance of the four mix design parameters of metakaolin-based geopolymers. To enhance reliability of the statistical analyses, another 36 metakaolin-based geopolymer mixes using sodium-based alkali as the activator with complete

information of mix design parameters and the corresponding value of compressive strength were collected from literature as shown in the Table A1 in appendix (Barbosa and MacKenzie 2003, Rowles and O'Connor 2003, Duxson 2006, Kriven, Bell et al. 2007, Yunsheng, Wei et al. 2010, Mo, He et al. 2014, Sarkar, Dana et al. 2015). Overall, a set of 71 data points (35 from the current study and 36 from published literature) was used for the statistical analyses. Two well-known statistical analyses methods, namely attribute evaluation and analysis of variance (ANOVA), were used in the current study and have been described below.

Attribute evaluation

Attribute evaluation is a data mining procedure which estimates the utility of attributes for a given task. In this study, correlation-based feature selection (CFS) algorithm, a filter method, was adopted as the attribute selection method for feature ranking, i.e. to rank the importance of the four parameters on compressive strength. Given a full attribute set, CFS searches an optimal subset of attributes which are highly correlated with the class label, but uncorrelated among them. The hypothesis behind attribute correlation evaluation performed by CFS is that “a good feature subset contains features highly correlated with (predictive of) the classification, yet uncorrelated with (not predictive of) each other”. This hypothesis relies on ‘attribute-class’ correlation, indicating the correlation of the attribute with the target class, and on the ‘inter-correlation’ amongst the attributes which indicates correlation between any two attributes.

The merit M_s for each subset of k features is calculated as below.

$$M_s = \frac{k\bar{r}_{cf}}{\sqrt{k + k(k-1)\bar{r}_{ii}}} \quad (1)$$

For each value of k , all possible subsets are chosen and merit values are computed. The subset which results in the highest value of the merit is given as the output by CFS. In Eqn. (1), $\bar{r}_{cf}$ is the average correlation between feature and class, and $\bar{r}_{ii}$ is the average inter-correlation between two features. The heuristic metrics $\bar{r}_{cf}$ and $\bar{r}_{ii}$ are calculated as the symmetrical uncertainty (SU) given in Eqn. (2) {Hall, 1999 #469.

$$SU = 2.0 \times \left[\frac{H(X) + H(Y) - H(X,Y)}{H(X) + H(Y)} \right] \quad (2)$$

Where, $H(X)$ is defined as entropy, given by:

$$H(X) = - \sum_{x \in X} p(x) \log_2(p(x)) \quad (3)$$

Here, $p(x)$ is the probability of an instance x being chosen at random from X ($x \in X$). The output of CFS is in the form of a subset (of the original attributes) which has the highest merit.

Attribute selection is performed using the implementation of CFS provided in the Weka machine learning suite. The final output of CFS is in the form of a single subset of attributes for each fold of the k -fold cross-validation ($k=5$) over the entire dataset. The k -fold cross-validation splits the dataset into k parts. The $(k-1)$ parts are used for building/training the model and the remaining one part is used for testing it. This is repeated k times and each time a different part is used for testing. The final result is an average over all k runs. Since the model is tested k times with a different test set in every run, this achieves a better learning model than a common training-testing split ratio of 2:1, i.e. two-third of the ‘labeled’ data is used to build and train the detection model while the remaining one-third (which is also labeled) is used to determine the accuracy of the model. Given a relatively small dataset of the current study, a 5-fold cross-validation was performed over the 71 datasets for attribute selection.

Analysis of variance (ANOVA)

Multivariate adaptive regression splines (MARS) technique developed by Jerome Friedman (Friedman 1991) in 1991 was used to model the dependence of compressive strength on multiple predictor variables, i.e. Si/Al ratio, water/solids ratio, Al/Na ratio and H₂O/Na₂O ratio in the current study. MARS is a method for flexible nonparametric regression modeling that can help to solve the current problem. For moderate sample size N ($50 \leq N \leq 1000$) and a moderate to high dimension n ($3 \leq n \leq 20$) as in the current study ($N = 71$ and $n = 4$), MARS is a suitable methodology (Friedman 1991). ARESLab (Jekabsons 2016) is a MATLAB Octave toolbox for building piecewise-linear and piecewise-cubic regression models using MARS technique. Some functions from this toolbox were used to build the MARS model in MATLAB and perform analysis of variance (ANOVA) on the collected compressive strength data. The most significant parameter affecting compressive strength was determined by comparing the value of generalized cross validation (GCV) score and standard deviation (STD) corresponding to the four parameters.

3.2.3 Strength prediction

Prediction of the compressive strength was performed using machine learning based classifiers. To facilitate easy and intuitive evaluation of the worth of the four attributes (Si/Al ratio, water/solids ratio, Al/Na ratio and H₂O/Na₂O ratio), numeric values of strength were divided into three categories of low, medium and high strength. Thus, the ‘target class’ for any 4-attribute tuple was represented by one of these categories. The three categories were made via a simple approach of dividing the numeric values of compressive strength into three equal-sized bins estimated from the full range of strength values of the 71 data points, i.e. from 0 to 81 MPa. Thus, the size of each bin was chosen to be 27 MPa and compressive strength less than 27 MPa was given a ‘low’ class label, strength between 27 and 54 MPa was categorized as ‘medium’, and strength above 54 MPa was labeled as ‘high’.

Three classifiers including the random forests classifier, the Naïve Bayes algorithm, and the k-nearest neighbor (k-nn) classifier were trained and the results were compared in this study. While decision trees are fast and easy to train, they tend to create complex tree structures and over-fit the data. In statistics, a good fit refers to how closely the model's predicted values are to the observed values. However, an over-fit model closely predicts training dataset, but it has poor fit with new dataset. Ideally, one wants a model which is at the sweet spot between under-fit and over-fit. The random forests classifier creates an ensemble of decision trees and output the final class that is the mode of the classes output by individual trees. The Naïve Bayes theorem is a simple probabilistic classifier based on applying Bayes' theorem. An advantage of Naïve Bayes method is that it requires a small amount of training data for classification, which is particularly useful for the current task. The k-nn classifier classifies instances based on the class label of k nearest neighbors. The k-nn method is a simple approach towards classification and does not over-fit the training data.

Similar to the attribute selection, all models were trained using a 5-fold cross-validation over the entire dataset, including selecting parameters for various models such as the value of k for the k-nn classifier. Random forests classifier was trained with multiple values of individual trees. The number of trees was incremented in each run. Value of ten trees was judged to be suitable since it achieved highest accuracy of classification of compressive strength. The value of k for k-nn was also determined via cross-validation and k=3 was found to give the highest accuracy of classification. For performance evaluation, established metrics such as Precision, Recall and False Positive rate were used. These are briefly defined as follows:

Precision is the ratio of the number of relevant records retrieved to the total number of relevant and irrelevant records retrieved. It is given by $TP / (TP+FP)$;

Recall (or True Positive Rate) is the ratio of the number of relevant records retrieved to the total number of relevant records in the complete dataset. It is given by $TP / (TP+FN)$; and

False Positive rate is given by the total number of relevant records missed over the total number of relevant records in the complete dataset. It is given by $FP / (FP+TN)$;

where TP stands for True Positive, a relevant record classified as relevant; TN stands for True Negative, an irrelevant record classified as irrelevant; FP stands for False Positive, an irrelevant record classified as relevant; and FN stands for False Negative, a relevant record classified as irrelevant.

3.3 Results and discussion

3.3.1 Experimental results

Figure 3.2 shows the influence of the four mix design parameters on compressive strengths of 7-day-old metakaolin-based geopolymers synthesized in the current study. As can be seen in **Figure 3.2(a)**, a clear trend shows that compressive strength increases with increasing Si/Al ratio first, peaks at Si/Al ratio close to 2, and decreases with increasing Si/Al ratio afterwards. It had been shown that as the Si/Al ratio is gradually increased from 1.15 to 2.15, due to an increase in Si-O-Si linkages (which are stronger than Si-O-Al linkages) as well as due to a simultaneous improvement in the geopolymer microstructure, the compressive strengths would keep increasing up to Si/Al = 1.90 (Duxson, Provis et al. 2005). It was also shown that a further increase in Si/Al ratio would cause an increase in the quantity of unreacted metakaolin. These unreacted metakaolin particles may in turn act as defect sites causing weakening of material and reduction in compressive strength. This suggests a strong influence of Si/Al ratio in determining the compressive strength of metakaolin-based geopolymers. Similar findings have been reported in previous literature (Duxson, Provis et al. 2005, Kriven, Bell et al. 2007).

Figure 3.2: Dependence of compressive strengths of metakaolin-based geopolymers on (a) Si/Al, (b) water/solids, (c) Al/Na, and (d) H₂O/Na₂O ratios

As for the dependence of compressive strength on water/solids ratio, while a general trend shows the strength decreases with increasing water/solids ratio, strong variation in compressive strength at the same water/solids is also observed as indicated by solid oval in **Figure 3.2(b)**. This indicates that water/solids ratio alone does not determine compressive strength of metakaolin-based geopolymers, which is in contrast to the OPC system where water-to-cement ratio is the chief factor controlling the micro-porosity and compressive strength. Detailed discussion can be found in section 3.3. The

general trend showing decrease in strength with increasing water/solids ratio is mainly attributed to simultaneous change in Si/Al ratio of the mix as shown in **Figure 3.3**. As can be seen, water/solids ratio in the current study generally increases with increasing Si/Al ratio. This is particularly true for Si/Al ratio larger than 2 and thus the strength decreases with increasing water/solids ratio.

Figure 3.3: Variation of water/solids ratio of the mix with the Si/Al ratio

As for the dependence of compressive strength on Al/Na ratio, **Figure 3.2(c)** indicates that the highest compressive strength can be attained when this ratio is close to one (as indicated by the rectangular box in the figure), which is the theoretical Al/Na ratio allowing charge balance between alkali cation and tetrahedrally coordinated aluminum as suggested in the literatures (Rahier, Simons et al. 1997, Duxson 2006, Provis and van Deventer 2009). When the amount of sodium is high, it causes efflorescence which is unsightly but may not always be harmful for the structural performance of the material (Provis 2009). However, compressive strength experienced significant variations (from 19.80 to 66.67 MPa) even at Al/Na ratio of unity as indicated by the oval in **Figure 3.2(c)**. This implies that although it is important for Al/Na ratio to be

close to unity, the values of the other three mix design parameters influence the development of compressive strength. As can be seen from **Figure 3.2(d)**, no obvious trend in compressive strengths versus $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio is observed indicating that $\text{H}_2\text{O}/\text{Na}_2\text{O}$ ratio did not significantly influence the development of compressive strength.

3.3.2 Statistical analysis

Attribute evaluation

Table 3.3 shows the results of attribute evaluation performed on the compressive strengths of the 71 metakaolin-based geopolymers (35 from the current study and 36 from published literature). Value in the second column (given by N) indicates the number of folds (out of 5) in which that particular attribute, which has the highest merit, was selected by CFS. Since the dataset is small, it is prudent to consider only those attributes as important which are selected by CFS in all the five folds of cross-validation. The output of CFS indicates that Si/Al is the most significant attribute since it was chosen in all 5 folds. The attributes Al/Na and water/solids were chosen in one-fold of CFS, and thus their significance is much less compared to Si/Al. The significance of $\text{H}_2\text{O}/\text{Na}_2\text{O}$ can be considered to be the least based on the CFS attribute evaluation method.

Table 3.3: Results of attribute evaluation by CFS

Attribute name	N*
Si/Al	5
Al/Na	1
water/solids	1
$\text{H}_2\text{O}/\text{Na}_2\text{O}$	0

* N denotes number of folds (out of 5) in which that particular attribute, which has the highest merit, was selected by CFS.

ANOVA

The output of ANOVA decomposition is given in **Table 3.4** below. ANOVA function number is listed in the first column. Standard deviation (STD) of the ANOVA function is given in the second column. This value gives a clue of its relative importance to the overall model. It can be interpreted in a way similar to a standardized regression coefficient in a linear model. Generalized cross validation (GCV) score for a model with all the basis functions corresponding to that particular ANOVA function removed is listed in the third column. The GCV score gives another indication of the importance of corresponding ANOVA function. It can help to evaluate whether that ANOVA function makes a significant contribution to the model, or whether it only slightly helps to improve the global GCV score (Friedman 1991).

Table 3.4: ANOVA decomposition results obtained from the MARS model developed for the compressive strength data

Function	STD	GCV	Variables in the function
1	45.8	530.7	Si/Al
2	26.5	514.0	Al/Na
3	92.4	332.6	Si/Al, water/solids
4	43.7	258.8	Si/Al, H ₂ O/Na ₂ O
7	28.6	257.6	H ₂ O/Na ₂ O
5	12.7	314.0	water/solids, Al/Na
6	11.5	386.8	water/solids, H ₂ O/Na ₂ O

Observing the STD and especially the GCV score in **Table 3.4**, the first and second ANOVA functions (corresponding to Si/Al ratio and Al/Na ratios respectively) are very important for the fit. The next two ANOVA functions have high standard deviation as well. Hence, removing these ANOVA functions would largely degrade the GCV score. In both these functions, Si/Al ratio is involved in interaction with water/solids and H₂O/Na₂O ratio respectively. Si/Al ratio is hence very significant parameter. Since last three functions have lower values of standard deviation and GCV score, the corresponding variables have lesser importance. Further analysis was carried out to give quantitative information about the relative importance of the variables (Jekabsons 2016) and the results are shown in **Figure 3.4**. It can be observed that Si/Al ratio is the most important parameter followed by Al/Na, H₂O/Na₂O and water/solids ratios.

Figure 3.4: Relative importance of the variables

In summary, both statistical analyses indicate that Si/Al ratio is a very significant parameter followed by Al/Na ratio. Water/solids ratio and H₂O/Na₂O ratio are of less importance among the four mix design parameters. Since Si/Al and Al/Na were found to be the most significant factors, a contour plot as shown in **Figure 3.5** was created to reveal the best ranges of Si/Al and Al/Na molar ratios suitable for the mix proportioning to design metakaolin-based geopolymers with desirable compressive strengths for any specific application. It was found that high strengths above 60 MPa could be attained by keeping Si/Al and Al/Na molar ratio of the geopolymer mixes roughly in the ranges of 1.7-2.2 and 0.8-1.2, respectively.

Figure 3.5: Compressive strength of metakaolin-based geopolymer as a function of Si/Al and Al/Na molar ratios (scale bar on the right indicates compressive strength in MPa)

3.3.3 Microstructure analysis

SEM micrographs of six geopolymers (mixes 1 to 3 and 22 to 24) are presented in **Figure 3.6**. As can be seen, geopolymers with Si/Al ratio of 1.03 (mixes 1 to 3) have very different microstructures than those with Si/Al of 2.0 (mixes 22 to 24). Microstructure of geopolymers with Si/Al ratio of 1.03 consists of dense particulates and large interconnected pores, whereas for geopolymers of Si/Al ratio of 2.0, the microstructure is more homogenous with smaller pores. As a result, compressive strength of geopolymers with Si/Al ratio of 2.0 (66-73 MPa) is much higher than that of geopolymers with Si/Al ratio of 1.03 (16-30 MPa). Similar findings were reported in previous literature (Duxson, Provis et al. 2005). Changes of other parameters, e.g. water/solids ratio from 0.48 to 0.67, only result in slight variation in morphology, porosity, and compressive strength.

Figure 3.6: Micrographs of metakaolin-based geopolymers with different mix design parameters and compressive strength (Si/Al=1.03-2.00, Al/Na=0.91-1.37, water/solids=0.48-0.67, H₂O/Na₂O=8.50-11.90, and f_c=15.97-72.51)

Microstructural similarity among the geopolymers with the same Si/Al ratio and a large difference with changes in Si/Al ratio indicates a strong influence of Si/Al ratio on the microstructure of geopolymers and the influences of the other three parameters (Al/Na, water/solids, and H₂O/Na₂O ratios) are not as significant. Unlike OPC system where water participates in cement hydration and determines overall porosity of paste (Neville 2011, Fang and Kayali 2013), geopolymer system is described as a biphasic gel of water and alumino-silicate binder where water acts as a reaction intermediate and is released during condensation to form pores and create the biphasic structure (Davidovits 1991). The porosity in geopolymers is determined by solution chemistry during geopolymerization, which is primarily a function of Si/Al ratio and alkali metal

cation type, while the absolute pore volume is determined by nominal water content (Duxson, Lukey et al. 2005, Duxson, Provis et al. 2005, Duxson, Lukey et al. 2006). The role of water in geopolymer system is therefore not the same as in OPC.

3.3.4 Strength prediction

The results obtained using Random forests classifier, Naïve Bayes classifier and k-nn classifier using the 4 attributes are given in **Table 3.5**. The precision obtained is as high as 83% indicating a good accuracy of prediction. Random forests classifier and k-nn classifier show higher precision than the Naïve Bayes classifier. This is because Naïve Bayes theorem holds a strong (naïve) independence assumption among the attributes; this is not valid for the four mix design parameters in the current study. As pointed out in Sec. 3.3, the four mix design parameters (Si/Al, water/solids, Al/Na and H₂O/Na₂O) are inter-dependent and it is not possible to keep three of them constant while varying only one parameter to reveal its influence. The false positives (FP) are in the range of 9 to 22% (with the majority being around 10-12 %) indicating not many misclassified instances. This is a moderate result keeping in view the limited dataset available. These results are encouraging and shed light on the suitability of using the four attributes (Si/Al, Al/Na, water/solids and H₂O/Na₂O ratios) in predicting compressive strength of metakaolin-based geopolymers through machine learning-based classifiers. The strength prediction potentially can guide preliminary mix proportioning of metakaolin-based geopolymers to achieve required strength grade without going through tedious (trial and error) mix formulation.

Table 3.5: Results of strength prediction of metakaolin-based geopolymer using machine learning-based classifiers

Class	Random forests of 10 trees			Naïve Bayes			k-nn (k=3)		
	Precision (%)	Recall (%)	FP rate (%)	Precision (%)	Recall (%)	FP rate (%)	Precision (%)	Recall (%)	FP rate (%)
Low	82	85	11	78	59	13	83	74	9
Medium	50	37	13	42	42	20	57	42	11
High	75	86	17	78	86	20	72	93	22

The results obtained through CFS or any other feature selection approaches are highly dependent on that particular dataset. Thus, the current results should be interpreted only for the current dataset. Availability of a larger dataset shall facilitate a more thorough understanding of the impact of different parameters in determining compressive strength of geopolymers. It should also be noted that the current study evaluated the impact of only four parameters. Further study is needed to understand the influence of factors such as metakaolin nature, curing time and temperature on the strength development.

3.4 Conclusions

This study evaluated the significance of four mix design parameters, namely, Si/Al ratio, water/solids ratio, Al/Na ratio and H₂O/Na₂O ratio, which influence compressive strength of metakaolin-based geopolymers through experiments and statistical analyses. Results showed that Si/Al ratio is the most significant parameter in determining compressive strength of geopolymers followed by Al/Na ratio. It was also found that unlike OPC, water/solids ratio is not a significant factor governing compressive strength of metakaolin-based geopolymers. Microstructure observations through SEM

facilitated physical reasoning of the statistics results and revealed that Si/Al ratio significantly influences the microstructure of geopolymers, while the other three parameters do have only minor influence on the morphology of geopolymers. Further, using the four attributes, compressive strength of geopolymers could be predicted by means of well-established machine learning approaches. The predictions could classify geopolymers into low, medium and high strength to a reasonable accuracy with high precision and false positives in range of 8 to 20% indicating not many misclassified instances. The strength prediction potentially can guide preliminary mix proportioning of metakaolin-based geopolymers to achieve required strength grade without going through tedious (trial and error) mix formulation.

Chapter 4

EFFECTS OF Si/Al MOLAR RATIO ON STRENGTH ENDURANCE AND VOLUME STABILITY OF METAKAOLIN GEOPOLYMERS SUBJECT TO ELEVATED TEMPERATURE

Good structural performance in a fire scenario necessitates that the structural material possesses chemical stability, deformation resistance and strength endurance. Excellent chemical stability for geopolymers has been reported in literature at a microscale. However, their performance at macroscale has not yet been systematically explored and the underlying mechanisms remain unexplained. In current study, effect of variation in Si/Al molar ratio on the meso- and macro-scale thermal stability of metakaolin geopolymers has been comprehensively investigated to discover the underlying mechanisms governing the performance. Results show that all the geopolymer samples experienced reduction in compressive strengths after exposure to high temperature up to 900 °C. Although, the geopolymer mixes exhibited good chemical stability at microscale, they possessed poor volume stability at mesoscale with very high thermal shrinkage. It was observed that thermal shrinkage induced crack formation dominates the residual strength for geopolymer mixes with Si/Al molar ratio ≤ 1.50 , while densification of matrix is the governing factor of the residual strength for geopolymer mixes with Si/Al molar ratio > 1.50 . Re-crystallization of nepheline at high temperature adversely affect the strength by inducing expansion and cracking of the geopolymer matrix. Geopolymer sample with Si/Al ratio 1.75 retained highest strength (6 MPa) because viscous sintering of geopolymer mixes with high Si/Al ratio at temperature beyond 600 °C enables localized healing of micro-cracks and densification of matrix which favored compressive strength gain after exposure to 900 °C. At an even higher Si/Al of 2.0, foaming of unreacted silica upon heating can lead to expansion and cracking of the sample which reduce the strength. It was observed that due to high

degree of cracking damage and low residual strength retention, it is essential to improve the macro-scale stability of metakaolin geopolymers for structural fire resistance applications.

4.1. Introduction

Geopolymer is a class of amorphous three-dimensional aluminosilicate material (Davidovits 1991, Kriven, Bell et al. 2006). The term "geopolymer" was first coined by Joseph Davidovits in 1976. The process of geopolymer formation involves a chemical reaction between various aluminosilicate oxides with silicates under high alkaline conditions, yielding polymeric Si-O-Al-O bonds (Xu and Van Deventer 2000). Metakaolin is the most commonly used model precursor for the study of geopolymers. Geopolymer binder is an attractive alternative to the ordinary Portland cement (OPC). Portland cement production is one of the principal causes of greenhouse gas emission. Geopolymer can be a greener construction material (Duxson, Provis et al. 2007, Weil 2007) because it can utilize industrial by-products such as coal fly ash (Provis and van Deventer 2009, Rickard, Williams et al. 2011) and/or ground granulated blast-furnace slag (Bernal, Rodríguez et al. 2011, Sakkas, Nomikos et al. 2013) as the aluminosilicate precursor. Use of wastes such as incinerated bottom ash (Chen. Z. 2016) for geopolymer synthesis has also been explored. Geopolymer thus has a great potential for sustainable infrastructure development. Geopolymer is understood to possess admirable mechanical properties and fire resistance (Davidovits 1989, Davidovits 2008). Research has been done to develop it as a heat resistant material (Davidovits 1991, Büchler 1999, Davidovits 1999, Liefke 1999, Barbosa and MacKenzie 2003, Barbosa and MacKenzie 2003, Cheng and Chiu 2003), as cement and concrete (Gourley and Johnson 2005, Pan, Sanjayan et al. 2009, Kong and Sanjayan 2010, Zhao and Sanjayan 2011), as thermal insulator (Buchwald, Hohmann et al. 2004, Temuujin, Rickard et al. 2011, Rickard, Vickers et al. 2013, Rickard and van Riessen 2014) and as a refractory material (Perera and Trautman 2005). Its use as a high-tech composite in aircrafts and

ships has also been investigated (Lyon, Balaguru et al. 1997, Flowerday, Ledger et al. 2006, Giancaspro, Balaguru et al. 2006).

To apply geopolymer as fire-resistant building material, its thermal performance should be examined at micro-, meso-, and macro-scales. Micro-scale refers to the micro-structural stability or chemical stability of the material subject to high temperature. Previous works have shown that geopolymers possess very good thermal stability at the micro-scale (Davidovits and Davidovics 1991, Barbosa and MacKenzie 2003, Barbosa and MacKenzie 2003, Bernal, Rodríguez et al. 2011). Geopolymers are generally amorphous at ambient conditions and on exposure to elevated temperature, they either retain their amorphous nature or transform to a crystalline microstructure. Whichever the case may be, the general agreement of researchers has been that geopolymers hold a stable inorganic framework after thermal exposure. This is in contrast to OPC which loses the stability of its hydration products (calcium silicate hydrate and calcium hydroxide) when exposed to elevated temperatures (Harmathy 1970, Harmathy 1993).

The ability of a material to resist volumetric change and thermally induced-cracking and to retain its compressive strength at elevated temperatures is referred to as the meso- and macro-scale thermal stability, respectively, in this study. Very limited studies have been published on high temperature response of metakaolin-based geopolymers at meso-scale (volume stability) and at macro-scale (strength endurance). This knowledge is necessary for any potential application of the material for structural applications. A previous study investigated the effect of high temperature on thermal shrinkage, weight loss, and composition of metakaolin-based geopolymers (Duxson, Lukey et al. 2007). However, such studies need to be extended to evaluate the thermal performance of the bulk geopolymeric material. An important study aimed towards this end was conducted by Kong et al. (Kong, Sanjayan et al. 2008). The study investigated effects of various factors such as kaolin calcination temperature, Si/Al ratio,

activator/metakaolin ratio on compressive strength (macro-scale) of metakaolin-based geopolymers subject to elevated temperatures. Yet, the fundamental mechanisms governing the strength performance at macro-scale were not clearly understood. Bernal et al. (Bernal, Rodríguez et al. 2011) studied the effect of temperature on compressive strength of geopolymers made from metakaolin/GGBS (Ground granulated blast furnace slag) blends. However, the study was conducted only for a single Si/Al ratio. Based on previous works (Duxson, Provis et al. 2005, Lahoti, Yang et al. 2017), Si/Al molar ratio strongly governs the microstructure and the mechanical properties of the geopolymer formed at ambient temperature. Hence, Si/Al molar ratio is likely to significantly affect the performance subject to elevated temperature as well.

The novelty of current work lies firstly in investigating the effect of variation in Si/Al molar ratio on the meso- and macro-scale thermal stability of metakaolin geopolymers in a systematic and comprehensive way, and secondly in discovering the underlying mechanisms governing the performance. To assess the thermal performance, residual compressive strengths of the geopolymer samples were measured subject to three temperature regimes. Damage and cracking patterns of samples before and after elevated temperature were observed. Thermal deformation of the geopolymer samples was measured using dilatometry. Micro-structural changes were observed using SEM and used to explain the thermal deformation characteristics. The chemical structure was characterized using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy to study the chemical stability of geopolymers.

4.2. Experiments

4.2.1 Raw materials

Metakaolin (MetaMax, BASF) was used as the precursor to synthesize geopolymer in current work. Metakaolin geopolymers are considered as model system to understand

geopolymer chemistry (Provis and van Deventer 2009). Metakaolin is produced by calcination of kaolinite clay at temperatures ranging from 500 to 800 °C depending on the purity and crystallinity of the precursor clay (Provis 2009). Metakaolin is largely X-ray amorphous. It easily takes part in geopolymerization reaction and is a purer system when compared to other geopolymer precursors such as coal fly ash or blast furnace slag. Chemical composition of metakaolin used in this study is given in **Table 4.1**.

Table 4.1: Chemical composition (by weight) of Metakaolin (MetaMax, BASF)

Composition	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	TiO ₂	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	SO ₃	LOI
Percent (%)	53.0	43.8	0.23	0.19	1.70	0.43	0.02	0.03	0.03	0.03	0.46

Sodium silicate solution was prepared by dissolving varying amounts of amorphous silica (fumed silica, Cabosil M5) into freshly prepared sodium hydroxide solution. The amorphous silica was more than 99.8 % pure SiO₂ in finely powdered form and was a manufactured product from Cabot Cooperation, Illinois, USA. Sodium hydroxide solution was prepared by dissolving a calculated quantity of NaOH pellets (99.8 % pure, Schedelco) into ultrapure water filtered through a Milli-Q water filtration station. The dissolution of fumed silica in sodium hydroxide solution was done to obtain a clear solution. The resulting sodium silicate solutions were stored for 24 h before use for geopolymer preparation to allow the solutions to cool down to room temperature and achieve equilibrium.

4.2.2 Mix design and sample preparation

The quantities of amorphous silica and NaOH pellets were taken such that the overall Si/Al molar ratio of metakaolin plus sodium silicate solution system was varied as 1.03,

1.25, 1.50, 1.75 and 2.0 for the five geopolymer mixes (mixes 1 to 5). The Al/Na molar ratios and H₂O/Na₂O molar ratios were kept constant at 1 and 11, respectively for the five mixes. Mix proportion of the five metakaolin geopolymers (mixes 1 to 5) is shown in **Table 4.2**.

Table 4.2: Mix proportion of metakaolin geopolymers

Mix No.	Metakaolin (kg/m ³)	NaOH (kg/m ³)	Fume silica (kg/m ³)	Water (kg/m ³)	Si/Al (molar ratio)	Water/solids (weight ratio)
1	743	256	0	575	1.03	0.67
2	707	243	81	547	1.25	0.62
3	670	231	163	519	1.50	0.56
4	637	219	237	493	1.75	0.52
5	608	209	304	470	2.00	0.48

Geopolymer specimens were prepared by adding metakaolin to the sodium silicate solution of various concentrations to obtain geopolymers with Si/Al molar ratios ranging from 1.03 to 2.0. The ingredients were mixed together in a Kenwood mixer (Titanium Timer Major KMM040) at a speed level 2 of the appliance for 10 min. The geopolymer slurry obtained was poured into cubic molds (50 mm) and cylindrical molds (8 mm diameter × 26 mm length) in two lifts. Molds were vibrated to remove the entrapped air and to consolidate the paste. Molds were then sealed using a plastic sheet to avoid the escape of moisture from the samples. The specimens were cured at ambient conditions (25-30 °C) for 24 h before de-molding. After that, they were de-molded and stored in plastic bags at ambient conditions (25-30 °C) till the date of testing.

4.2.3 Test methods

The 7-day old metakaolin geopolymer specimens (50 mm cube) were heated in a furnace to the target temperatures at a heating rate of 5 °C/min, held at that temperature for an hour, and then allowed to cool down slowly to room temperature in the furnace. Two target temperatures chosen were 300 and 900 °C. After removing the specimens from the furnace, visual observation was made first and images were taken using a Nikon camera. Residual compressive strength of 50 mm cubic specimens were measured using Tony Technik compression testing machine with loading rate of 60 kN/min (ASTM 2016). At least four specimens was tested for each mix at each temperature and the average value and standard deviation were reported. The specimen density was recorded for each specimen by dividing its weight by the volume prior to the compressive strength test. Specimens without exposure to elevated temperature were also documented and tested as the control.

Thermal deformation of geopolymers was measured using a TA Instruments Dilatometer (DIL 802L) at a constant heating rate of 5 °C/min up to a maximum temperature of 900 °C in an atmosphere of air. Cylindrical specimens of diameter 8 mm and length 25 mm were used. The results presented herein are an average of at least three measurements. Scanning electron microscopy (SEM) was conducted using a field emission-SEM (JSM-7600F) at magnification level 10,000 to observe the microstructure of the geopolymer at room temperature and after exposure to elevated temperatures. Geopolymer samples were taken from the fractured surface after the compression test. The samples were first oven dried and then mounted on a stub using a carbon tape and were coated with a platinum layer using a JEOL sputter coater (JFC-1600 Auto fine coater) using 20 mA current for duration of 30 s prior to SEM imaging. X-ray diffraction (XRD) powder diffractograms were obtained using Bruker D8 Powder XRD diffractometer with CuK α radiation. Samples were step scanned from 10 ° to 60° (2 θ) at 0.02° (2 θ) increment. FTIR spectra were obtained from 4000 to 400 cm⁻¹

using a Nicolet iS50 FT-IR spectrometer in attenuated total reflectance (ATR) mode. Spectra were collected with 64 transients at a resolution of 4 cm^{-1} in absorption mode at room temperature.

4.3. Results

4.3.1 Residual Strength

Figure 4.1 shows the compressive strength of the geopolymer samples before and after exposure to high temperature. It can be observed from the figure that the compressive strength of the unexposed samples increased with increasing Si/Al molar ratio from 1.03 to 2.0. Similar increase in ambient temperature mechanical strength of geopolymer samples with increase in Si/Al molar ratio has also been observed in published literatures (Duxson, Provis et al. 2005, He, Wang et al. 2016, Lahoti, Narang et al. 2017). This is related to the gel microstructure becoming more homogenous and pore sizes reducing with the increase in Si/Al ratio from 1.03 to 2.0, as observed in the SEM micrographs (**Figure 4.5**). This causes gel skeletal density to increase and the increase in gel volume would allow the material to bear higher compression loads. Furthermore, the Si-O-Si bonds in geopolymers, which are stronger than Si-O-Al bonds, increased in number as the Si/Al ratio was increased (Duxson, Provis et al. 2005).

Figure 4.1: Compressive strength of geopolymers after high temperature exposure

Further, after exposure to 300 °C, without any exception all the geopolymer samples experienced reduction in compressive strengths. The absolute values of strengths observed after exposure to 300 °C continued to follow the trend in compressive strength as observed for the unexposed samples, i.e. higher Si/Al ratio samples exhibited higher residual strengths. **Figure 4.2** plots the normalized compressive strengths of the geopolymer samples. For each Si/Al molar ratio, compressive strengths of the geopolymer samples were normalized by the compressive strength of the geopolymer sample at 25 °C. As can be seen, after exposure to 300 °C, the normalized compressive strength of the geopolymer samples first decreased and then increased with increasing Si/Al molar ratio.

Figure 4.2: Normalized compressive strength of geopolymers

After exposure to 900 °C temperature regime, geopolymer samples experienced even larger reduction in compressive strengths as compared to after exposure to 300 °C temperature regime. However, all the samples could maintain structural integrity. Geopolymer sample with Si/Al molar ratio equal to 1.75 retained highest strength (6 MPa) after exposure to 900 °C.

4.3.2 Crack pattern

Figure 4.3 shows the visual appearance of geopolymer samples and reveals the damage pattern and change of sample color after exposure to the high temperature regimes. Due to exposure of geopolymer samples to 300 °C, free water from the pores evaporated and escaped out of the samples generating cracks. Several fine and wide cracks in the order of 10s and 100s of microns respectively were observed. After exposure to 900 °C, geopolymer samples display more perceivable cracking damage than after exposure to 300 °C. All geopolymer samples barely showed fine cracks and were predominated by wide cracks in the order of 100s and 1000s of microns. Besides, mix 5 also

underwent some expansion events in contrast to other four mixes. Largely, it revealed that metakaolin geopolymers exhibit significant cracking damage after exposure to high temperature.

Figure 4.3: Visual observation of geopolymer samples (50 mm cubes) after high temperature exposure

4.3.3 Thermal deformation

Figure 4.4 shows the thermal deformation of the geopolymer samples with five different Si/Al molar ratios recorded through dilatometry. Shrinkage in metakaolin

geopolymers could be attributed to capillary stress, dehydroxylation reactions and viscous sintering for different temperature regions (Duxson, Lukey et al. 2007). The first shrinkage event was due to capillary stress caused by the dehydration of freely evaporable water. In **Figure 4.4**, up to 300 °C, it can be observed that all the five mixes experienced shrinkage in a narrow range of 5.5 to 7.5 %. This finding corresponds well with the previous research in which all geopolymer samples with Si/Al molar ratio in the range 1.15 to 2.15 experienced shrinkage in a narrow range too (Duxson, Lukey et al. 2007). In the temperature range 300-600 °C, continued shrinkage was observed in all the geopolymer samples due to the condensation of the hydroxyl groups present in these samples, to form shorter T-O-T linkages (where 'T' is aluminum or silicon atom) (Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007, Vickers, van Riessen et al. 2015).

Figure 4.4: Thermal deformation of the geopolymer samples observed using dilatometry

In the temperature range 600-900 °C, geopolymer samples with higher Si/Al ratios (mix 3 and mix 4) showed greater amount of shrinkage (3.5% and 6%, respectively) as compared to lower Si/Al ratio geopolymer samples (mix 1 and mix 2) with shrinkage 2% and 1.5%, respectively. This is because for lower Si/Al ratio geopolymer samples ($\text{Si/Al} \leq 1.40$) exposed to high temperature ($> 600^\circ\text{C}$), viscous sintering alone contributes to thermal shrinkage, while for geopolymers with Si/Al molar ratio > 1.40 , along with viscous sintering, collapse of highly distributed pore network is another factor contributing to thermal shrinkage (Duxson, Lukey et al. 2007). Thus in **Figure 4.4**, in general, higher Si/Al ratio mixes experienced higher extent of shrinkage in the temperature range 600-900 °C.

Further, mix 5 was noted to exhibit lowest shrinkage due to the presence of an expansion peak overlaid on its shrinkage curve. This expansion peak was possibly caused by foaming of unreacted silica upon heating, as the free water was removed (Provis, Harrex et al. 2012). The amount of unreacted phase has been found to increase with Si/Al ratio (Duxson, Lukey et al. 2005). Since mix 5 has highest Si/Al ratio, it is expected that it would have largest amount of unreacted phase that would cause the expansion peak superimposed on the shrinkage curve for this mix.

4.3.4 SEM observations

SEM images of metakaolin geopolymers with different Si/Al molar ratios before and after exposure to elevated temperatures are shown in **Figure 4.5**. As can be seen, prior to exposure to high temperature, for geopolymers with higher Si/Al molar ratio (> 1.50), the pores observed in SEM images were smaller compared to those with lower Si/Al molar ratio (≤ 1.50) due to the change in the lability of silicate species during the process of geopolymer formation (Duxson, Provis et al. 2005). Thus, for Si/Al ratio ≤ 1.50 , higher lability allows greater gel reorganization and densification during

geopolymerization which results in a microstructure with dense gel particles and large interconnecting pores. For $\text{Si}/\text{Al} > 1.50$, due to higher concentration of silicate species the lability of gel is low. This results in homogenous microstructure with porosity distributed in small pores.

Figure 4.5: Influences of Si/Al molar ratio and temperature on microstructure of metakaolin geopolymers

After exposure to high temperature, the common trend noted for all the geopolymer samples was a reduction in porosity and a more compact microstructure. This was more evident for samples exposed to 900 °C temperature regime and could be reasoned to the process of viscous sintering (He, Jia et al. 2011). Viscous sintering causes collapse of nano-pores, a stronger inter-particle bonding, healing of micro-cracks and densification of geopolymer matrix (Riessen, Rickard et al. 2009). It also leads to formation of a compact microstructure and smoother texture (Duxson, Lukey et al. 2006, Kong, Sanjayan et al. 2007) as observed in the current study as well.

Further, it could be observed through the SEM images that after exposure to high temperature, geopolymers with Si/Al molar ratio > 1.50 had lesser porosity and more compact gel structure compared to those with Si/Al molar ratio ≤ 1.50 . This could be explained based on literature that for geopolymers with Si/Al molar ratio < 1.40 , viscous sintering was the chief reason causing thermal shrinkage while for geopolymers with Si/Al molar ratio > 1.40 , along with viscous sintering, collapse of highly distributed pore network also contributed to thermal shrinkage at elevated temperature beyond 600 °C (Duxson, Lukey et al. 2007). The collapse of pore network can also be explained using Young-Laplace equation which states that the capillary pressure is inversely proportional to pore radius (Adamson and Gast 1997). Larger capillaries or pores have a larger volume-to-surface ratio and they develop smaller capillary stresses. Smaller capillaries have smaller capillary volumes and they develop larger stresses. Since, in current study, geopolymers with Si/Al ratio > 1.50 exhibited smaller pores at ambient temperature; when exposed to elevated temperature, they would develop larger stresses and would be easier to collapse compared to geopolymers with Si/Al ratio < 1.50 exhibiting larger pores at ambient temperature.

4.3.5 XRD analysis

Figure 4.6: XRD patterns of geopolymers corresponding to Si/Al ratios of (a) 1.03, (b) 1.25, (c) 1.50, (d) 1.75 and (e) 2.0, respectively, before and after exposure to high temperature

Material characterization using XRD was conducted to gain better understanding of the transformations in the geopolymers. Figure 4.6 displays the XRD patterns for the original metakaolin and geopolymer matrix before and after exposure to high temperature for all five geopolymer mixes. It could be observed in the figure for all the five geopolymers that the amorphous hump in the precursor metakaolin (centered around 22 degree 2θ) shifts to right (centered around 28-30 degrees 2θ) as a result of geopolymerization. After exposure to 300 °C, all the geopolymer samples exhibited good thermal stability and minimal phase changes. Whereas on exposure to 900 °C, formation of nepheline could be noted for all the geopolymer mixes (Duxson, Lukey et al. 2006).

4.3.6 FTIR analysis

Figure 4.7 shows the FTIR spectra of the original metakaolin and geopolymer matrix before and after exposure to high temperature for all the five geopolymer samples. It can be noted that the main asymmetric stretching band for T-O-T bond (where T is ‘Si’ or ‘Al’) in initial metakaolin is at 1054 cm^{-1} . This band was found to become narrower and shift to longer wavelengths 957, 957, 961, 961 and 970 cm^{-1} for geopolymer mixes 1, 2, 3, 4 and 5, respectively as a result of geopolymerization. Similar shifts have been observed previously by Fernandez-Jimenez et al. (Fernández-Jiménez, Palomo et al. 2008).

Figure 4.7: FTIR spectra of geopolymers corresponding to Si/Al ratios of (a) 1.03, (b) 1.25, (c) 1.50, (d) 1.75, and (e) 2.0, respectively, before and after exposure to high temperature

Due to exposure to 300 °C, for all the geopolymer mixes, the main asymmetric stretching band showed only slight broadening and little shift in the peak positions (962, 956, 960, 960 and 970 cm^{-1}) for mixes 1, 2, 3, 4 and 5, respectively. This chemical stability observed after exposure of samples to 300°C was consistent with the XRD observations. The slight broadening of the main asymmetric stretching band may be related to the structural changes caused by the dehydration of physically and chemically bonded water (Fernández-Jiménez, Pastor et al. 2010).

On exposure to 900 °C, slight broadening and small shift in the main asymmetric stretching band peak position (942, 955, 960, 957 and 958 cm^{-1}) were observed for the geopolymer mixes 1, 2, 3, 4 and 5, respectively. The formation of nepheline observed through XRD was confirmed by the appearance of peaks around 450 and 675 cm^{-1} and a shoulder at 1080 cm^{-1} (Farmer 1974) for all geopolymer mixes in the FTIR spectra.

4.3.7 Discussion

As shown in **Figure 4.1**, all the geopolymer samples experienced reduction in compressive strengths after exposure to 300 °C. While metakaolin geopolymer mixes possessed good chemical stability at microscale as shown from the XRD and FTIR results (**Figures 4.6** and **4.7**), they exhibited poor volume stability at mesoscale with very high thermal shrinkage (**Figure 4.4**), which causes crack formation (**Figure 4.3**) and reduces mechanical strength at macroscale (**Figure 4.1**). On the other hand, thermal shrinkage may lead to densification of matrix as shown in the SEM images (**Figure 4.5**) which favors compressive strength gain by allowing more uniform stress gradients during load application (Van Riessen, Rickard et al. 2009). Such densification of matrix is more pronounced for mixes with high Si/Al ratio (**Figure 4.5**). As a result, the normalized residual compressive strength of the geopolymer samples first decreased and then increased with increasing Si/Al molar ratio (**Figure 4.2**, 300 °C).

This suggests that thermal shrinkage induced crack formation dominates the residual strength for geopolymer mixes with Si/Al molar ratio ≤ 1.50 , while densification of matrix is the governing factor of the residual strength for geopolymer mixes with Si/Al molar ratio > 1.50 .

While geopolymer mixes did not decompose after exposure to 900 °C temperature regime, they experienced severe cracking (**Figure 4.3**) and strength reduction (**Figure 4.1**). This is attributed to continuous shrinkage at elevated temperature (**Figure 4.4**). Furthermore, re-crystallization of nepheline at high temperature as shown from the XRD and FTIR results (**Figures 4.6 and 4.7**) would cause expansion and thus cracking of the geopolymer matrix as well. The structural changes or rearrangement corresponding to the partial transformation of amorphous to semi-crystalline aluminosilicate gel to crystalline framework (**Figure 4.4**) would have deteriorated the mechanical properties of the geopolymers (Van Riessen, Rickard et al. 2009). Geopolymer sample with Si/Al molar ratio equal to 1.75 retained highest strength (6 MPa) after exposure to 900 °C. This is because viscous sintering of geopolymer mixes with high Si/Al ratio at temperature beyond 600 °C enables localized healing of micro-cracks and densification of matrix (**Figure 4.5**) which favored compressive strength gain after exposure to 900 °C. At an even higher Si/Al of 2.0, foaming of unreacted silica upon heating can lead to expansion (**Figures 4.3 and 4.4**) and cracking of the sample which reduce the strength.

The underlying mechanisms causing the variegated compressive strength performance of the five metakaolin geopolymer mixes subject to elevated temperature can be summarized as shown in **Table 4.3**.

Table 4.3 Underlying competing mechanisms causing compressive strength performance of the five MK-geopolymer mixes

After exposure to	Competing mechanisms		Observation in strength
	Favoring strength gain	Favoring strength loss	
300°C	Densification of matrix (SEM images); more pronounced for high Si/Al mixes	High shrinkage and severe Cracking damage due to high water content	
900°C	Healing of micro-cracks, stronger inter-particle bonding (SEM) at local scale	Formation of very wide cracks, structural rearrangement due to re-crystallization of nepheline	

The current findings are also significant in showing that good micro-scale or chemical stability, as observed for the metakaolin geopolymer mixes (**Figure 4.6** and **4.7**), does not necessarily mean good meso-scale / volume stability (**Figure 4.3** and **4.4**) or macro-scale / strength stability (**Figure 4.1** and **4.2**). In fact, the geopolymer mixes exhibited poor volume stability and reduced mechanical strengths although they did not show any chemical structure breakdown. However, poor chemical stability does hamper the volume stability and compressive strength. Further, it can also be noted that volume stability (meso-scale stability) strongly influences the strength endurance (macro-scale stability). Thus, to ensure good thermal performance of metakaolin geopolymers for structural applications, it is important to ensure good strength endurance which depends on volume and chemical stabilities.

4.4. Conclusions

The effect of variation in Si/Al molar ratio on meso-scale (volume stability) and macro-scale (strength endurance) properties of metakaolin geopolymers has been explored in detail in this work and the underlying mechanisms have been revealed. It was observed that all the geopolymer samples experienced reduction in compressive strengths after exposure to 300 °C. Although, the geopolymer mixes exhibited good chemical stability at microscale as shown from the XRD and FTIR results, they possessed poor volume stability at mesoscale with very high thermal shrinkage. It was observed that thermal shrinkage induced crack formation dominates the residual strength for geopolymer mixes with Si/Al molar ratio ≤ 1.50 , while densification of matrix is the governing factor of the residual strength for geopolymer mixes with Si/Al molar ratio > 1.50 .

Further, all geopolymer samples retained their structural integrity even after exposure to 900 °C temperature regime. However, they experienced severe cracking and strength reduction attributed to continuous shrinkage at elevated temperature. Re-crystallization

of nepheline at high temperature was also thought to adversely affect the strength by inducing expansion and cracking of the geopolymer matrix. Geopolymer sample with Si/Al ratio 1.75 retained highest strength (6 MPa) after exposure to 900 °C. It was observed that due to high degree of cracking damage and low residual strength retention, it is essential to improve the macro-scale stability of metakaolin geopolymers for structural fire resistance applications.

Chapter 5

EVALUATING THE TOTAL REACTIVE CONTENT IN LOCAL FLY ASH FOR GEOPOLYMERIZATION

Evaluating the reactive content in fly ash helps to determine values of the mix design parameters such as Si/Al ratio and Al/Na ratio of the geopolymer, which in their turn affect the performance of geopolymers subject to elevated temperature. This chapter reports on an investigation conducted on a locally available fly ash to study its potential reactive content and estimate the reactive Si/Al ratio. A procedure involving dissolution of fly ash in sodium hydroxide (NaOH) solution followed by a hydrochloric acid (HCl) attack was applied. The dissolution of fly ash in 10 M NaOH solution at 80°C for increasing time duration (0.5, 1, 1.5, 2, 4 and 8 h) was examined. It was found that maximum dissolution of fly ash happens at around 2 h. Scanning electron microscopy was used to get a deeper insight into the mechanisms. The amount of geopolymer or zeolite formed during the dissolution of fly ash was evaluated using the test data from HCl extraction. The results from NaOH dissolution and HCl extraction combined together provide information about the total reactive content in the fly ash. Inductive coupled plasma optical emission spectrometer analysis on the solutions obtained from dissolution test and HCl extraction test was used to estimate the reactive Si/Al ratio. It was found that the Si/Al ratio is dependent on the duration of dissolution test. These Si/Al values were compared with the Si/Al value obtained using a combination of quantitative XRD and X-ray fluorescence techniques.

5.1 Introduction

Concrete is the most used man-made material in the world and ordinary Portland cement (OPC) is conventionally used as the binder material for producing concrete. Production of OPC; however, causes serious environmental impact by increasing the carbon dioxide (CO₂) content in atmosphere (Scrivener and Kirkpatrick 2007). It has been reported that producing a ton of cement generates nearly the same amount of carbon dioxide and cement industry accounts for around 5-8% of global CO₂ emissions (Yang, Yang et al. 2007).

The term “geopolymer” was first coined by Davidovits in 1978 to represent a wide range of materials characterized by a presence of inorganic polymeric system (Davidovits 1991). These materials could be produced by a polymeric reaction of alkaline liquids with silicon and aluminum in source materials of geological origin such as kaolin clay or in by-product materials such as fly ash, blast furnace slag and rice husk ash. The aluminosilicate precursor reacts with alkaline solution to form an inorganic poly-sialate material with SiO₄ and AlO₄ tetrahedra being the structural units. The main reaction product formed in this process is an X-ray amorphous alkaline aluminosilicate gel characterized by somewhat limited short-range structural order (Granizo, Alonso et al. 2002). In addition, Na-Herschelite-type zeolites and hydroxysodalite are formed as secondary reaction products particularly when fly ash is used as the precursor (Fernandez-Jimenez and Palomo 2003, Palomo, Alonso et al. 2004). Geopolymer is considered as a green binder because many aluminosilicate rich industrial by-products such as fly ash can be used as precursors for geopolymer synthesis. Consequently, geopolymer may be used as an alternative binder to replace OPC (Duxson, Provis et al. 2007).

Dissolution of aluminosilicate source leading to formation of individual alumina and silicate species is the first step in geopolymerization. These species then co-polymerize to form geopolymers. It requires presence of alkaline solution for the dissolution of

aluminosilicate source as well as for catalysis of the condensation reaction (Xu and Van Deventer 2000). When metakaolin is used as the aluminosilicate precursor for geopolymerization, due to its being almost fully amorphous, its reactive Si/Al ratio can be easily evaluated. This Si/Al ratio has been found to be very significant in determining the mechanical properties and microstructure of geopolymers (Duxson, Provis et al. 2005). When fly ash is used as the geopolymer precursor; however, the estimation of reactive Si/Al ratio is not straightforward because fly ash is not entirely amorphous. Furthermore, the total reactive Si and Al content available for geopolymerization may vary for fly ash sourced from different thermal power plants. Therefore, it is important to estimate the potential reactivity of fly ash for geopolymerization.

Few researchers have conducted studies to assess the reactivity of fly ash. Fernandez-Jimenez et al. (Fernandez-Jimenez, de la Torre et al. 2006) chemically treated two different fly ashes with hydrofluoric acid (HF). Quantitative X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) were also used to quantify the amorphous aluminosilicate content in the fly ashes and the results were compared with the amorphous content obtained through the HF chemical treatment. It was concluded that the chemical attack and XRD methods were more accurate in quantifying the amorphous content as compared to the NMR technique. However, this method does not provide information about the reaction mechanism of fly ash in the alkaline environment. Moreover, the practical application of this method to assess the reactivity is hindered by the usage of extremely hazardous hydrofluoric acid.

Fernandez-Jimenez et al. (Fernandez-Jimenez, de la Torre et al. 2006) also suggested the following method to determine the phase composition of alkaline-activated fly ash. Fly ash was activated with an 8 M NaOH solution with “alkaline solution/ash” ratio equal to 0.56. After thermal curing (at 85°C), HCl extraction was carried out on the alkaline-activated fly ash to determine the amount of ash that had reacted to form

binder based on the previous study by Palomo et al. (Palomo, Alonso et al. 2004). The residue from HCl extraction was re-activated with 8 M NaOH with “alkaline solution/ash” ratio of 0.56 for three days at 85°C. The re-activated material was then subject to HCl extraction. Residues from HCl extraction were analyzed using XRD and NMR to quantify the crystalline and amorphous reaction products. This method can be utilized to assess the phase composition of a hardened alkaline-activated material. However, it does not provide the information about total reactive content in the fly ash.

Rickard et al. (Rickard, Williams et al. 2011) used quantitative XRD to determine the amorphous content of fly ash with fluorite as internal standard. Elemental composition of amorphous phase was obtained by subtracting the content of crystalline phases obtained from XRD data from the X-ray fluorescence (XRF) data. This is not a totally correct approach to determine the reactive content since available Si and Al content may vary with different reaction conditions, for example, with pH, temperature or duration of experiment.

Nigel et al. (Chen-Tan, Van Riessen et al. 2009) suggested a dissolution method followed by XRD analysis to estimate the reactivity of fly ash. In this method, two different set of dissolution experiments were conducted, one at room temperature and another at 75°C. XRD/XRF results showed that close to 52 wt% of fly ash was amorphous aluminosilicate material while dissolution experiments gave a lower value of 39 wt%. Quantitative evaluation of minerals by scanning electron microscopy results indicated that amorphous iron does not participate in the geopolymerization process. The limitation of this work lies in the fact that while estimating the reactivity of fly ash, it does not consider the reaction products formed due to the precipitation of aluminosilicate gel that simultaneously occurs along with the dissolution of fly ash in alkaline medium.

The scope of the current preliminary study is to estimate the total reactive content in the locally available fly ash and to estimate the reactive Si/Al ratio through the use of dissolution and chemical extraction experiments conducted for different time intervals. Dissolution experiment alone is not sufficient to estimate the total reactivity of fly ash. Hence, the current approach was considered appropriate. The reactive Si/Al ratio in fly ash was also estimated using a combination of quantitative XRD and XRF techniques for purpose of comparison. Quantification of reactive silica and alumina content in the fly ash was done using ICP-OES analysis. XRD and SEM characterizations have been carried out to support the experimental investigation.

5.2 Experimental Investigation

5.2.1 Raw Materials

Class F Fly ash was provided by Bisley Asia Pte Ltd. The reagent grade sodium hydroxide pellets (> 99% purity) used were obtained from Merck. Sodium hydroxide solution was prepared by dissolving sodium hydroxide pellets in deionised water. The solution was allowed to cool down before using for the experiment the next day.

5.2.2 Experimental Procedure

7.5 g of fly ash was added to 200 ml of 10 mol/L sodium hydroxide solution in a closed beaker. The mix was continuously stirred using a magnetic stirrer. The dissolution experiment was conducted at 80 °C using a hot plate and thermometer, for various time durations, namely, 0.5, 1, 1.5, 2, 4 and 8 h. The solution was filtered using a vacuum filtration system equipped with a Rocker Chemker 400 vacuum pump and a 0.22 µm membrane filter (Millipore). The insoluble residue after filtration was collected and washed with nano-pure water for 3 times. The residue (FA-NaOH) was dried at 100°C for 1 h, then weighed and recorded. Hydrochloric acid (HCl) extraction was used to dissolve geopolymer/zeolite formed during alkaline activation. The HCl extraction

procedure used for this experiment was a modification of the method used by Polomo et al. (Palomo, Alonso et al. 2004). In the present study, 1 part concentrated HCl acid (37%) was diluted with 20 parts de-ionized water. 2 g of residue was added to 500 ml of HCl solution (1:20). The mix was stirred using a magnetic stirrer for three h at 500 rpm speed, after which it was filtered using the same vacuum filtration system (Rocker chemker 400 vacuum pump with 0.22 μm membrane filter). The insoluble residue after filtration was collected and washed with nano-pure water for 3 times. The residue (FA-NaOH-HCl) was dried at 100 °C for 1 h, then weighed and recorded.

5.2.3 Characterization techniques

Particle size distribution of fly ash was measured using a Malvern 2000 Laser Particle Size Analyzer. 5 g of fly ash mixed with 20 ml of dispersing solution (deionized water) was sonicated for 10 min to break up aggregates before the analysis. The instrument default optical parameters were used with a refractive index of 1.33 for water.

Scanning electron microscopy (SEM) was conducted using a thermal FE-SEM (JSM-7600F) at various magnification levels on the fly ash as well as other residue sample. Samples were first oven dried at 50 °C for 24 h and then were mounted on a stub using a carbon tape and coated with a platinum layer using a JEOL sputter coater (JFC-1600 Auto fine coater) with 20 mA current for a duration of 30 s prior to SEM imaging.

Powder x-ray diffraction (XRD) analysis was performed on fly ash. Fly ash sample was spiked using silica (5% by weight) obtained from National Institute of Standards and Technology (NIST) to quantify the different phases in the fly ash. XRD analysis was performed with Siemens-Bruker D5000 that had a Cu K α source at a voltage of 40 kV and a current of 30 mA. Samples were scanned from 5° to 120° (2 θ) at 0.02° (2 θ) step size with a scan speed of 1°/min. Quantitative analysis of XRD patterns for crystalline

phases was performed using a software TOPAZ, which is commonly used to perform basic XRD analysis. For positive crystalline phase identification, a minimum of three main peaks must be matched to a crystalline phase, which can be obtained from the literature of powder diffraction database.

Inductive coupled plasma optical emission spectroscopy (ICP-OES) was carried out on Optima 8300 provided by Perkin Elmer. Calibration tests were performed at first to check the accuracy of the results using standard solution and distilled water. The solutions obtained from the reactivity tests were diluted 100 times for carrying out the ICP-OES test so as to find out the amount of silicon, aluminum and iron dissolved in the solution. The dilution is necessary since the ICP-OES analysis gives best results when readings are below 100 ppb. Quantitative analysis was performed on the solution using the software Winlab provided by Perkin Elmer to analyze the elements in the solution.

5.3 Results and Discussion

5.3.1 Fly ash characterization

Particle size plays an important role as it determines the surface area that is available for alkaline activation. It is known from the previous studies (Hemmings and Berry 1987) that the fly ash particles with smaller size ($< 20\mu\text{m}$) have a high glassy composition which is ideal for geopolymerization. The particle size distribution of fly ash is presented in **Figure 5.1**. As can be seen, fly ash used in the current study shows a well graded or continuous particle size distribution with particle size ranging from 0.2 to $10\mu\text{m}$ with $d_{10} = 0.74\mu\text{m}$, $d_{50} = 2.5\mu\text{m}$ and $d_{90} = 6\mu\text{m}$.

Figure 5.1: Particle size distribution of fly ash

An SEM micrograph showing the typical morphology of fly ash is presented in **Figure 5.2**. It suggests that the fly ash is round and has a high surface area. Spherical morphology of fly ash is advantageous as it helps to achieve good workability at low liquid to solid mix ratios (Kong, Sanjayan et al. 2007, Rickard, Williams et al. 2011).

Figure 5.2: SEM image of fly ash

XRF analysis was carried out to determine the chemical composition of fly ash (**Table 5.1**). As can be seen from the table, the fly ash is composed of silicates, aluminates, iron oxides and other minor oxides. Major components include SiO_2 and Al_2O_3 which contribute almost 90% of the total weight of fly ash. Fe_2O_3 content is less than 5% of the total weight of fly ash. This is a class F fly ash according to ASTM C618.

Table 5.1: Chemical composition of fly ash

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	CaO	MgO
Content (wt %)	58.59	30.44	4.66	2.02	1.51	1.21	0.78
Oxide	P_2O_5	SO_3	ZrO_2	MnO	Cr_2O_3	CuO	ZnO
Content (wt %)	0.53	0.09	0.04	0.04	0.03	0.03	0.02

XRF provides information only about the total oxide contents in the fly ash, but does not provide any information about the reactive content in the fly ash. Previous research (Chen-Tan, Van Riessen et al. 2009) has indicated that only amorphous aluminosilicates in the fly ash are reactive. To analyze the phase composition and the reactive components, XRD analysis was carried out. The XRD pattern for fly ash is shown in **Figure 5.3**. The two major crystalline phases observed were Mullite ($\text{Al}_{4.66}\text{Si}_{1.39}\text{O}_{9.75}$) and Quartz (SiO_2). The hump in the XRD pattern is indicative of the amorphous phases which are considered as the potential reactive components for alkaline activation.

Figure 5.3: XRD pattern of fly ash

Silica was used as internal standard to conduct the quantitative analysis of fly ash. The total percentages of crystalline and amorphous phases for the fly ash obtained using TOPAZ software are displayed in **Table 5.2**. Elemental composition of amorphous phase was obtained by subtracting the content of crystalline phases obtained from XRD data (**Table 5.2**) from the XRF data (**Table 5.1**). **Table 5.3** summarizes the calculation for Si/Al molar ratio.

Table 5.2: Phase composition of fly ash from XRD

Phase	Formula	Weight%
Mullite	$\text{Al}_{4.66}\text{Si}_{1.39}\text{O}_{9.75}$	27.29
Quartz	SiO_2	6.43
Amorphous	-	66.28

Table 5.3: Calculation of Si/Al molar ratio

Description	Moles of Si (per 100 g fly ash)	Moles of Al (per 100 g fly ash)	Si/Al molar ratio
Total content (XRF)	0.9765	0.5969	1.63
Crystalline content (XRD)	0.2255	0.3965	0.57
Amorphous content	0.7510	0.2004	3.75

The amorphous silicon to aluminum ratio (Si/Al) is found out to be 3.75. Previous research by Hardjito et al. (Hardjito, Wallah et al. 2004) directly calculated the Si/Al ratio using XRF data; however, it can be observed from **Table 5.3** that the value of reactive Si/Al ratio obtained using XRF data alone largely differs from that obtained using a combination of XRF and XRD techniques. In the technique used by Hardjito et al. (Hardjito, Wallah et al. 2004), the Si/Al ratio included the crystal phases as well. The latter technique using XRD and XRF has been previously used by Rickard et al. (Rickard, Williams et al. 2011). It is considered better approach since it takes into consideration only the amorphous part of fly ash. Yet, it is not totally correct approach since available Si and Al content may vary with different reaction conditions, for example, with pH, temperature, duration, etc. Therefore, it is essential to study the reactivity of fly ash based on the proposed method.

5.3.2 Reactivity of fly ash

Dissolution test results

Dissolution tests for fly ash were conducted to study the extent of dissolution of fly ash in 10 M NaOH solution for different time durations, viz. 0.5, 1, 2, 4, 8 h and also to

find out the reactive Si/Al ratio. The results for the dissolution test showing percentage of fly ash dissolved against the duration of dissolution has been plotted in **Figure 5.4**.

Figure 5.4: Weight% of fly ash dissolved in NaOH versus duration

From the **Figure 5.4** it can be observed that the amount of fly ash dissolved in NaOH first increases and then decreases as the duration of dissolution is increased from 0.5 to 8 h. The maximum dissolution (around 44%) is observed for 2 h duration. It has been explained in literature that the dissolution of fly ash involves the severance of Si-O-Si, Al-O-Al and Si-O-Al bonds due to the action of OH^{-1} ions. The amorphous component of fly ash will tend to dissolve first, releasing aluminates and silicates, probably as monomers. The monomers will interact to form dimers, and further to form trimers, tetramers and so on. At the saturation point, the precipitation of aluminosilicate gel will initiate (Duxson, Provis et al. 2007). This reaction mechanism helps to explain the trend in fly ash dissolution as observed in **Figure 5.3**. The extent of fly ash dissolution will increase at first and then decrease after 2 h duration. The decrease is apparently due to the beginning of precipitation of the aluminosilicate gel. For 8 h duration experiment, a large reduction in the extent of dissolution was observed perhaps due to

continuous formation of aluminosilicate gel after the saturation point. The SEM micrographs shown in **Figure 5.5** help to better comprehend the phenomenon of fly ash dissolution.

Figure 5.5: SEM micrographs showing fly ash particles (a) before (b) after 1 h (c) after 2 h and (d) after 8 h dissolution in 10 M NaOH solution

From the micrographs, it can be observed that the spherically shaped fly ash particles, shown in **Figure 5.5(a)**, start to dissolve in the NaOH solution. **Figure 5.5(b)** clearly shows that a small amount of amorphous content from fly ash has started to dissolve after 1 h dissolution test. **Figure 5.5(c)** depicts a large change in the fly ash morphology explaining the maximum dissolution observed for 2 h duration. **Figure**

5.5(d) illustrates the precipitation of aluminosilicate gel on the fly ash particles after 8 h dissolution.

HCl extraction results

It has been suggested in previous research (Fernández-Jiménez and Palomo 2005, Fernández-Jiménez, Palomo et al. 2005, Duxson, Fernández-Jiménez et al. 2007) that the geopolymerization process involves various stages comprising dissolution, speciation equilibrium, gelation, reorganization, polymerization and hardening. All these stages are simultaneous and overall process is heterogeneous. This means that during the dissolution of fly ash, there will be a simultaneous precipitation of aluminosilicate gel. Hence, to estimate the amount of aluminosilicates precipitated during the dissolution experiments, HCl extraction was carried out. This method has been previously used by Granizo et al. (Granizo, Alonso et al. 2002) to find out the reactive contents in alkali activated metakaolin. The HCl extraction results, presented in **Figure 5.6**, show that with the increase in duration of dissolution experiment the amount of aluminosilicate gel precipitated increases monotonically.

Figure 5.6: HCl extraction results

Total available reactive content in fly ash

Figure 5.7 shows the plot of total available reactive content in fly ash against the duration of dissolution. The overall reactive fly ash was calculated by compiling the results from the dissolution test and the HCl extraction test. Previous research by Nigel et al. (Chen-Tan, Van Riessen et al. 2009)(Chen-Tan, van Riessen et al. 2009) calculated the total reactive content using only the data from dissolution experiment. However, as explained previously, there is a simultaneous precipitation of aluminosilicate gel along with the dissolution of the reactive components from the fly ash. Hence, it is essential to integrate the results from the HCl extraction test to the dissolution test.

Figure 5.7: Total available reactive content in fly ash (wt %)

From **Figure 5.7**, it can be observed that up to the 2 h duration, which was found to be the saturation point for the fly ash dissolution in NaOH, there is a linear increase in the

total available reactive content in the fly ash. After the saturation point, there is only a diminutive increase in the available reactive content in the fly ash.

The SEM images of the residue after HCl extraction for 1 h, 2 h and 8 h duration are shown in **Figure 5.8**. The residue from HCl extraction is supposed to contain only the unreacted component of fly ash. It can be observed from the SEM micrographs that the morphologies of fly ash in **Figure 5.8** (C and D) and (E and F) are similar to each other while they are very different from that in **Figure 5.8** (A and B). **Figure 5.8** (A and B), show a spherical fly ash particle almost fully unreacted. This indicates that large amount of fly ash remains unreacted after 1 hour dissolution in NaOH. While **Figure 5.8** (C and D) demonstrate largely reacted fly ash particles after 2 h dissolution. **Figure 5.8** (E and F) show that the morphology of unreacted fly ash after 8 h dissolution is similar to that of 2 h dissolution which explains why their total reactivity (**Figure 5.7**) was nearly the same.

Figure 5.8: SEM images of the residue after HCl extraction test for (A) 1 h at 5000x (B) 1 h at 25,000x (C) 2 h at 5000x (D) 2 h at 25,000x (E) 8 h at 5000x (F) 8 h at 25,000x

Calculation of Si/Al molar ratio

The results presented above provide information about the total available reactive content in the fly ash. However, it does not provide any information about the individual reactive components in the fly ash. In order to find out the reactive Si/Al ratio, it is essential to determine the total available amount of Si and Al in the fly ash. This was found out by carrying out ICP-OES analysis on the solutions obtained from the dissolution test and the HCl extraction test. **Figure 5.9(a)** and **5.9(b)** illustrate the results of ICP-OES analysis carried out on the solutions obtained after the dissolution and HCl attack experiment respectively.

Figure 5.9: Amount of Si, Al and Fe identified in (a) NaOH solution (b) HCl solution

From **Figure 5.9(a)** it can be observed that the maximum dissolution of Si and Al occurs at the saturation point (2 h). After this point, a reduction in the amount of dissolved Si and Al is observed which is evidently due to the precipitation of aluminosilicate gel. This observation ascertains the findings from the dissolution experiment. It can also be noted that the amount of iron dissolved in NaOH solution is very meager.

Further, from **Figure 5.9(b)** it can be observed that there is a continuous increase in the concentration of both Si and Al in the solution. This is reasonable since the amount of aluminosilicate gel formed keeps increasing continuously with the duration of dissolution. Also, a significant amount of iron is found to dissolve in the solution. This is apparently due to the dissolution of the amorphous iron content in the fly ash (Chen-Tan, Van Riessen et al. 2009).

Table 5.4, column 2, 3 and 4, summarizes the calculated values of Si/Al ratios from dissolution experiment, HCl extraction experiment and total reactive content respectively. The values in column 2 of **Table 5.4** were obtained using the dissolution test results (**Figure 5.4**) and ICP-OES results (**Figure 5.9a**). The values in column 3 of Table 6 were obtained using the HCl extraction results (**Figure 5.6**) and ICP-OES results (**Figure 5.9b**). Column 4 gives the total available Si/Al ratio calculated by summing up column 2 and column 3 values after proper mass proportioning.

Table 5.4: Reactive Si/Al molar ratio

Duration (hours)	Reactive Si/Al molar ratio		
	From NaOH dissolution	From HCl extraction	Total
1	3.2	1.95	2.98
2	3.1	2.12	2.85
8	3.3	1.94	2.65

It can be observed that the values of Si/Al ratio after dissolution of fly ash in NaOH after 1 h, 2 h and 8 h dissolution lie in close proximity (around 3.2). Further, Si/Al ratio in column 3 for all the three time durations is found to be close to 2. For metakaolin based geopolymer, it had been suggested that the microchemistry of aluminosilicate gel frequently observed by TEM/EDS corresponded to a Si/Al ratio of 2:1 {Kriven, 2003

#476. The current results suggest that even when the fly ash is used as a precursor the Si/Al ratio of the aluminosilicate gel formed is close to 2.

Column 4 of **Table 5.4** gives the total reactive Si/Al ratio based on the available silicon and aluminum content obtained from NaOH dissolution experiment and HCl extraction experiment. It can also be observed that the total reactive Si/Al ratio values differ from that calculated using XRD and XRF analysis (**Table 5.3**). This suggests that XRD and XRF analysis may not give a correct estimation of the Si/Al ratio of fly ash. Besides, it is also observed that the total reactive Si/Al ratio found out using NaOH dissolution and HCl extraction method is not a constant value. It is found to be dependent on the time period of dissolution. Further, this value may also depend on other reaction parameters such as temperature and alkalinity. The current study provides a more accurate estimation of the total reactive Si/Al ratios which may be used for fly ash geopolymer mix design.

In Chapters 6 and 7, the value of Si/Al ratio equal to 2.98 has been considered for fly ash geopolymer mix design, which was the value calculated for 1 h experiment. Si/Al value obtained for 1 h represents a scenario where fly ash has been only partially reacted, which is a common observation when fly ash is used as precursor for geopolymer synthesis. Hence, this value was selected for fly ash geopolymer mix design.

5.4 Conclusions

Dissolution test in conjunction with HCl extraction method has been used in this investigation to facilitate the evaluation of potential reactivity in locally available fly ash. It was found that the amount of fly ash dissolved in NaOH first increases, reaches maximum (around 44%) for 2 h duration and then decreases with the duration of dissolution. The reduction in the extent of dissolution was attributed to the continuous formation of aluminosilicate gel after the saturation point. SEM micrographs revealed the changes in fly ash morphology such as dissolution of fly ash particles and precipitation of aluminosilicate gel occurring during the dissolution experiment. Further, HCl extraction was considered necessary to estimate the amount of aluminosilicates precipitated during the dissolution experiments. By combining the results from dissolution and HCl extraction tests, the total reactive content in fly ash was calculated. Further, the reactive Si/Al ratio of fly ash was calculated using results from ICP-OES analysis along with those from NaOH dissolution and HCl extraction experiments. Si/Al ratio was found to be dependent on the duration of dissolution. The current study provides a more accurate estimation of the total reactive Si/Al ratios which may be used for fly ash geopolymer mix design.

Chapter 6

Effect of alkali cation type on strength endurance of fly ash geopolymers subject to high temperature exposure

Choice of alkali cation in mix design of geopolymers is critical for their thermal performance. However, the influence of alkali cation type on strength endurance of geopolymers subject to high temperature exposure and the underlying governing mechanisms have not been studied. This study investigated the effects of alkali cation type on high temperature response of fly ash geopolymers aiming towards structural applications. In-depth investigation was carried out to discover the underlying mechanisms governing the strength endurance of fly ash geopolymers subject to high temperature exposure and its correlation with their volume stability and chemical stability. Results showed that potassium geopolymer exhibited significant strength enhancement (30-40%) and sodium geopolymer displayed reduced strength (10%), and the strength of mixed sodium and potassium geopolymer remained unchanged after exposure to elevated temperature. While the binders were chemically stable without deterioration and formation of new crystal phases after high temperature exposure, the volume stability varied with the type of alkali cation used. Formation of cracks and gel densification due to shrinkage, and healing of micro-cracks and change of pore sizes due to sintering were identified as responsible mechanisms at different temperature ranges. While crack development and enlargement of pores lowered the strength, densification of matrix and healing of micro-cracks favored strength gain. These competing mechanisms determine the strength endurance of geopolymers depending on the type of alkali cation used. Overall, it shows that geopolymers can be tailored, such that stable (or even enhanced) strengths upon thermal exposure are realized, for structural applications.

6.1 Introduction

Fire damage can be critical in structures and in all cases the protection of people and property is essential (Sakkas, Nomikos et al. 2013). Concrete is the most used construction material on Earth (Mindess, F. et al. 2003). It is non-combustible and has a relatively low thermal conductivity. However, cracking, spalling and loss in mechanical strength of concrete after exposure to fire are key concerns especially with high strength concrete (Khoury 1992, Ulm, Coussy et al. 1999, Chan, Luo et al. 2000, Khoury 2000, Vydra, Vodak et al. 2001, Komonen and Penttala 2003, Odelson, Kerr et al. 2007, Khoury 2008). Degradation of cement hydration products after high temperature exposure is another serious issue with ordinary Portland cement (OPC) (Harmathy 1970, Harmathy 1993).

Geopolymer with mechanical strength more than 60 MPa (Fernandez-Jimenez and Palomo 2007) is an alternative binder to OPC (Duxson, Fernández-Jiménez et al. 2007). It has been shown that geopolymer can be greener than OPC because many industrial by-products can be the precursor for the synthesis of geopolymer (Duxson, Provis et al. 2007, Weil, Jeske et al. 2007). Moreover, fire resistance potential of geopolymer is remarkable (Davidovits 1991, Davidovits 1991, Lyon, Balaguru et al. 1997, Davidovits 1999, Giancaspro, Balaguru et al. 2004, Giancaspro, Balaguru et al. 2006) and its applications as heat-resistant material (Davidovits 1989, Büchler 1999, Liefke 1999, Cheng and Chiu 2003, Gourley and Johnson 2005), thermal insulator (Buchwald, Hohmann et al. 2004, Temuujin, Rickard et al. 2011, Rickard, Vickers et al. 2013, Sakkas, Nomikos et al. 2013, Rickard and van Riessen 2014), refractory material (Perera and Trautman 2005) and precursor to ceramic formation (Bell, Driemeyer et al. 2009, Bell, Driemeyer et al. 2009) have been reported.

Geopolymer has been shown to be largely chemically stable on exposure to high temperature (Barbosa and MacKenzie 2003, Barbosa and MacKenzie 2003, Duxson,

Lukey et al. 2006, Duxson, Lukey et al. 2007, Krivenko and Kovalchuk 2007). Chemical stability means that geopolymer does not undergo decomposition of the binder phase as experienced by OPC paste on high temperature exposure. However, volume stability, especially for metakaolin-based geopolymer, is a serious concern (Bernal, Rodriguez et al. 2011, Lahoti, Yang et al. 2017). In absence of volume stability material would experience thermal deformation and cracking damage. Coal fly ash-based geopolymer has shown better high temperature performance than metakaolin-based geopolymer in terms of their volume stability and residual strength (Kong, Sanjayan et al. 2007, Rickard, Williams et al. 2011, Zhang, Kodur et al. 2014). It was reported that fly ash-based geopolymers experienced less damage, as compared to their metakaolin counterparts, due to their possessing large numbers of interconnected pores which facilitated moisture escape on high temperature exposure (Kong, Sanjayan et al. 2007). Additionally, sintering of unreacted fly ash particles was thought to be another reason for better performance of fly ash geopolymers. Sintering enhances mechanical strength due to stronger bonding among the particles. Comparative assessment of fly ash from different sources to produce geopolymers for high temperature applications has been reported (Rickard, Williams et al. 2011, Rickard, Temuujin et al. 2012).

It has been shown for metakaolin-based geopolymers that the choice of alkali cation (whether sodium, potassium or a mixture of two), while designing a geopolymer mix, affects thermal shrinkage and phase stability subject to elevated temperatures (Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007). However, for fly ash-based geopolymers, there has been very limited research investigating the effect of mixed alkali cation on their high temperature performance. Furthermore, the influence of alkali cation type on strength endurance of geopolymers subject to high temperature exposure and the underlying governing mechanisms have not been studied even for metakaolin-based geopolymers. Strength endurance of material subject to high temperature exposure is of particular importance for structural applications.

Construction materials need to satisfy required strength criteria (e.g. 30 MPa) at ambient condition and also must endure sufficient strength to continue to serve as a structural material after exposure to elevated temperature. Geopolymers synthesized in many previous works with low strength (e.g. 10 MPa) were not aiming towards structural applications (Bakharev 2006). Therefore, there is a need to carry out a careful investigation on geopolymers designed using different alkaline activators to not only meet the strength endurance criteria but also to reveal the underlying mechanisms that govern their thermal performance.

Hence, this study investigated the effects of alkali cation type (whether sodium, potassium or a mixture of two) on high temperature response of fly ash-based geopolymers aiming towards structural applications. In-depth investigation was carried out to discover the underlying mechanisms governing the strength endurance of the fly ash geopolymers subject to high temperature and its correlation with their volume stability and chemical stability. Various experimental techniques, namely x-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), mercury intrusion porosimetry (MIP), dilatometry, and scanning electron microscopy (SEM) were utilized in this research.

6.2 Materials and methods

6.2.1 Fly ash

Class F Fly ash was used as a precursor to synthesize geopolymers in this research. The particle size distribution of fly ash is shown in **Figure 5.1**. It illustrates a well graded or continuous particle size distribution with particle size ranging from 0.2 to 80 μm with $d_{10} = 0.74 \mu\text{m}$, $d_{50} = 2.5 \mu\text{m}$ and $d_{90} = 6 \mu\text{m}$.

Chemical composition of fly ash based on X-ray fluorescence spectroscopy (XRF) is given in **Table 5.1**. As can be seen, the fly ash has low CaO and the total content of

SiO₂, Al₂O₃, and Fe₂O₃ is more than 70%, which indicates it is a class F fly ash according to ASTM C618. The high SiO₂ and Al₂O₃ content (~ 90%) implies the fly ash may potentially be a suitable geopolymer precursor.

The XRD pattern for fly ash is shown in **Figure 5.3**. Almost all crystalline peaks could be identified and were classified into either Mullite (Al_{4.66}Si_{1.39}O_{9.75}) or Quartz (SiO₂). The hump in the XRD pattern is indicative of the amorphous phases which are considered as potential reactive components for alkaline activation (Chen-Tan, Van Riessen et al. 2009). Amorphous phases were quantified by means of the internal standard method. Fly ash samples were spiked with silica (5% by weight) obtained from the U.S. National Institute of Standards and Technology (NIST). The total percentages of crystalline and amorphous phases for the fly ash obtained using TOPAZ software are presented in **Table 5.2**. Elemental composition of amorphous phase was obtained by subtracting the content of crystalline phases obtained from XRD data (**Table 5.2**) from the XRF data (**Table 5.1**). **Table 5.3** summarizes the calculation for Si/Al molar ratio. This method to calculate the Si/Al ratio has been previously used by Rickard et al. (Rickard, Williams et al. 2011). The amorphous silicon to aluminum ratio (Si/Al) is found out to be 3.75. This value has been used to design the geopolymer mixes in current work.

6.2.2 Alkali Activators

In this study, sodium hydroxide, sodium silicate, potassium hydroxide and potassium silicate were used as alkali activators. Sodium hydroxide solution was prepared by dissolving calculated quantity of NaOH pellets (99.8% in purity, purchased from Merck) into distilled water. Extra pure sodium silicate solution containing Na₂O = 7.5-8.5% by weight and SiO₂ = 25.5-28.5% by weight was purchased from Merck. Potassium hydroxide solution was prepared by dissolving KOH pellets (> 85% in

purity, purchased from Schedelco Pte. Ltd) into distilled water. Potassium silicate solution containing $K_2O = 13\%$ by weight and $SiO_2 = 27\%$ was purchased from Merck. The silicate solution was mixed with the freshly prepared hydroxide solution and stored for 24 h before casting to allow the solution to cool down to room temperature and achieve equilibrium.

6.2.3 Mix proportion and sample preparation

Three geopolymer mixes were prepared for experimental investigation as shown in **Table 6.1**. All the mixes had the same Si/Al ratio, Al/M ratio and H_2O/M_2O molar ratios equal to 4.15, 1.15 and 16, respectively (where 'M' represents the total Na+K content). These ratios were calculated considering reactive Si/Al ratio of fly ash equal to 3.75 as discussed previously. It has been observed in this research and has been previously reported that K-based activators exhibit increased workability compared to Na-based (Rodriguez, Bernal et al. 2013). Hence to achieve similar workability, water/solids ratio for the three mixes with increasing K content were, 0.251, 0.225, and 0.220, respectively.

Table 6.1: Mix proportions and density of fly ash geopolymer

Mix	$\frac{Na}{Na + K}$	Fly ash (kg/m ³)	NaOH pellets (kg/m ³)	Na- silicate solution (kg/m ³)	KOH pellets (kg/m ³)	K-silicate solution (kg/m ³)	Water (kg/m ³)	ρ (kg/m ³)
K	0.0	1445	-	-	100	266	188	1841±21
NaK	0.5	1453	51	-	30	260	193	1784±28
Na	1.0	1407	80	258	-	-	206	1820±34

Geopolymer samples were prepared by mixing fly ash with silicate solution for 15 min in a Kenwood mixer (Titanium Timer Major KMM040) at speed level two of the mixer. Geopolymer slurry was poured in cubic molds (50 mm dimension) and cylindrical molds (8 mm diameter and 26 mm length). The molds were first half filled and vibrated and then fully filled and vibrated to ensure proper compaction and removal of entrapped air bubbles. Molds were then covered with plastic sheets to prevent any loss of moisture. The samples were allowed to cure for 3 days at 60°C in an environmental chamber with 98% relative humidity. After that samples were de-molded and stored in plastic bags at ambient conditions (25-30°C) for another four days before testing.

6.2.4 Test Methods

For elevated temperature exposure, 50 mm cube samples were heated in the furnace to the target temperature at a heating rate of 5 °C/min, held at that temperature for 1 h, and then allowed to cool down gradually to room temperature. The target temperatures were chosen as 500°C and 900°C because literature suggests that major volume changes in geopolymer are attributable to two phenomena, namely, dehydration (between 100°C-300°C) and sintering (between 550-900°C) (Komnitsas and Zaharaki 2009, Rickard, van Riessen et al. 2010, Vickers, Riessen et al. 2015). To clearly segregate and bring to light the influence of each of the two phenomena, it was important to study the thermal performance at intermediate temperature of 500°C. Densities were determined by measuring weight loss and dimension change of the geopolymer sample before and after exposure to high temperature.

Chemical stability of the three geopolymers subject to high temperature exposure was evaluated by means of XRD and FTIR. XRD analysis was performed on the geopolymer samples before and after elevated temperature exposure with a Bruker AXS D8 advance powder diffractometer by using Cu K α radiation. Samples were step

scanned from 5° to 65° (2 θ) at a scan rate of 2.5°/min. FTIR spectra for the geopolymer samples before and after elevated temperature exposure were obtained from 4000 to 400 cm⁻¹ using a Nicolet iS50 FT-IR spectrometer in ATR (attenuated total reflectance) mode. Spectra were collected with 64 transients at a resolution of 4 cm⁻¹ in absorption mode at room temperature.

Change of pore structure of the three geopolymers subject to high temperature exposure was evaluated by means of mercury intrusion porosimetry (MIP). MIP analysis was performed on the geopolymer samples before and after elevated temperature exposure to measure the pore size distribution and cumulative pore volume. Mercury porosimeter from Micromeritics (AutoPore IV 9500 V1.09) was used at a maximum head pressure of 307 MPa. The contact angle and surface tension of mercury used for calculations were 130° and 0.485 N/m, respectively.

Volume stability of the three geopolymers subject to high temperature exposure was evaluated by means of dilatometry. Thermal deformation of geopolymers was measured using a TA Instruments Dilatometer (DIL 802L) at a constant heating rate of 5 °C/min up to a maximum temperature of 900°C in an atmosphere of air. Cylindrical specimens of diameter 8 mm and length 25 mm were used. The results presented herein are an average of at least three measurements.

Visual appearances as well as the internal microstructure of geopolymer samples were assessed before and after exposure to elevated temperature. To observe the crack pattern and porosity of the samples, a small specimen measured 15 by 15 mm was cut from the center of the cube sample and coated with epoxy. The epoxy coated sample was then cut and polished to obtain a thin and flat specimen. This specimen was first dried at 40°C and then mounted on a stub using a carbon tape and coated with a

platinum layer using a JEOL sputter coater (JFC-1600 Auto fine coater) with 20 mA current for duration of 45 s prior to SEM imaging using a field emission scanning electron microscope (FESEM), JSM-7600F at magnification level 2500x in BSE imaging mode. Nine continuous images were taken and combined into one micrograph by computerized program to capture a larger area of 100 μm by 125 μm at 2500x and to reveal fine micro-cracks and porosity in the sample.

The 7-day compressive strengths of 50 mm geopolymer cubes were measured before and after exposure to high temperature regime. A compression testing machine from Tony Technik was used at a loading rate of 60 kN/min in accordance with ASTM C109/109M. For each mix, at least three samples were tested and the average value of compressive strength with the standard deviation was reported.

6.3 Results

6.3.1 Chemical stability

Material characterization techniques, XRD and FTIR, were used to acquire a better understanding of possible transformations occurring in the geopolymers. **Figure 6.1** shows the XRD patterns for the original fly ash and geopolymer matrix before and after exposure to high temperature for Na-, NaK- and K-geopolymer samples. The crystalline phases (mullite and quartz shown in **Figure 5.3**) present in the initial fly ash were barely affected by either geopolymerization or high temperature exposure. As a result of geopolymerization, the characteristic halo due to the amorphous phase in the initial fly ash shifted from 20°-30° 2 θ range to 25°-35° 2 θ range. This shift is indicative of geopolymer formation (Duxson, Fernández-Jiménez et al. 2007). The intensity of this halo changes only slightly with elevated temperature exposure and the changes are difficult to quantify. However, it can be noted that while K-geopolymer had almost no changes in this halo, NaK- and Na-geopolymers showed very slight changes in the halo for 900°C samples, possibly due to a higher degree of sintering observed in these

samples compared to the K-geopolymer. These results imply that largely, the three geopolymers have good thermal stability and nominal phase changes upon thermal exposure (Rickard, Temuujin et al. 2012). The presence of free alkali in geopolymers can reduce the onset temperature of re-crystallization of feldspars such as nepheline (Krivenko and Kovalchuk 2007). Current results indicate that the geopolymer mixes considered in this study are well-reacted, thereby leaving few free alkali cations and manifesting good phase stability.

Figure 6.1: XRD patterns of (a) Na-geopolymer, (b) NaK-geopolymer, and (c) K-geopolymer before and after high temperature exposure

Figure 6.2 shows the FTIR spectra for the original fly ash and geopolymer matrix before and after exposure to high temperature for Na-, NaK-, and K-geopolymer samples. The main asymmetric stretching band for T-O-T bond (where T is 'Si' or 'Al') in initial fly ash is observed at 1040 cm^{-1} . This band was found to become narrower and shift to longer wavelengths 1003 , 1005 and 1004 cm^{-1} for Na-, NaK-, and K-geopolymers, respectively, as a result of alkaline activation (Fernández-Jiménez, Palomo et al. 2008). As a result of elevated temperature exposure to 500 and 900°C , a broadening in the T-O-T bond band for three geopolymers was observed, which may be a consequence of structural disorder caused by the heating of material. It can be observed that for K-geopolymer, this band showed only slight broadening. For NaK-geopolymer, broadening was more than K sample while for Na-geopolymer broadening was more clearly observed. This is because Na-based sample experienced the highest structural disorder such as densification caused by dehydration of free water and viscous sintering as will be shown in SEM and dilatometry results. The increase in structural disorder of geopolymers ($\text{Na} > \text{NaK} > \text{K}$) would cause appearance of a wider T-O-T bond vibration band in FTIR spectra.

Figure 6.2: FTIR patterns of (a) Na-, (b) NaK-, and (c) K-geopolymer before and after high temperature exposure

6.3.2 Pore structure

Figure 6.3 shows the pore size distribution in the geopolymer samples. It can be observed that at 25°C, NaK-geopolymer has smaller pore sizes than Na- and K-geopolymers. This is perhaps due to use of mixed alkali cations, causing mixed alkali effect (Duxson, Mallicoat et al. 2007), in this geopolymer.

(a)

(b)

(c)

Figure 6.3: Pore size distribution in (a) Na-, (b) NaK-, and (c) K-geopolymers before and after high temperature exposure

After exposure to 500°C, Na and NaK samples showed an increase in pore size and cumulative volume. This increase was perhaps due to formation of cracks which led to opening up of closed pores and interconnection of pores. The intrusion data used in MIP analysis gives information about pore throat size and not pore radii (Anovitz and Cole 2015). Formation of micro-cracks perhaps resulted in an increase in pore throat size (depending on the intensity of crack) and may also cause opening up of closed pores, resulting in observing an increase in ‘pore size’ and ‘cumulative pore volume’ measured through MIP. Interestingly, K-geopolymer did not show an increase in pore size which was possibly because of the least cracking damage of the sample (**Figures 6.5 and 6.6**). Contrarily, it showed some reduction in pore size probably because capillary stress due to dehydration caused contraction of geopolymer gel (Duxson, Lukey et al. 2006).

After exposure to 900°C, all the three samples, irrespective of the alkali cation type, experienced significant increase in the pore size. This increase was perhaps due to the micro-structural rearrangement during the viscous sintering process. Small pores apparently clubbed together to form large pores. The influence of alkali cation on total pore volume (cumulative intrusion) could also be noted. The reduction in cumulative pore volume observed in samples after exposure to 900°C was in the order of Na > NaK > K. This was probably a consequence of densification caused by sintering process. As will be explained in Section 3.3, the total amount of densification followed the order Na > NaK > K, and thus the reduction in cumulative intrusion followed the same sequence.

6.3.3 Volume stability

Thermal deformation characteristic of geopolymers is of particular significance when evaluating the potential for high temperature applications. Thermal deformation can

cause stresses and weaken the construction material. Examining the overall thermal shrinkage, it can be noted that K-geopolymer has the minimum thermal deformation followed by NaK- and Na-geopolymers, respectively. Thermal deformation characteristics of the three geopolymers (**Figure 6.4**) were quite similar except that the extent of deformation differed in the various temperature regions. In region 1 (25-150°C), practically no dimensional changes could be observed in the geopolymer samples, possibly because the material was strong enough to resist the stresses generated in this temperature range.

Figure 6.4: Thermal deformation of the geopolymers observed by dilatometry

Region 2 (150-300°C) involved first major shrinkage in the order $K < NaK < Na$ due to dehydration of physically bound water. It has been revealed by nuclear magnetic resonance (NMR) and thermo-gravimetric analysis (TGA) that most of the water in geopolymer is physically and not chemically bound, at least in highly reacted samples (Komnitsas and Zaharaki 2009). Since Na-geopolymers required more water, porosity in these samples should be higher than that in NaK and K samples and hence after

dehydration, thermal shrinkage is higher. Thermal shrinkage was also associated with densification of geopolymer matrix and pore structure changes because the removal of free water is associated with release of energy which contributes to densification of gel (Brinker and Scherer 1990).

Slight expansion was observed in 300-600°C (Region 3) which may be attributed to two phenomena. First, phase transformations in the secondary phases in fly ash such as quartz were recognized (Vickers, Riessen et al. 2015). It has been reported that quartz, a commonly found crystalline phase in fly ash, undergoes transformation from low to high quartz at 573°C causing thermal expansion (Deer, Howie et al. 2013). Secondly, slight shrinkage due to the physical contraction of geopolymer caused by condensation reactions of the hydroxyl groups present in geopolymers to form shorter T-O-T linkages (where 'T' is aluminum or silicon atom) was reported (Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007). In the current results, for all the three geopolymers, only a slight expansion was observed in the region 3. This is may be attributed to that thermal expansion from phase transformations in the secondary phases in fly ash was compensated by condensation reactions of the hydroxyl groups.

Region 4 (600-900°C), involves densification and sintering and is the cause of second major shrinkage experienced. It can be observed that the choice of alkali cation has a significant effect on the onset temperature of densification. While the onset of densification for NaK and Na geopolymers occurs at temperatures around 600°C, the K-geopolymer is more stable and its onset temperature of densification seems higher than 850°C. The total amount of densification and shrinkage observed in region 4 was in the order $K < NaK < Na$. It has been suggested in literature that due to increased strength of Al-O bonds in the presence of potassium compared to sodium, K-geopolymer is more resilient to densification (Duxson, Lukey et al. 2007). Thus, the reduction in cumulative pore volume observed in samples after exposure to 900°C

(Figure 6.3) followed the same sequence of the total amount of densification (i.e., $K < NaK < Na$).

6.3.4 Visual appearance and microstructure observations

Clearly observable changes in the appearance of all the three samples can be observed in **Figure 6.5** subjected to three different temperature exposures. Especially after 900°C, the geopolymer samples turn reddish-brown with the intensity of color in the order $Na > NaK > K$. This change of color may be attributed to oxidation of iron in the fly ash (Rickard, Williams et al. 2011). Crack pattern and damage to the geopolymer matrix can also be observed in **Figure 6.5** due to dehydration of free water from the pores, contraction of pores and development of cracks that resulted in overall shrinkage of the geopolymer samples. The water vapor escaping from the samples and the shrinkage of pore led to development of cracks. The K-geopolymer; however, show lesser damage after exposure to 500 and 900°C as compared to the NaK- and Na-geopolymer. This observation corresponds well with the dilatometry observations related to the higher volume stability (**Figure 6.4**) of the K-geopolymer mixes.

Figure 6.5: Visual observation of samples before and after exposure to elevated temperature

Figure 6.6: SEM-BSE micrographs of geopolymers before and after high temperature exposure (solid arrows showing micro-cracks)

Figure 6.6 gives more clear information about damage to the matrix by showing the cross-section of 50 mm geopolymer cube before and after exposure to high temperature. Perceivable micro-structural differences and transformations could be observed in the SEM micrographs. Before high temperature exposure, all the three geopolymers (Na, NaK and K) exhibited a homogenous microstructure containing geopolymer gel, voids and unreacted fly ash particles. Such a microstructure allows high load carrying capacity (Duxson, Provis et al. 2005, Lahoti, Yang et al. 2017) and favors development of good compressive strengths at ambient temperature. When exposed to 500°C temperature regime, geopolymer samples developed micro-cracks (yellow arrows in **Figure 6.6**). This is because high temperature exposure up to 500°C caused dehydration of free water from the pores, contraction of pores and development of cracks that resulted in overall shrinkage of the geopolymer sample. The water vapors escaping from the samples and the shrinkage of pore led to development of cracks. However, it was observed that damage was more extensive for Na-containing samples, while K-geopolymer showed very fine micro-cracks. This is attributed to higher dehydration shrinkage of the Na-containing geopolymers observed in region 2 (**Figure 6.4**). Higher the shrinkage, the higher is cracking damage.

Na, NaK and K samples after exposure to 900°C showed an evident transformation in the microstructure. A smoother texture without any cracks and enlarged pores could be observed in all geopolymer samples after exposure to 900°C (**Figure 6.6**). This was mainly attributed to softening and sintering mechanisms taking place above 600°C. Viscous sintering causes local tight packing of the particles, thereby healing the micro-cracks and causing a smooth texture (Duxson, Lukey et al. 2006, Kong, Sanjayan et al. 2007). K-geopolymer; however, showed lesser amount of 'smooth texture' compared to NaK- and Na-geopolymers. This is because K-geopolymer is more resilient to densification due to increased strength of Al-O bonds in the presence of potassium compared to sodium (Duxson, Lukey et al. 2007). The micrographs show that all the

micro-cracks, even those for Na-geopolymer, have been healed up after exposure to 900°C.

6.3.5 Compressive strength

Figure 6.7: Compressive strengths for the Na, NaK and K geopolymers before and after exposure to 500°C and 900°C temperature regimes

Figure 6.7 shows the compressive strength of Na, NaK and K geopolymer samples before and after exposure to elevated temperature regimes. It can be observed that all specimens possess strength above 30 MPa before and after high temperature exposure which qualifies the geopolymers in the current study as structural materials. After exposure to 500°C, the effect of potassium was to increase the compressive strength in K-geopolymer (from 40 to 59 MPa, i.e. 50% enhancement). NaK-geopolymer sample experienced lesser increase in strength (from 49.5 to 51 MPa, i.e. 5% enhancement) while Na-geopolymer sample experienced a slight strength loss (from 38 to 35.5 MPa, i.e. 7% reduction). Furthermore, when samples were exposed to 900°C temperature

regime, Na and NaK samples could more or less maintain their compressive strengths, while K-geopolymer undergoes slight reduction in compressive strength from 59 to 54 MPa (8% reduction) as compared to that observed after exposure to 500°C. This observation suggests that the mechanisms occurring before 500°C (such as dehydration) were more significant than those occurring after 500°C (such as viscous sintering) in governing the compressive strength of geopolymer.

To obtain the clear trend of the strength performance of the material, two additional geopolymer mixes with Na/Na+K ratio of 0.25 and 0.75 were prepared and evaluated (**Figure 6.8a**). It can be observed that before high temperature exposure, with the increase in Na/Na+K ratio, compressive strength first increased, reached the maximum at Na/Na+K ratio of 0.5 and then decreased. Highest strength observed for the geopolymer sample with Na/Na+K ratio equal to 0.5 was due to mixed-alkali effect which leads to improvement in the geopolymer microstructure (Duxson, Mallicoat et al. 2007). As observed in **Figure 6.3**, geopolymer sample with Na/Na+K ratio equal to 0.5 had also possessed smaller pore size than the Na or K samples. After exposure to 900°C, geopolymers with Na/Na+K ratio < 0.5 showed increased compressive strength while geopolymers with Na/Na+K ratio > 0.5 exhibited reduced compressive strength. For instance, the pure K-geopolymer revealed 40% enhancement of compressive strength while the pure Na-geopolymer showed 10% reduction of compressive strength after exposure to 900°C as shown in **Figure 6.8(b)**. Compressive strength of geopolymer with Na/Na+K ratio = 0.5 remained unchanged after exposure to 900°C. These observations are significant. Firstly, they show that compressive strengths for geopolymers after elevated temperature exposure can be even higher than before high temperature exposure. This is in contrast to OPC samples which always show decreasing strengths after high temperature exposure. Secondly, the compressive strength results show that the increase or decrease of compressive strengths after elevated temperature is highly dependent on the cation type and mixing ratio.

(a)

(b)

Figure 6.8: (a) Compressive strengths for the five geopolymer before and after exposure to 900°C, and (b) normalized compressive strengths

6.4 Discussion

The densification of geopolymer matrix (**Figure 6.4**) would result in changes in the gel/space ratio (X), a concept used in OPC system. From cement chemistry, it is well-known that gel-to-space ratio has direct correlation with compressive strength of the OPC paste (Mindess, F. et al. 2003). It is likely or potentially that gel/space ratio would similarly influence the compressive strength of geopolymer matrix. Gel/space ratio (X) can be defined in the following way:

$$\text{Gel/space ratio} = \frac{\text{Volume of geopolymer gel}}{\text{Volume of geopolymer gel} + \text{Volume of capillary pores}}$$

Volume of geopolymer gel can be calculated by subtracting the volume of capillary pores from the volume of the cube sample. At room temperature, the cumulative volume of capillary pores can be estimated using the MIP test results (**Figure 6.3**). After exposure to 500°C, since MIP analysis does not give reliable information about the cumulative pore volume due to formation of cracks in the sample, it is assumed that the shrinkage or densification observed in the geopolymer sample after heating was caused by a corresponding shrinkage of pores. Thus, volume of capillary pores is estimated by subtracting the amount of shrinkage of cube sample (dilatometry results at 500°C, **Figure 6.4**) from the volume of capillary pores measured at 25°C (MIP results at 25°C, **Figure 6.3**). After exposure to 900°C, since the micro-cracks are healed by sintering, MIP results are used to evaluate the volume of capillary pores. There are some possible errors due to not considering the closed pore volume in calculation of capillary pore volume.

The values of gel/space ratio evaluated using the MIP results in conjunction with dilatometry observations are shown in **Table 6.2**. As can be seen, the gel/space ratio for all three geopolymers has increased after exposure to 500°C due to matrix densification. Na-geopolymer shows a further increase in gel/space ratio after 900°C exposure, while NaK and K samples show a reverse trend. This is because Na-

geopolymer experienced reduction in cumulative pore volume, while K-geopolymer showed slightly increased cumulative intrusion.

Table 6.2: Calculation of gel/space ratio in geopolymers before and after exposure to elevated temperature

	Volume of geopolymer gel + capillary pores (ml)*			Volume of capillary pores (ml)#			Gel/space ratio (X)		
	25°C	500°C	900°C	25°C	500°C	900°C	25°C	500°C	900°C
K	125	122.76	122.76	40.11	37.87	42.02	0.679	0.691	0.658
NaK	125	121.29	119.10	42.42	38.70	38.73	0.661	0.681	0.675
Na	125	119.82	115.50	41.98	36.80	30.11	0.664	0.693	0.739

*Volume of geopolymer gel + capillary pores = volume of the cube sample. At 25°C, volume of cube is 5 x 5 x 5 cm³. After exposure to 500°C and 900°C, volume of cube samples is calculated using % change in length observed using dilatometry (**Figure 6.4**).

#Volume of capillary pores at 25°C is calculated based on the MIP results. Since after 500°C, due to crack formation, the capillary volume measured by MIP is not accurate, it is assumed that whatever shrinkage of geopolymer cube sample is equal to the shrinkage of capillary pores. Volume of capillary pores at 500°C is thus evaluated by subtracting dilatometry results at 50°C from the MIP results at 25°C. After exposure to 900°C, since the micro-cracks are healed by sintering, MIP results are used to evaluate the volume of capillary pores.

Table 6.3: Underlying competing mechanisms causing variegated compressive strength performance of the three geopolymer mixes

Temperature Exposure	Competing mechanisms		Observation in strength
	Favoring strength gain	Favoring strength loss	
500°C	Densification of matrix leading to increase in gel/space ratio	Cracking damage (K < NaK < Na)	K: 50% gain NaK: 5% gain Na: 7% loss
900°C	Healing of micro-cracks, stronger inter-particle bonding, increase gel/space ratio	Formation of bigger pores, changes in cumulative pore volume, reduction in gel/space ratio	K: 8% loss NaK: maintains Na: maintains

The underlying mechanisms causing the variegated compressive strength performance of the three geopolymer mixes subject to elevated temperature are summarized in **Table 6.3**. High temperature exposure to 500°C caused dehydration of free water from the pores and capillary stress. Densification of geopolymer matrix caused by capillary stress leading to an increase in the gel/space ratio favored compressive strength gain. Dehydration of free water was also associated with crack formation which adversely affected the compressive strengths depending on the intensity of cracks. The two competing mechanisms, namely, cracking damage and densification determined the residual strength. While minimal cracking damage (**Figures 6.5** and **6.6**) more or less did not affect the compressive strength of K-geopolymer, densification (and thus increased gel-to-space ratio) possibly led to significant strength gain from 40 MPa at 25°C to 59 MPa after exposure to 500°C (50% enhancement). Contrarily, NaK and Na samples experienced higher cracking damage (**Figures 6.5** and **6.6**). The reduction in strength caused by cracking damage was compensated by the increase in gel/space ratio for these samples. Therefore, even with perceivable cracking damage, NaK- and Na-geopolymers experienced 1 MPa strength gain (5% enhancement) and 3 MPa strength loss (7% reduction), respectively.

Exposure of geopolymer samples up to 900°C led to viscous sintering and stronger inter-particle bonding (Van Riessen, Rickard et al. 2009). As a consequence, healing of micro-cracks was observed (**Figure 6.6**). On the other hand, viscous sintering caused formation of some bigger pores and changes in cumulative pore volume as observed using MIP (**Figure 6.3**). While crack healing and densification favored strength gain, enlargement of pores reduced strength. Reduced value of gel/space ratio for K-geopolymer and also increase in its pore sizes (**Figure 6.3c**) caused slightly more reduction (8% reduction) in compressive strength as compared to that observed after

exposure to 500°C. Na and NaK samples could more or less maintain their compressive strengths from 500 to 900°C. While both samples showed increase in pore size (**Figure 6.3a-b**), healing of micro-cracks (**Figure 6.6**) and enhanced inter-particle bonding potentially favored regain of strength. Furthermore, gel/space ratio for NaK sample showed only slight reduction while for Na sample the value even increased. These competing mechanisms determined the strength endurance of geopolymers after exposure to 900°C depending on the type of alkali cation used.

6.5 Conclusions

This research reported the influence of alkali cation (sodium, potassium or a mixture of two) on the strength endurance of fly ash-based geopolymers subject to high temperature exposure aiming towards structural applications. The underlying mechanisms were revealed by studying their volume stability and chemical stability before and after exposure to elevated temperature through various microstructure analysis and characterization techniques including XRD, FTIR, MIP, dilatometry, and SEM. Results showed alkali cation (i.e. Na/Na+K ratio) has a strong influence on the compressive strength of fly ash-based geopolymers after exposure to elevated temperature. In general, K-geopolymer showed strength enhancement and Na-geopolymer exhibited reduced strength, while the strength of NaK-geopolymer remained unchanged after exposure to elevated temperature.

While the binders are chemically stable without deterioration and formation of new crystal phases after high temperature exposure, the volume stability varies with the type of alkali cation used. Before 500°C, dehydration of free water caused formation of cracks, pore size changes and densification of geopolymer gel. While crack development lowered the strength, densification of geopolymer matrix favored strength gain by increasing the gel/space ratio. These competing mechanisms determine the

compressive strength performance. Since K-geopolymer only exhibited very fine cracks, significant strength gain (50% enhancement) for K-geopolymer was observed due to increase in the gel/space ratio after exposure to 500°C. Contrarily, NaK and Na samples experienced higher cracking damage. The reduction in strength caused by cracking damage was compensated by the increase in gel/space ratio for these samples. Therefore, even with perceivable cracking damage, NaK- and Na-geopolymers experienced 1 MPa strength gain (5% enhancement) and 3 MPa strength loss (7% reduction), respectively. After 500°C, healing of micro-cracks due to viscous sintering potentially favored regain of strength while enlargement of pores reduced strength. These two mechanisms compensated with each other. As a result, all geopolymers could more or less maintain their compressive strength after exposure to 900°C as compared to that observed after 500°C temperature exposure. Overall, it shows that geopolymers can be tailored, such that stable (or even enhanced) strengths upon thermal exposure are realized, for structural applications.

Chapter 7

TAILORING SODIUM-BASED FLY ASH GEOPOLYMERS WITH VARIEGATED THERMAL PERFORMANCE

Sodium-based fly ash geopolymers show great fire resistance potential and commercial advantage for structural applications. Hence, in current research, tailoring of sodium-based geopolymer mix design using the same fly ash source has been studied. It was found that a wide variety of residual compressive strength ranging from significant reduction (~80%) to maintaining to significant enhancement (~150%) after exposure to 900°C was observed. The underlying mechanisms were revealed by studying their chemical stability, pore structures, volume stability, and strength endurance before and after exposure to elevated temperature through various microstructure analysis and characterization techniques including XRD, FTIR, MIP, dilatometry, and SEM. Crack formation, pore shrinkage, and re-crystallization of nepheline adversely affected compressive strength. Matrix densification due to shrinkage of pore and stronger inter-particle bonding due to viscous sintering, favored compressive strength gain. This work discusses at length these competing mechanisms influencing the residual compressive strength.

7.1 Introduction

Protection of structures from fire is essential since fire is one of the most serious environmental conditions that a structure may be exposed to (Sakkas, Nomikos et al. 2013). Despite of all the technological advancements and measures for fire prevention, there remains a threat of fire outbreak always. Several fire events have been experienced in the past which lead to safety concerns not just for the occupants but also for the fire rescuers. Ordinary Portland cement (OPC) concrete is the most widely used

structural material that can provide passive fire protection (Mindess, F. et al. 2003). It is incombustible and possesses a relatively low thermal conductivity; however, spalling and loss of mechanical strength remain key concerns, especially for high strength concrete (Khoury 1992, Ulm, Coussy et al. 1999, Chan, Luo et al. 2000, Khoury 2000, Vydra, Vodak et al. 2001, Komonen and Penttala 2003, Odelson, Kerr et al. 2007, Khoury 2008). Moreover, it has been shown that the OPC hydration products, namely calcium silicate hydrate and calcium hydroxide, degrade when the material is subjected to high temperature. It is very difficult to avoid this deterioration of OPC concrete micro-structure (Harmathy 1970, Harmathy 1993).

Geopolymer, an alkali aluminosilicate binder, is a novel building and construction material (Duxson, Fernández-Jiménez et al. 2007). Production of geopolymers by activating fly ash using alkaline silicate solution is an effective method to produce concrete which is environmentally friendly (Duxson, Provis et al. 2007, Weil, Jeske et al. 2007, Provis, Harrex et al. 2012) and possesses promising mechanical and engineering properties (Fernandez-Jimenez and Palomo 2007). This binder is an attractive alternative to OPC and is available at a comparable performance and cost (Rodriguez, Bernal et al. 2013). Besides, geopolymer binder also has promising fire resistance. Geopolymer has shown significant chemical stability on high temperature exposure (Barbosa and MacKenzie 2003, Barbosa and MacKenzie 2003, Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007, Krivenko and Kovalchuk 2007, Rodriguez, Bernal et al. 2013). Fernandez-Jimenez et al. (Fernández-Jiménez, Palomo et al. 2008) demonstrated that geopolymer binders possess better mechanical performance exposed to elevated temperature as compared to OPC binder. In other reported literature (Davidovits 1991, Lyon, Balaguru et al. 1997, Davidovits 1999, Giancaspro, Balaguru et al. 2004, Giancaspro, Balaguru et al. 2006), excellent properties of geopolymers in terms of incombustibility, inflammability and no smoke generation were highlighted. Geopolymer has found many applications as a heat-resistant material (Davidovits 1989, Büchler 1999, Liefke 1999, Cheng and Chiu 2003,

Gourley and Johnson 2005), thermal insulation (Buchwald, Hohmann et al. 2004, Temuujin, Rickard et al. 2011, Rickard, Vickers et al. 2013, Sakkas, Nomikos et al. 2013, Rickard and van Riessen 2014), refractory material (Perera and Trautman 2005) and ceramic precursor (Bell, Driemeyer et al. 2009, Bell, Driemeyer et al. 2009)).

It has been reported that coal fly ash-based geopolymers are more suitable than metakaolin-based geopolymers for high temperature applications (Kong, Sanjayan et al. 2007, Rickard, Williams et al. 2011, Rickard, Temuujin et al. 2012, Zhang, Kodur et al. 2014). Kong et al. (Kong, Sanjayan et al. 2007) found that fly ash geopolymers, as compared to their metakaolin counterparts, have larger number of interconnected pores which facilitate the escape of moisture on high temperature exposure. Sintering of unreacted fly ash particles was another factor contributing to better performance of fly ash geopolymers. On the other hand, higher water demand of metakaolin geopolymers was thought to make them more prone to cracking. Fernandez-Jimenez et al. (Fernández-Jiménez, Pastor et al. 2010) and Kovalchuk et al. (Kovalchuk and Krivenko 2009) suggested that total alkali content is significant in determining the high temperature properties such as onset temperature of crystallization and sintering temperature. The importance of reactive Si/Al ratio and iron content of the fly ash was to some extent investigated by Rickard et al. (Rickard, Williams et al. 2011, Rickard, Temuujin et al. 2012). In these works, fly ashes from different sources were assessed for their suitability to produce geopolymers for high temperature applications. Development of fire-resistant fly ash-based geopolymer concrete is a potential solution for construction of important structures such as tunnels, underground caverns and high-rise buildings which necessitate greater fire safety.

Previous study (Bakharev 2006) found regarding effects of alkali type on thermal performance of fly ash geopolymer that the samples prepared using sodium-containing activators experienced rapid deterioration of strength at 800°C while those prepared

using potassium-containing activators experienced significantly increased strength. That finding gives a notion that sodium-based geopolymers are not as good as potassium-based in terms of compressive strength performance. However, potassium-based activators are more expensive and less easily available in market as compared to sodium-based activators.

In this study, tailoring of the geopolymer mix design to attain variegated thermal performance using sodium as the alkali cation has been discussed. The thermal performance of geopolymer mixes with same Si/Al ratio but different alkali content and water content in terms of their chemical stability, volume stability, change of pore structure, damage and crack pattern, and residual compressive strengths has been reported. Efforts have been made to reveal the underlying mechanisms causing the variegated performances using experimental techniques, such as x-ray diffractometry (XRD), Fourier transform infrared (FTIR) spectroscopy, mercury intrusion porosimetry (MIP), dilatometry, and scanning electron microscopy (SEM).

7.2 Materials and methods

7.2.1 Fly ash

Fly ash used in this research had a continuous particle size distribution as shown in **Figure 5.1**. Particle size ranged from 0.2 to 80 μm with $d_{50} = 2.5 \mu\text{m}$. The chemical composition of fly ash is shown in **Table 5.1** and it shows that the fly ash is rich in SiO_2 and Al_2O_3 . These two components constitute around 90% of the total weight of fly ash. According to ASTM C618, this fly ash belongs to the class F category since the total content of SiO_2 , Al_2O_3 , and Fe_2O_3 is more than 70%. The CaO content in fly ash is low.

Based on previous research (Chen-Tan, Van Riessen et al. 2009), only amorphous aluminosilicates in the fly ash are reactive. XRD analysis was carried out to evaluate the amorphous content in the fly ash. XRD pattern for fly ash is presented in **Figure 5.3**. The crystalline peaks primarily correspond to Mullite ($\text{Al}_{4.66}\text{Si}_{1.39}\text{O}_{9.75}$) and Quartz (SiO_2). A hump can also be observed in the XRD pattern which is indicative of the amorphous phases present in the fly ash. Quantitative analysis was performed using Silica (5% by weight) from NIST. **Table 5.2** shows the amorphous and crystalline content in the fly ash obtained using TOPAZ software. Composition of amorphous phase was obtained by subtracting the crystalline content obtained from XRD data (**Table 5.2**) from the XRF data (**Table 5.1**). Calculation for Si/Al molar ratio is shown in **Table 5.3** and is based on method previously used by Rickard et al. (Rickard, Williams et al. 2011). The calculated value for Si/Al molar ratio equal to 3.75 has been used to design all the geopolymer mixes prepared in this work.

7.2.2 Alkali activators

Sodium hydroxide (NaOH) and sodium silicate were used as alkali activators in the current investigation. NaOH pellets (99.8% in purity, purchased from Merck) were dissolved in distilled water to prepare the sodium hydroxide solution. Extra pure sodium silicate solution consisting of 7.5-8.5% Na_2O by weight and 25.5-28.5% SiO_2 by weight was procured from Merck. Freshly prepared sodium hydroxide solution was mixed with the silicate solution. The solution obtained was kept undisturbed for 24 h to let it cool down to room temperature and attain equilibrium before being used for geopolymer synthesis.

7.2.3 Mix proportion and sample preparation

Table 7.1 shows the mix proportion of five geopolymer mixes synthesized in this study. The value of Si/Al molar ratio was kept constant at 4.15 while water content and

alkali content (i.e. Al/Na ratio, water/solids ratio, and H₂O/Na₂O ratio) varied. These ratios were evaluated taking Si/Al molar ratio of fly ash equal to 3.75. For geopolymer synthesis, the precursor fly ash was mixed together with the silicate solution in a Kenwood mixer (Titanium Timer Major KMM040) for 15 minutes at speed level two. The homogenous slurry obtained was casted into cubic molds of 50 mm dimension and cylindrical molds of 8 mm diameter and 26 mm length. Proper compaction was ensured by removing the entrapped air bubbles. Molds were covered with a plastic sheet and kept in an environmental chamber at 60°C for an initial 3 days of curing at a relative humidity of 98%. After 3 days, samples were removed from the environment chamber and de-molded. They were cured for another four days in a plastic bag at ambient temperature (25-30°C) before testing. Density of each sample was calculated by dividing the sample weight by its volume. An average value of density with standard deviation has been reported in **Table 7.1**.

Table 7.1: Mix proportion of geopolymers

Mix	Fly ash (kg/m ³)	NaOH pellets (kg/m ³)	Na-silicate solution (kg/m ³)	Water (kg/m ³)	Si/Al molar ratio	Al/Na molar ratio	H ₂ O/ Na ₂ O ratio	water/ solids weight ratio	ρ (kg/m ³)
1	1290	163	229	233	4.15	0.55	9.9	0.280	1852±17
2	1293	126	236	245	4.15	0.69	12.6	0.290	1883±11
3	1407	80	258	206	4.15	1.0	16.0	0.251	1820±34
4	1443	77	256	195	4.15	1.12	16.3	0.238	1822±30
5	1450	70	242	227	4.15	1.15	17.0	0.244	1817±13

7.2.4 Test methods

The 50 mm cube geopolymer samples were exposed to a slow heating rate of 5°C/min in an electric furnace. Two target temperatures, 500°C and 900°C, were chosen. Since major factors governing the thermal performance of geopolymers reported in literature (Komnitsas and Zaharaki 2009, Rickard, van Riessen et al. 2010, Vickers, Riessen et al. 2015) are dehydration (occurring between 100°C-300°C) and sintering (occurring between 550°C-900°C); to clearly segregate and elucidate the mechanisms controlling the performance of these samples subject to elevated temperature exposure, these two specific target temperatures (500°C and 900°C) were selected. Samples were held at the target temperature for one hour and then gradually cooled down.

Chemical stability of the five geopolymers subject to high temperature exposure was evaluated by means of XRD and FTIR. Bruker AXS D8 advance powder diffractometer was used to carry out the XRD analysis on the powdered geopolymer samples before and after elevated temperature exposure using Cu K α radiations. Samples were step scanned from 5° to 65° (2 θ) at a scan rate of 2.5°/min. FTIR analysis on the geopolymer samples, before and after elevated temperature exposure, was carried out using a Nicolet iS50 FTIR spectrometer in attenuated total reflectance (ATR) mode. Spectra were collected with 64 transients at a resolution of 4 cm⁻¹ in absorption mode in wave number range 4000 to 400 cm⁻¹.

Change of pore structure of the five geopolymers subject to high temperature exposure was evaluated by means of mercury intrusion porosimetry (MIP). MIP analysis was performed using a Mercury porosimeter from Micromeritics (AutoPore IV 9500 V1.09) at a maximum head pressure of 307 MPa. The pore size distribution and cumulative pore volume of the geopolymer samples were measured before and after elevated temperature exposure. The contact angle and surface tension of mercury used for calculations were 130° and 0.485 N/m.

Volume stability of the five geopolymers subject to high temperature exposure was evaluated by means of dilatometry. Cylindrical geopolymer specimens of diameter 8 mm and length 25 mm were used for dilatometry tests. TA Instruments Dilatometer (DIL 802L), which can precisely measure the thermal deformations, was used at a constant heating rate of 5°C/min up to the maximum temperature of 900°C in an atmosphere of air. Each result presented herein is an average of three tests.

Visual appearances of geopolymer samples were assessed before and after high temperature exposure. Images of the bulk sample were taken using a Nikon camera. In addition, 50 mm cube sample was cut across its cross-section to observe the internal cracks. Field emission scanning electron microscope (FESEM), JSM-7600F was used, in the BSE imaging mode, to observe the internal microstructure of geopolymer samples. A magnification level of 2500x was chosen. Small specimens measuring 15 by 15 mm were cut from the centre of the geopolymer cubes, coated with epoxy and polished. After drying at 40°C, the specimens were mounted on a stub using carbon tape. JEOL sputter coater (JFC-1600 Auto fine coater) with 20 mA current was used for a duration of 45 s to coat the specimens with platinum layer before the SEM imaging. Mass loss was determined by measuring weight loss and dimension change of the geopolymer sample before and after exposure to high temperature.

Compressive strengths of the samples were measured at age of 7 days, using a Tony Technik compression testing machine, before and after high temperature exposure. The loading rate was 60 kN/min based on ASTM C109/109M. At least three samples have been tested for each mix and the average value of compressive strength along with the standard deviation has been reported.

7.3 Results

7.3.1 Chemical stability

Material characterization techniques, XRD and FTIR were used to gain better understanding of possible transformations in the geopolymers. **Figure 7.1** displays the XRD patterns for the original fly ash and geopolymer matrix before and after exposure to high temperature for all five geopolymer mixes. It can be observed that the crystalline phases present in the precursor fly ash (mullite and quartz) were essentially neither affected by geopolymerization nor by high temperature exposure. Further, hardly any new crystal peak was formed after high temperature exposure for mixes 3, 4 and 5 indicating good thermal stability and minimal phase changes in these geopolymer mixes. For mixes 1 and 2, after exposure to 900°C, formation of nepheline (N) was observed. The formation of nepheline in these two mixes may be related to a higher alkali content in these geopolymer mixes as suggested in literature (Kovalchuk and Krivenko 2009). Alkalis can act as very good flushing agent, that is, they reduce the temperature of crystallization in geopolymers. Therefore, excessive alkali content in geopolymers would favor crystallization of nepheline when material is subject to high temperature. On the other hand, it is also well-known that lower alkali content adversely affects the compressive strengths at ambient temperature. Therefore, optimum alkali content is required in geopolymers to balance between the development of strength at ambient temperature and thermal stability subject to elevated temperatures.

Figure 7.1: XRD patterns before and after high temperature exposure for mixes 1-5 (M: Mullite; Q: Quartz; N: Nepheline)

Figure 7.2 (1-5) shows the FTIR spectra of the original fly ash and geopolymer matrix before and after exposure to high temperature for all five geopolymer samples. It can be noted that the main asymmetric stretching band for T-O-T bond vibrations (where T is 'Si' or 'Al') in initial fly ash is at 1040 cm^{-1} . This band was found to become narrower and shift to longer wavelengths 979 , 991 and 1000 , 1000 and 1000 cm^{-1} for geopolymer mixes 1, 2, 3, 4 and 5, respectively, as a result of alkaline activation.

Similar shifts have been observed previously by Fernandez-Jimenez et al. (Fernández-Jiménez, Palomo et al. 2008). The larger shift for mixes 1 and 2 as compared to the other 3 mixes might be related to their higher alkalinity which favors a higher degree of reaction and a corresponding shift in peak position at ambient temperature conditions (Kovalchuk and Krivenko 2009).

Due to exposure to 500°C, for geopolymer mixes 1 and 2, the main asymmetric stretching band showed significant broadening and considerable shift in the peak position (967 and 980 cm⁻¹ respectively) while for mixes 3, 4 and 5, this band showed only slight broadening and no variation in the peak position (1000 cm⁻¹ for 3 mixes). This broadening may be related to structural changes caused by dehydration of physically- and chemically-bonded water, the content of which is higher in mixes 1 and 2 as compared to the other three mixes (Fernández-Jiménez, Pastor et al. 2010).

On exposure to 900°C, for all the geopolymer mixes, only slight broadening and almost no shift in the main asymmetric stretching band peak position was observed. However, for mixes 1 and 2, the peak is more sharply defined as compared to mixes 3-5, confirming that the material in these mixes was more crystalline due to crystallization of nepheline (Fernández-Jiménez, Palomo et al. 2008).

Figure 7.2: FTIR spectra before and after high temperature exposure for mixes 1-5

7.3.2 Pore structure

Figure 7.3: Pore structure analysis using MIP

Further, from the plots (Figure 7.3) it can be observed that the pore size and cumulative pore volume for all the mixes increased after samples were exposed to 500°C. The increase was perhaps due to interconnection of pores, opening up of closed pores and formation of cracks. Mix 1 showed larger increase in pore size as compared to other mixes. Mixes 2, 3, 4, and 5 exhibited similar pore size distributions after exposure to 500°C.

After exposure to 900°C (Figure 7.3), all geopolymer samples showed an increase in the pore sizes and a reduction in the cumulative pore volume as a consequence of viscous sintering. On a local scale viscous sintering-caused collapse of nano-pores, a stronger inter-particle bonding, and densification of geopolymer matrix, while on global scale it caused formation of large pores. Mixes 3, 4, and 5 showed similar increases in pore sizes and similar reduction in total pore volume.

7.3.3 Volume stability

Dilatometric curve for the five geopolymers is shown in **Figure 7.4**. In the temperature range 100-300°C, thermal shrinkage was mainly attributed to dehydration of free water which led to shrinkage of pores (Van Riessen, Rickard et al. 2009) and consequent densification of matrix. The extent of thermal shrinkage in this region is dependent on

the water-to-solids ratio. Since, mixes 1 and 2 have higher water-to-solids than mixes 3, 4, and 5; higher shrinkage (**Figure 7.4**) as well greater structural changes in FTIR spectra (**Figure 7.2**) were observed for these mixes.

Figure 7.4: Thermal deformation of the geopolymers observed by dilatometry

(Corresponding mix no. has been indicated)

A slight expansion was observed in the temperature range 300-600°C (**Figure 7.4**). This expansion was a resultant of expansion of crystalline phase such as quartz present in the original fly ash (Deer, Howie et al. 2013) and a slight shrinkage due to condensation of the hydroxyl groups in geopolymers to form shorter T-O-T linkages (where 'T' is aluminum or silicon atom) (Duxson, Lukey et al. 2006, Duxson, Lukey et al. 2007, Vickers, Riessen et al. 2015).

After 550-600°C, shrinkage was attributed to densification caused by viscous sintering inside geopolymer specimens. Sintering-caused collapse of nano-pores, formation of larger pores and reduction in cumulative pore volume (**Figure 7.3**). For mixes 1 and 2, respectively, a severe and a very mild expansion peak were observed around 700°C in **Figure 7.4**, which were not observed for the other 3 mixes. This could be expansion caused by either crystal growth (Komnitsas and Zaharaki 2009), e.g. formation of nepheline (**Figures 7.1** and **7.2**), or by swelling of unreacted silica phases in these geopolymers (Provis, Yong et al. 2009), or simply a combination of both processes.

It can also be observed in **Figure 7.4** that the onset temperature of ‘sintering caused shrinkage’, more or less decreased for geopolymer mix 1 to 5. It has been suggested that total alkali content in the system is critical in determining the onset temperature of crystallization, sintering temperature and the amount of viscous sintering (Fernández-Jiménez, Pastor et al. 2010). Higher alkali content in mixes 1 and 2 is thus the reason for these two mixes exhibiting lower onset temperature of sintering and higher amount of sintering than mixes 3-5.

7.3.4 Visual appearance and microstructure observations

Figure 7.5 shows that all five geopolymer samples experienced perceivable transformations after exposure to elevated temperature. It can be observed that the samples turned reddish-brown in color after exposure to 900°C which is attributed to the oxidation of iron present in the precursor fly ash (Rickard, Williams et al. 2011). Crack pattern and damage to the geopolymer matrix can also be observed in **Figure 7.5** due to dehydration of free water from the pores, contraction of pores and development of cracks that resulted in overall shrinkage of the geopolymer sample. The water vapors escaping from the samples and the shrinkage of pore led to development of cracks. Mixes 3, 4, and 5; however, show lesser damage after exposure to 500 and 900°C as compared to mixes 1 and 2. This observation corresponds well with the XRD and FTIR

results related to the higher chemical stability (**Figures 7.1 and 7.2**) and with the dilatometry observations related to the higher volume stability (**Figure 7.4**) of these mixes.

Figure 7.5: Visual appearance of geopolymer samples before and after exposure to elevated temperature

Figure 7.6: Crack patterns observed before and after exposure to elevated temperature

Figure 7.6 gives more clear information about damage to the matrix by showing the cross-section of 50 mm geopolymer cube before and after exposure to high temperature. As can be seen, mixes 1 and 2 exhibited large extent of cracking damage after exposure to 500 and 900°C. The crack pattern was similar to map cracking which is often observed in case of alkali-silica reaction in concrete and here this map cracking may be associated with the formation of Nepheline observed for mixes 1 and 2 (**Figure 7.1**). Mix 3 exhibited lesser damage in terms of the crack number and crack widths as compared to mixes 1 and 2. Mixes 4 and 5 experienced even lesser damage than mix 3. The degree of cracking damage observed in the five mixes was strongly related to water-to-solids ratio of the samples. Higher degree of damage and cracks were observed for high water-to-solids ratio samples (mixes 1 and 2), as compared to lower water-to-solids ratio samples (mixes 3, 4, and 5) on high temperature exposure.

Figure 7.7 presents typical SEM micrograph observed for the geopolymer samples before and after high temperature exposure. The microstructure at ambient temperature consisted of aluminosilicate gel, unreacted fly ash particles and void spaces. After exposure of the samples to 500 and 900°C, changes in the morphology of the aluminosilicate gel as well as the pore size distribution could be observed. The formation of a 'smoother texture' caused by viscous sintering has been reported in literature (Duxson, Lukey et al. 2006, Kong, Sanjayan et al. 2007) and was also observed in the current study.

Figure 7.7: Typical microstructure of geopolymers observed using SEM

7.3.5 Compressive strength

Figure 7.8a presents the compressive strength of five geopolymer mixes before and after exposure to elevated temperature regime. It can be observed that all geopolymers possessed good strengths at ambient temperature (30-50 MPa) which is a positive note for their potential structural applications. Mix 2 possessed the highest strength followed by mixes 3, 4, 5, and 1. This is mainly attributed to the smallest mean pore size (**Figure 7.3**), higher degree of reaction and highest density (**Table 7.1**) observed for mix 2 as compared to other mixes. After high temperature exposure, a wide variety of compressive strength was observed. As can be seen in **Figure 7.8b**, mixes 1 and 2 exhibited significant strength loss by 47% and 80%, respectively, while mixes 4 and 5

showed great strength gain by 54% and 148% after exposure to 900°C. Mix 3, however, showed a relatively stable thermal performance in terms of the residual strengths.

(a)

(b)

Figure 7.8: (a) Compressive strength of geopolymers at 25°C and after exposure to 500°C and 900°C, and (b) normalized compressive strength gain (%) of geopolymers after exposure to 500°C and 900°C

The underlying mechanisms causing the variegated compressive strength performance of the five geopolymer mixes subject to elevated temperature are summarized in **Table 7.2**. Exposure to 500°C causes dehydration of free water accompanied by shrinkage of pores, densification of geopolymer matrix and development of cracks in the geopolymer samples. Crack formation adversely affected compressive strength, while matrix densification allowed for more uniform stress gradients during load application and favored compressive strength gain. These two competing mechanisms determined the compressive strength of the geopolymer samples exposure to 500°C. Moderate reduction in compressive strength of geopolymer mixes 1 and 2 (~20%, **Figure 7.8**) was related to large damage of the geopolymer matrix (plenty of wide cracks) as observed in **Figures 7.5** and **7.6**, and structural changes observed in FTIR spectra

(**Figure 7.2**). Mixes 4 and 5 exhibited moderate gain in compressive strength (~10%) which may be attributed to densification of matrix and much lesser damage (fewer and finer cracks) and less significant structural transformations. Mix 3 showed the minimal changes in compressive strength after exposure to 500°C, perhaps due to the balanced compensation of the two competing mechanisms.

When geopolymer samples were exposed to 900°C, along with experiencing dehydration of free water and densification of matrix, the specimens also experienced transformations caused by viscous sintering, and in some cases changes caused by formation of new phase such as nepheline. Viscous sintering leads to stronger inter-particle bonding and crack healing (Van Riessen, Rickard et al. 2009) and matrix densification allowed for more uniform stress gradients during load application. Both favor compressive strength gain. Re-crystallization of nepheline; however, can lead to expansion and cracking of matrix, which adversely affect compressive strength. These competing mechanisms determined the compressive strength of the geopolymer samples exposure to 900°C. Mixes 1 and 2, thus exhibited significant reduction in compressive strengths due to severe cracking and damage of matrix (**Figures 7.5 and 7.6**). This is mainly attributed to re-crystallization of nepheline (**Figures 7.1 and 7.2**) which leads to poor volume stability (expansion peaks in **Figure 7.4**). Mixes 4 and 5; however, showed much better volume stability with much fewer and finer cracks as compared to mixes 1 and 2. Matrix densification (**Figure 7.3**), and stronger inter-particle bonding due to viscous sintering lead to significant strength gain of geopolymer mixes 4 and 5 (up to ~150%). Mix 3 again showed the minimal changes in compressive strength after exposure to 900°C, perhaps due to the balanced compensation of these competing mechanisms.

Table 7.2 Underlying competing mechanisms causing variegated compressive strength performance of the five FA-geopolymer mixes

After exposure to	Competing mechanisms		Observation in strength
	Favoring strength gain	Favoring strength loss	
500°C	Matrix Densification	Crack formation, structural changes (FTIR spectra) (Mix 1,2 > mix 3 > mix 4,5)	Mix 1, 2: 20% loss (plenty wide cracks) Mix 3: Minimal changes (balanced compensation) Mix 4,5: 10% gain (fewer and finer cracks, densification)
900°C	Stronger inter-particle bonding, crack healing and densification	Re-crystallization of nepheline causing expansion and matrix cracking	Mix 1, 2: 47%, 80% loss (severe cracking, nepheline formation) Mix 3: Minimal changes (balanced compensation) Mix 4,5: Up to 150% gain (no nepheline formation, crack healing)

The results demonstrate that water content and alkali content play a key role in determining the performance of geopolymers after subjected to high temperature heating. Tailoring of mix design factors is thus essential to realize good thermal performance. By tailoring the mix design, it is possible to attain not only a stable mechanical performance of geopolymers exposed to high temperature (as observed for Mix 3) but even enhanced performances (as observed for Mixes 4 and 5) using sodium as an alkali cation. Furthermore, the current observations also suggest that while assessing the suitability of any fly ash for high temperature applications, it is important to consider various permutation and combinations of mix design factors. By properly controlled mix design factors, the good high temperature performance can be realized.

7.4 Conclusions

Current research discussed tailoring of geopolymer mix using sodium as alkali cation to realize variegated compressive strength behavior subject to elevated temperature. The underlying mechanisms were revealed by studying their chemical stability, pore structures, volume stability, and strength endurance before and after exposure to elevated temperature through various microstructure analysis and characterization techniques including XRD, FTIR, MIP, dilatometry, and SEM. Results showed that mix design (i.e. Al/Na ratio, water-to-solids ratio, and H_2O/Na_2O ratio) has a strong influence on the compressive strength of sodium-based fly ash geopolymers after exposure to elevated temperature. A wide variety of residual compressive strength ranging from significant reduction (~80%) to maintaining to significant enhancement (~150%) after exposure to 900°C was observed. Crack formation due to water vapors escaping from the samples, the shrinkage of pore, and re-crystallization of nepheline adversely affected compressive strength. Matrix densification due to shrinkage of pore allowed for more uniform stress gradients during load application. Viscous sintering led to stronger inter-particle bonding and crack healing. Both of the phenomena

avored compressive strength gain. These competing mechanisms determined the compressive strength of the geopolymer samples on exposure to elevated temperature.

Chapter 8

CONCLUDING REMARKS

Current research has focused towards developing geopolymer as an innovative material to enhance structural fire resistance. Accordingly, the influence of geopolymer mix design on its mechanical performance subject to high temperature heating was investigated. It was possible to realize good strength endurance, deformation resistance and stability of chemical structure by proper tailoring of the mix design factors.

Research activities can be divided into two task groups, namely, those related to metakaolin-based geopolymers (**Chapters 3 and 4**) and those related to fly ash-based geopolymers (**Chapters 5, 6, and 7**). Investigation on metakaolin-based geopolymers addressed the knowledge gaps associated with their performance at ambient temperature and subjected to elevated temperature. Since, metakaolin easily participates in geopolymerization compared to fly ash; metakaolin-based geopolymer system is considered a model system and provides more fundamental understanding about geopolymer performance. Assessment of factors affecting compressive strength of metakaolin-based geopolymers was discussed in **Chapter 3**. Strength endurance and volume stability of metakaolin-based geopolymers was discussed in **Chapter 4**.

In second task group, performance of fly ash-based geopolymer was investigated. Study about fly ash-based geopolymer is very significant since their performance, subject to high temperature, is much superior to their metakaolin-based counterpart. **Chapter 5** discussed the mechanism of fly ash dissolution in alkaline environment as well as the different methods to evaluate the Si/Al ratio. **Chapter 6** discussed improving the thermal performance of fly ash-based geopolymers by tailoring the alkali

cation type. Further, **Chapter 7** discussed how to tailor the fly ash-based geopolymer mix design using sodium as alkali cation to regulate the performance subjected to high temperature.

8.1 Major findings

Important findings and accomplishments through this thesis are summarized in the following section:

8.1.1 Improvement in knowledge about what governs compressive strength of metakaolin-based geopolymers

Geopolymer is a promising alternative binder to Portland cement. Unlike OPC binders, the importance of mix design factors affecting the compressive strength of geopolymer binder are not yet quantitatively assessed. The novelty of study discussed in **Chapter 3** lies in evaluating the four inter-dependent mix design parameters and their importance to the compressive strength of metakaolin-based geopolymer. In a geopolymer mix design, it is not possible to keep three of the four parameters (Si/Al, Al/Na, H₂O/Na₂O, and water/solids) constant while varying only one parameter to study its influence. Most of the previous studies; however, have not considered this significant point and only study the influence of Si/Al, Al/Na, and H₂O/Na₂O. Those studies evaluate effects of each individual parameter by fixing the other two parameters. However, the simultaneously changing in water/solids was not recognized and got neglected. In the current work, the inter-dependency of the parameters was noted and statistical analyses were engaged to evaluate the relative importance of the four inter-dependent mix design parameters including water/solids ratio. The approach used in this study is more systematic and appropriate than previous researches. Furthermore, the importance of water/solids ratio in a metakaolin-based geopolymer binder system as compared to the OPC systems was clarified, which had not been clearly understood by previous studies.

In addition, machine learning-based classifiers were engaged for strength predictions. The predictions could classify geopolymers into low, medium and high strength to a reasonable accuracy with high precision and false positives in range of 8 to 20% indicating not many misclassified instances. The strength predictions can potentially guide preliminary mix proportioning of metakaolin-based geopolymers to achieve required strength grade without going through tedious (trial and error) mix formulation.

8.1.2 Strength endurance and volume stability of metakaolin-based geopolymers subject to elevated temperature

To apply geopolymer as fire-resistant building material, its thermal performance should be examined at micro, meso and macro-levels. Most of the previous studies reported thermal stability of geopolymers only at micro-level. The significance of current work is to extend the understanding to higher levels. The thermal performance of bulk geopolymeric material was assessed by studying the mechanical strength retention, resistance to crack development, and volumetric changes. This had not been systematically taken up in literature and it brings us a step forward towards application of geopolymers as a fire-resistant construction material for macro-scale applications.

Metakaolin-based geopolymer specimens underwent reduction in compressive strengths due to experiencing severe crack-induced damage. The damage could be clearly perceived by observing the cross-section of the geopolymer samples and damage varied with the Si/Al molar ratio and the exposure temperature. SEM micrographs also helped to describe the performance. Thermal deformations of the geopolymer samples were noted using dilatometry and were found to be substantial. Transformation of some part of the amorphous aluminosilicate gel into crystalline material along with cracking damage, and presence of unreacted phases were found to be the possible reasons influencing the thermal performance. The need to impart

sufficient mechanical strength and volume stability to metakaolin-geopolymers for high-temperature application was realized in this work.

8.1.3 Studying the reactivity of the locally available fly ash and evaluating its Si/Al ratio

The values of mix design parameters such as Si/Al ratio, Al/Na ratio, etc. affect the performance of geopolymers at ambient temperature as well as when subjected to elevated temperature. Since fly ash is not entirely amorphous like metakaolin, reactive silicon and aluminum content and mix design parameters cannot be determined in a straightforward way. Significance of this work (**Chapter 5**) lies in assessing the reactive silicon and aluminum available in fly ash using a detailed experimental technique to estimate value of reactive Si/Al ratio. Available silicon and aluminum content was found to be dependent on the duration of dissolution. This study provides a more accurate method to estimate the reactive Si/Al ratio as compared to using a combination of quantitative XRD and XRF techniques to predict the Si/Al ratio of fly ash.

8.1.4 Enhancing thermal performance of fly ash geopolymers using mixed alkali cations

This work, presented in **Chapter 6** of this thesis, has the following key findings:

First, the current work deeply investigated the effect of using mixed-alkali cation on the thermal performance of fly ash-based geopolymers. Importance of alkali cation type for metakaolin-based geopolymers had been reported in literature; however a comprehensive study for fly-ash based geopolymers had been missing. The only one prominent research on this topic had found that due to large changes in compressive

strength and volume, the fly ash-based geopolymers were not suited for refractory applications. However, evaluating their suitability for structural applications was placed as a future work. Furthermore, that study was not comprehensive and studied performance of only one mix. Current work addressed the research gap by investigating the effect mixed-alkali cation on thermal stability of fly ash-based geopolymers in detail. It was shown in current work that large changes in the compressive strength and volume of the material subject to high temperature exposure could be prevented by a careful mix design. Stable and promising thermal performance could be achieved. The underlying mechanisms were explained by establishing the link between performances at macro-, meso- and micro-scales.

Next, it is found that investigating the performance of geopolymers at an intermediate temperature (500°C in current work) was essential to clearly explain the mechanisms governing high temperature performance of geopolymers. The effect of dehydration and viscous sintering could be clearly isolated. Especially, the SEM images could clearly explain the mechanism of crack development and crack healing and also how the performance changed with the alkali cation. These results are novel and significant and have not been previously reported.

XRD and FTIR analysis revealed that geopolymers had good chemical stability and very nominal phase transformations subject to elevated temperature exposure. Performance of these geopolymers was found to be promising for structural fire applications.

8.1.5 Regulating the high temperature performance of fly ash geopolymers by tailoring the mix design

While K-based geopolymer perform better than Na-based geopolymer, there is still a need to design Na-based geopolymers for enhanced thermal performance because Na-based alkali activators are cost-effective and easily available compared to their K-based alkali activators. For structural application of geopolymers, Na-based geopolymers show a commercial advantage. Moreover, there is very limited research conducted on tailoring the Na-geopolymer mix design to achieve good thermal performance using fly ash from one particular source. Since, not all geopolymer formulations possess good thermal resistance and performance depends greatly on the mix design factors, this work on tailoring the mix design factors was very significant. The novelty of this work (presented in **Chapter 7**) was in showing that using a single fly ash source and sodium as an alkali cation type it is possible to attain variegated high-temperature performance. And by proper tailoring of mix design factors, not only stable but even enhanced residual compressive strengths could be attained.

It was found that an initial high strength geopolymer mix could end up with either high strength or low strength after exposure to heating depending on the mix design. Conversely, an initial low strength mix ending up with either high or low strength was also possible. Further, a geopolymer mix without any significant change in compressive strength after high temperature exposure was also achievable. Detailed investigation using image analysis, dilatometry, SEM, MIP, XRD and FTIR was carried out to explain the underlying mechanisms controlling the variegated thermal performance. Those samples with high residual compressive strength after exposure to high temperature markedly showed fine cracks compared to samples with low residual strength. It was found that the extent of damage, signified by the crack pattern, thermal deformations and phase transformations, was highly dependent on water content and alkali content. The findings are significant and indicate that using a particular fly ash

source, by proper mix design selection (Si/Al ratio, water content and alkali content), it is possible to attain geopolymers with adequate performance at ambient temperature and after exposure to high temperature.

8.2 Impact of this research

Current research enhances the understanding about performance of the novel material, *geopolymer*, at ambient temperature and when subjected to high temperature heating. Specifically, the properties of geopolymers at micro-, meso- and macro-scale, namely, stability of chemical structure, deformation resistance and strength endurance, respectively, have been investigated and their relation has been established with the mix design factors (**Figure 8.1**).

Figure 8.1: Establishing the relationships between geopolymer mix design and strength endurance, volume stability and chemical stability subject to elevated temperature

The influence of mix design factors on compressive strength at ambient temperature and material properties after high temperature exposure for metakaolin-based geopolymer has been studied in detail. Tailoring of mix design to attain good performance for fly ash-based geopolymers has also been investigated. Through the understanding and knowhow gained in this research, it is possible to design geopolymers using precursor from a particular source to achieve desired thermal performance. This systematic study brings us a step forward towards application of geopolymers as a fire-resistant construction material for macro-scale applications.

Although the focus was placed on enhancing the compressive strength and fire-resistance of the material, the research approach can also be applied to enhance other properties of this material such as tensile ductility, impact resistance and durability.

8.3 Recommendations for future Research

Other than the mix design factors governing the compressive strength of metakaolin-based geopolymers considered in **Chapter 3**, factors such as curing duration, curing temperature and metakaolin type may have certain influence on the strength development. Current statistical analyses of mix design factors could be further strengthened by considering the effect of more parameters.

Another interesting area of research is to evaluate the significance of mix design factors for fly ash-based geopolymers. Fly ash-based geopolymers are highly cost-effective than metakaolin based; however fly ash based system is more complex due to material variability among different fly ash sources. A study on mix design factors for fly ash-based geopolymers would be very meaningful, involving experimental work, microstructure analysis and statistical analysis, to answer the fundamental question about what governs the compressive strength of fly ash-based geopolymers. It can potentially guide preliminary mix proportioning of fly ash-based geopolymers to

achieve required strength grade without going through tedious (trial and error) mix formulation. This study can also consider the use of rock powder as filler, as discussed in **Chapter 3** for metakaolin-based geopolymers, to achieve a wide range of mix design factors.

Further studies are required to tailor the high temperature performance of fly ash-based geopolymers using potassium (K) as alkali cation. As reported in **Chapter 6**, K-based geopolymers experienced strength gain and lower deformations than sodium (Na)-based geopolymers due to elevated temperature exposure. It would be interesting to further tailor the performance of K and NaK-based geopolymers. That would necessitate detailed microstructure investigation using FE-SEM, MIP, XRD and FT-IR. Current study considered the performance of geopolymer binder. The use of suitable fibers, fillers and aggregates should be considered to produce geopolymer composites or geopolymer concrete. A variety of fibers, fillers and aggregates with different thermal properties are commercially available and the effect of their addition on the thermal stability of geopolymer composites can be investigated.

At structural scale, the performance of this novel material needs to be examined by conducting fire tests based on standard fire curves to measure the spalling resistance and heat conductivity. Tests to measure permeability of the geopolymer composite at high temperature will also be helpful to evaluate the macro-structural stability of the geopolymer composites. Other added functions such as high tensile ductility and self-healing can be considered to make this material more versatile and enhance the safety and durability infrastructure build with geopolymer composite. Such studies on fire-resistant geopolymer concrete might provide a potential solution for construction and safety of important structures such as tunnels, underground caverns, high-rise buildings etc.

Appendix

Table A1: Mix design and compressive strength of the thirty-six (36) metakaolin-based geopolymers from published literature

Mix No.	Si/Al	water/solids	Al/Na	H ₂ O/Na ₂ O	f'_c (MPa)	Age at testing (days)	Reference
1	1.08	0.50	1.96	22.04	0.40	7	(Rowles and O'Connor 2003)
2	1.08	0.50	1.39	16.14	2.20	7	(Rowles and O'Connor 2003)
3	1.08	0.50	1.00	11.46	4.40	7	(Rowles and O'Connor 2003)
4	1.50	0.50	1.39	17.62	6.20	7	(Rowles and O'Connor 2003)
5	1.50	0.50	1.00	12.51	23.40	7	(Rowles and O'Connor 2003)
6	1.50	0.50	0.65	8.18	29.80	7	(Rowles and O'Connor 2003)
7	2.00	0.50	1.00	13.76	51.30	7	(Rowles and O'Connor 2003)
8	2.00	0.50	0.78	10.67	53.10	7	(Rowles and O'Connor 2003)
9	2.00	0.50	0.50	8.99	11.80	7	(Rowles and O'Connor 2003)
10	2.50	0.50	0.78	11.64	64.00	7	(Rowles and O'Connor 2003)
11	2.50	0.50	0.65	9.81	49.00	7	(Rowles and O'Connor 2003)
12	3.00	0.50	0.65	11.77	2.60	7	(Rowles and O'Connor 2003)
13	3.00	0.50	0.50	9.01	19.90	7	(Rowles and O'Connor 2003)
14	1.15	0.63	1.00	11.00	15.79	7	(Duxson 2006)
15	1.40	0.57	1.00	11.00	38.93	7	(Duxson 2006)
16	1.65	0.53	1.00	11.00	57.91	7	(Duxson 2006)
17	1.90	0.49	1.00	11.00	81.60	7	(Duxson 2006)
18	2.15	0.46	1.00	11.00	66.83	7	(Duxson 2006)

19	1.00	0.67	1.00	11.00	14.18	7	(Kriven et al., 2007)
20	1.25	0.62	1.00	11.00	36.57	7	(Kriven et al., 2007)
21	1.50	0.56	1.00	11.00	55.22	7	(Kriven et al., 2007)
22	1.75	0.52	1.00	11.00	74.63	7	(Kriven et al., 2007)
23	2.00	0.48	1.00	11.00	62.69	7	(Kriven et al., 2007)
24	1.58	0.73	0.44	8.53	2.00	28	(Sarkar, Dana et al. 2015)
25	2.20	0.67	0.61	11.71	28.00	28	(Sarkar, Dana et al. 2015)
26	2.75	0.25	1.25	8.50	6.00	28	(Yunsheng, Wei et al. 2010)
27	2.75	0.26	1.00	7.00	34.90	28	(Yunsheng, Wei et al. 2010)
28	2.75	0.43	0.83	10.00	0.80	28	(Yunsheng, Wei et al. 2010)
29	3.00	0.20	1.25	7.00	5.40	28	(Yunsheng, Wei et al. 2010)
30	3.00	0.34	1.00	10.00	13.60	28	(Yunsheng, Wei et al. 2010)
31	3.00	0.34	0.83	8.50	13.90	28	(Yunsheng, Wei et al. 2010)
32	3.25	0.27	1.25	10.00	8.60	28	(Yunsheng, Wei et al. 2010)
33	3.25	0.28	1.00	8.50	21.70	28	(Yunsheng, Wei et al. 2010)
34	3.25	0.27	0.83	7.00	31.20	28	(Yunsheng, Wei et al. 2010)
35	1.65	0.47	1.11	10.56	61.95	7	(Mo, He et al. 2014)
36	1.65	0.41	1.21	10.00	54.00	Few h	(Barbosa and MacKenzie 2003)

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