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Mechanical and Thermal Properties of Fly Ash-based Geopolymer Cement

Fenghong Fan
Louisiana State University and Agricultural and Mechanical College, fanfenghong@163.com

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MECHANICAL AND THERMAL PROPERTIES OF FLY ASH-BASED GEOPOLYMER CEMENT

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Civil Engineering

in

The Department of Civil and Environmental Engineering

by

Fenghong Fan
B.S., Hunan University, 2007
M.S., Hunan University, 2010
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ABSTRACT

The geopolymer concrete is a more durable and green material with less CO₂ emission and less energy consuming as compared with the widely used Portland cement (PC) concrete. In this thesis, an experimental study of the thermo-mechanical properties of a cement prepared using a class F fly ash and three different alkali-activators (NaOH activator, NaOH and Na₂SiO₃ mixture activator, and KOH and Na₂SiO₃ mixture activator) is presented. The mechanical properties, including the compressive strength, shrinkage, weight loss, and chemical composition, are investigated utilizing several key tools, such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDXS) measurements. The effects of the water/ash ratio, curing methods, cooling methods, and sealing degree on the compressive strength and thermal properties of the geopolymer products are studied and analyzed in details.

The tested results show that the geopolymer cement cured at appropriate conditions can reach a compressive strength of more than 100MPa and it also has an excellent heat resistance with a remarkable strength after the 500°C heating. In addition, it is found that the studied geopolymer cement possesses a much higher spallation resistance when suddenly cooled down by water after the high temperature heating than the ordinary Portland cement concrete which has a high spallation tendency. These findings indicate that the geopolymer cement may be an excellent construction material for the fire-protection and fire-prone structures.
CHAPTER 1 INTRODUCTION

1.1 Geopolymer Technology

Currently, the Portland cement concrete is extensively used with a general life of about 100 years and maybe 150 years for bridge engineering. In real life, the lifetime of concrete structures is less than the expect design time owing to the original design and construction errors, potential damages caused by mechanical actions and environmental effects, and changes in functionality, etc. However, many previous studies reveal that old Egyptians already knew how to build huge concrete blocks which can last for thousands of years. It has been proven by the book titled “Why the pharaohs built the pyramids with fake stones?” (Davidovits, 1984, 2009) that the building material used in the construction of the pyramids at Giza as well as in other ancient constructions is made of geopolymer concrete. During the summer of 2002, one team from the Geopolymer Institute experimented with the fabrication of five blocks, 12 tones in total, resembling those of the pyramids of Giza by using only those tools that have been found by archaeologists: a hoe to collect the aggregate, a basket to transport it, a wooden mold, a trough, a ladder, a square, a plumb line, a level, a float etc. It is well expected that geopolymers have great potential to replace Portland cement concrete as the main building materials to build new structures in the future.

Geopolymer, first coined by the French scientist Joseph Davidovits, is a class of inorganic polymers formed by reacting silica-rich and alumina-rich solids with a high alkaline solution, which combines the properties of polymers, ceramics, and cements (Davidovits, 1994; Lecomte et al. 2003; Verdolotti, 2008). Prof. Davidovits, a French scientist, proved that the Pyramids in Egypt 5000 years ago and the Great Wall in China in Song Dynasty 600 years ago were all built by geopolymer technology (Davidovits,
The geopolymer concrete has been recognized as a more durable “green” material with less CO₂ emission and less energy consuming as compared with the widely used Portland cement (PC) concrete. It is predicted that the geopolymer will replace the traditional cement and will lead to a revolution in civil engineering. Every great breakthrough in the civil engineering history is due to the research and application of new materials in civil engineering, such as the occurrence of concrete and steel, etc.

Geopolymers in general possess excellent physical and chemical properties: (1) exceptional heat/fire performance; (2) nontoxic, thus will not release toxic gas when on fire or heating; (3) better durability (thus can last for five thousand years as the pyramids): not degrade under the UV light, and highly corrosion-resistant, which can resist all organic solvents and acids resistant (Hardjito, 2004, 2005; Song X-J, Marosszeky M, Brung M, Chang Z-T, 2005); (4) less energy consuming and could be synthesized from various low-cost materials, for instance, the fly ash-based geopolymer concrete is estimated to be about 10 to 30 percent cheaper than that of the Portland cement concrete, according Rangan, (2008). In addition, they have less greenhouse gas CO₂ emission, six to nine times less than the traditional Portland cement based on the study by Davidovits(1993); (5) the heat-cured fly ash-based geopolymer undergoes low creep and very little drying shrinkage (Hardjito 2004, 2005); (6) no Alkali-Aggregate-Reaction (Davidovitts, 2013); (7) chemically compatible with concrete, and also adhere well to carbon, glass fabrics, wood, and steel; (8) unlike Ca-based cements, the water is present only to facilitate the workability and does not incorporate in the geopolymer crystal structure, which renders the geopolymer more resistant to the water penetration and the heat/fire (Davidovits 2008; Lloyd et al. 2009).
Geopolymers can be taken as a new binder for coating and adhesives, fiber composites, and waste encapsulation. The usage and properties of geopolymers are being explored in many scientific and industrial areas: chemistry, mineralogy, and geology. As stated by Davidovits (2011) that “The wide variety of potential applications includes: fire resistant materials, decorative stone artifacts, thermal insulation, low-tech building materials, low energy ceramic tiles, refractory items, thermal shock refractories, foundry applications, cements and concretes, composites for infrastructures repair and strengthening, high-tech composites for aircraft interior and automobile, high-tech resin systems, radioactive and toxic waste containment, arts and decoration, cultural heritage, archaeology and history of sciences.”

Nowadays, geopolymer is being paid extensive attention due to its potential and diverse applications to replace organic polymers and inorganic cements. Its exceptional features, including high thermal and chemical stability, competitive mechanical strength, adhesive behavior and long-term durability, make it a viable economical and environmentally friendly material. Many industrial by-products and other kinds of minerals can be utilized to produce the geopolymers (Cheng and Chiu 2003; He, J. et al. 2012).

1.2 Factors Affecting the Geopolymerization

The properties of constituent materials and the chemical composition in the geopolymers dominate the mechanical properties of the geopolymer end products, the same way for the Portland cement concrete. The experimental data with various properties are essential to make the general guidance and further explorations can be made based on the justification and verification with the as-established acknowledgement (Hadjito et al. 2004).
The geopolymerization reaction is very sensitive to different raw materials (particle size and distribution, crystallization degree, etc.), different alkali-activators (Sodium/potassium hydroxide, Sodium/potassium silicate, and the ratio of these two, etc.), different Si/Al ratios, different water/ash ratios, different curing conditions (temperature, moisture degree, opening or healing condition, curing time, etc.). Different mechanical and thermal properties of geopolymer cement will be produced according to different raw materials, alkali-activators, Si/Al ratios, water/ash ratios, and curing conditions.

1.2.1 Raw Materials

Raw materials must constitute a large portion of Aluminum and Silica, inorganic non-metallic minerals and industrial waste, of which the main active ingredient is aluminum silicate. There are different kinds of raw materials that can be used to produce geopolymer cement, such as fly ash, red mud, metakaolin, natural pozzolan, blast steel slag, rice husk ash, and etc. In this study, the class F fly ash is used to form the geopolymer cement. Geopolymers possess different mechanical and thermal properties due to different raw materials, such as their variable chemical composition, particle size (fineness) and particle shape. Most of the recent studies are found focusing on the mechanical and thermal properties of the fly ash based geopolymers.

It is observed that a higher content of the glass phase will ensure a higher degree of geopolymerization, and thus resulting in a higher compressive strength. In addition, finer fly ash balls will lead to a relatively larger contacting surface area and hence higher reactivity can be guaranteed. Both the utilization of higher combustion temperatures and the grinding of the fly ash can make the fly ash balls much finer (Diaz, 2010). Further, a small portion of unburned coal in the fly ash will require a higher ratio of the alkali-
activators to the fly ash, resulting in detrimental influence on the mechanical properties of the final geopolymer products (Diaz, 2009).

1.2.2 Alkali-activators

For the alkali-activators, several choices are adopted. Alkali metal hydroxide (sodium hydroxide), carbonate, sulfate, phosphate, and fluoride (few studies) can be used as the activators. Silicate and aluminum silicate enrich the alkaline activator species in a large degree.

1.2.2.1 NaOH

Higher NaOH dosages can result in a better workability, higher 1-, 7-, and 8-day strengths, and shorter demolding time. But too much (excessive) NaOH concentration would adversely affect the strength. The optimal NaOH content depends on other mixture constituents. The concentration of sodium hydroxide (NaOH) liquid measured in terms of Molarity (Mol/L) is better in the range of 8 to 16 M (Mol/L). To check which one influences the properties of the geopolymers more, the Na\(^+\) or the OH\(^-\), the study by Hardjito (2004) concluded that it is the OH\(^-\) that influences the compressive strength of the geopolymers most.

1.2.2.2 KOH

The compressive strength of the K-containing geopolymers is generally higher than the Na counterparts because Na-containing pastes are more viscous and harder to mix. In order to reach the same compressive strength level, the amount of Na-solution must increases by 50% as compared to the K-solution, which means that the Na-based geopolymers are less user-friendly than the K-based geopolymers (Davidovits, 2011).

1.2.2.3 Na\(_2\)SiO\(_3\)

The higher ratio of the sodium silicate to the sodium hydroxide liquid by mass, the
higher the compressive strength of the geopolymer concrete is. The reason maybe that Na$_2$SiO$_3$ improves the Si:Al ratio and hence the compressive strength.

1.2.2.4 Si: Na

Some papers (Hardjito, and Rangan, 2005) mentioned about the increase of Na$_2$O:Si$_2$O$_3$ decreases the compressive strength of geopolymer.

1.2.3 Si/Al Ratio

Silica and alumina are the main precursors for the geopolymeric reaction, and the ratio of Si and Al is the fundamental influence factor for the properties of geopolymer. The Silicon oxide (SiO$_2$) to the aluminum oxide (Al$_2$O$_3$) ratio by mass in the source material (fly ash) should preferably be in the range of 2.0 to 3.5 to make a good concrete (Si:Al by Mol is equal to 1.733 to 3.033). The ratios of Si and Al by mol in the geopolymer concrete produced by Hardjito (2004) are about 1.779 and 1.883.

1.2.4 Water/ash Ratio

The added water remains outside of the geopolymeric network, acting as a lubricating element (Davidovitts, 2011). While the mechanism of the polymerization is yet to be fully understood, a critical feature is that water is present only to facilitate the workability and does not become a part of the resulting geopolymer structure. In other words, water is not involved in the chemical reaction and instead is expelled during curing and the subsequent drying.

It is well accepted that the addition of water decreases the compressive strength. However, water plays an important role in the dissolution and transportation process, indicating that the water influences the first two essential steps of geopolymerization. There must be a proper range of water/ash ratio that an optimum compressive strength of geopolymer cement can be warranted. The lower the water/ash ratio, the less fluidity is.
The water/ash ratio affects the volume of pores and the porosity in the matrix which directly influences the strength of the geopolymer concrete (Kong et al. 2008b). However, consider the mechanical property and workability together, it is important to study the optimum water/ash ratios for the geopolymer cement, the same as that for the ordinary Portland cement.

1.2.5 Curing Regimes

There are many studies about the effects of the heat curing on the compressive strength of the fly ash based geopolymer (Davidovits 2011; Jiang et al. 1992; Duxson et al. 2007; Bakharev 2005). Jiang et al. (1992) explained the reason for the need of the heat treatment is that the activation of the fly ash is an endothermic reaction so that the heat curing is very important for the geopolymerization of the fly ash based geopolymer cement. Hardjito et al. (2004) studied the compressive strength of the fly ash based geopolymer cement with the curing temperature ranging from 30°C to 90 °C and concluded that the compressive strength of the geopolymer cement increases when the curing temperature increases. It is also proved that a longer heat curing time improves the degree of geopolymerization and hence results in higher compressive strength. However, the increase in the compressive strength beyond 24 hours heat curing time is not significant. Therefore, the heat-curing time is better to be set as less than 24 hours in the practical applications. Long pre-curing process at the room temperature before the heat treatment is also beneficial for the strength development of the fly ash based geopolymer cement. Bakharev (2005) proved that the compressive strength is significantly higher with the geopolymer cement samples stored 24 hours at the room temperature before the heat curing.
1.2.6 Plasticizers and Retardants

Plasticizers: sodium naphthalene sulfonate is a well-known plasticizer, which increases the fluidity of geopolymer resins and cement pastes (Davidovits, 2011).

Retarders: delay the setting time of geopolymer cement without affecting the long-term mechanical properties. Retarding admixtures are mainly based on materials having lignosulfonic acids and their salts, hydroxyl-carboxylic acids, tartaric acid, citric acid, and their salts, sugar and their derivatives and inorganic acids and their salts such as borates, phosphates. Several Fe$^{2+}$ salts can be used as the retardants. Adding NaCl can retard the curing time for 20 mins and also decrease the compressive strength of geopolymer concrete (Davidovits, 2011).

1.3 Thermal Properties of Geopolymers

A 28-storey building caught fire and at least 42 people were killed and 90 more people were critically injured on November 15$^{th}$ 2010 in Shanghai, China, which aroused a great concern on the fire performance of structures. Another tragedy in this century is the twin towers in New York destroyed in 9/11 attacks, 2001. The steel building collapsed quickly within two hours in fire. Moreover, most organic matrix cannot bear the temperature more than 200°C and will issue poison gas when on heat/fire. Therefore, there is an urgent necessity to enhance the fire/heat resistant performance of structures. Geopolymer concrete, coating, and matrix may resolve these problems. The geopolymers discovered recently are reported to possess excellent fire resistant performance due to their ceramic like characteristics and they are prepared using alkali activation and alumino-silicate raw materials (Davidovits et al. 1984, 1994, 1996, 2008; Cheng et al. 2003; Barbosa et al. 2003a, 2003b; Bakharev, 2005, 2006; Kong et al. 2007, 2008a, 2008b, 2010). Foden, et al. (1996) first examined the mechanical properties of the carbon
composites made using an inorganic polymer, including strengths in tension, flexure, and shear. It is reported that the carbon composite made with geopolymer matrix retains considerable strength even at 1000°C.

Recent work by Bakharev (2005, 2006), Kong et al. (2007, 2008a, 2008b, 2010), Provis et al. (2009), Pan et al. (2010), Guerrieri et al. (2010), and Zhao et al. (2011) reported that the heat resistance of the fly ash based geopolymer materials is better than that of the metakaolin-based geopolymers. Kong, et al (2007) reported that the fly-ash based geopolymer paste had a strength increase of 6% while the metakaolin-synthesized geopolymer paste counterparts showed a strength reduction of 34% after the exposure to 800°C. This is because the high porosity and proper pore size of the fly-ash based geopolymer matrix accelerate the dehydration of free and chemically-bound water when heated, thus decreasing the damage to the matrix. The strength increase and high heat resistant performance of the fly ash based geopolymers are also partly attributed to the large proportion of hollow spheres and the sintering reactions of un-reacted fly ash particles. Compared with metakaolin, the fly ash has a lower cost and less environmental pollution.

The studies by Kong (2008b) and Xu et al. (2000) showed that KOH-based pastes perform better at the room temperature and high heating temperature (after elevated temperature exposure till 850°C) than NaOH-based pastes. However, Kong et al. (2008) and Rahier et al. (2001) both proved that the sodium-silicate based geopolymer provides better compressive strength than its potassium silicate-based equivalent, both before and after exposed to the elevated temperature (850°C). The reason was described by Rahier et al. (1997) that Na₂SiO₃-based geopolymer synthesized at a faster rate and may underwent
further progression of geopolymerization reaction than those K$_2$SiO$_3$-based geopolymers.

Portland cement concrete can spall when exposed to fire or high temperature heating, especially when subjected to a rapid temperature rise simulating fire (Zhao et al. 2011), like in an accidental fire. Portland cement concrete after heating or fire will also be fatally damaged by rapid water cooling just like the real fire-fighting method in our daily life. Geopolymer is reported to be an environmentally friendly and fire resistant material which possesses higher spalling resistance in a rapid temperature rise simulating fire (Zhao et al. 2011). However, the spalling behavior of geopolymer cement cooled suddenly by water after high temperature heating is not reported in the literature.

1.4 Limitations
While numerous geopolymer systems have been proposed (many are patented), most of them are difficult to work with and require great care in their production. In addition, the polymerization reaction is very sensitive to the temperature and usually requires that the geopolymer concrete should be cured at elevated temperature under a strictly controlled temperature regime (Hardjito et al. 2004; Tempest et al. 2009; Lloyd and Rangan 2009). In many respects, these facts may limit the practical applications of the geopolymer concrete in the transportation infrastructure to the precast applications.

1.5 Overview of the Thesis
The goal of this research is to develop a geopolymer material-based “GeoCement” that may replace the traditional Portland cement. This study first in Chapter 2 presents the mechanical properties of the class F fly ash based geopolymer materials prepared using different alkali-activators, such as NaOH solution, NaOH and Na$_2$SiO$_3$ mixed solution, and KOH and Na$_2$SiO$_3$ mixed solution. The effects of water/ash ratio, curing methods, and sealing degree on the compressive properties of geopolymer are investigated.
The geopolymer cement with a good thermo-mechanical performance is developed in Chapter 3 in order to improve the fire performance of structures based on the good mechanical performance of the class F fly ash based geopolymer materials as formed. The effects of different factors on the thermo-mechanical properties of the geopolymer cement are discussed. The compressive strength, shrinkage, and the weight loss before and after the heating process are tested as well as the microstructures and the chemical composition of the final products are investigated by employing the X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDXS) measurements. Potential applications of the formed geopolymer cement are also discussed in Chapter 4 with the conclusions.
CHAPTER 2 THE PROPERTIES OF GEOPOLYMER CEMENTS ACTIVATED BY DIFFERENT ALKALI-ACTIVATORS

2.1 Introduction

Alkali-activators play an important role in the geopolymerization, which determines the mechanical and thermal properties of geopolymer cements. Alkali-activators have the following choices: alkali metal hydroxide (sodium hydroxide, potassium hydroxide), carbonate, sulfate, phosphate, fluoride (very few studies), silicate and aluminum silicate. Two alkali metal hydroxides, sodium hydroxide and potassium hydroxide, are commonly used and the sodium silicate is adopted in many studies. In this chapter, three kinds of geopolymer cements will be discussed, which are activated by sodium hydroxide activator, sodium hydroxide and sodium silicate mixed activators, and potassium hydroxide and sodium silicate mixed activators.

2.2 Materials and Experimental Methods

2.2.1 Materials

The raw materials used for geopolymer synthesis include a low calcium Class F fly ash (Boral Material Technologies, Inc.), sodium hydroxide (purity quotient: 99%, Sigma-Aldrich Co., USA), potassium hydroxide (purity quotient: 88%, Sigma-Aldrich Co., USA), sodium silicate solution (9.07 wt.% Na₂O and 29.35 wt.% SiO₂, Aqua Solutions Inc, USA) and deionized water. The chemical composition of the low calcium Class F fly ash is shown in Table 2.1, the molar ratio of Si/Al is 2.154, and the gravity density is 2.46.

The XRD traces of the fly ash and one mixture of 5% quartz and 95% glass are compared as shown in Figure 2.1. In this figure, a very huge and nonsymmetrical hump at 5-40° 2θ can be clearly observed for the XRD trace of the fly ash, along with several sharp peaks identified as quartz and Kaolinite. The high peaks of the quartz in the fly ash and the mixture of 5% quartz and 95% glass are 785, and 664, respectively. Therefore, it
is predicted that the raw material of the Class F fly ash is almost amorphous with a percentage of about 6% (785/664*5%=5.9%) of crystalline (mainly quartz). Figure 2.2 shows the particle size distribution (PSD) curve of the fly ash determined by the ASTM standard test method combining both sieving and hydrometer analyses (ASTM 2010). For this fly ash, 20% of the raw material are sand-sized (>75 µm) coarse particles and the median particle size ($D_{50}$) is 22 µm.

Table 2.1 Composition of the fly ash (wt.%) by ASTM C 618 test report.

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>LOI</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>52.06</td>
<td>20.54</td>
<td>5.50</td>
<td>14.07</td>
<td>3.29</td>
<td>0.57</td>
<td>0.94</td>
<td>0.69</td>
<td>0.10</td>
<td>0.01</td>
</tr>
</tbody>
</table>

LOI: Loss of ignition

Figure 2.1 Comparisons of the XRD traces between the fly ash and a mixture of 5% quartz and 95% glass (Q=quartz, QTZ=quartz, K=Kaolinite)
2.2.2 Sample Preparation

During this part, three groups of cement samples are illustrated and prepared based on different materials used in the process. According to the source materials as used, they are named in different groups. The NaOH activated fly ash geopolymer cement samples are named Group 1 (G1), the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples are named Group 2 (G2), and the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples are named Group 3 (G3). The details about the preparation process will be discussed separately as follows.

2.2.2.1 NaOH Activated Fly Ash Geopolymer Cement Samples (G1)

For the NaOH activated fly ash based geopolymer cement (Group 1), a number of 35 small size cylinder samples (Ø0.75*2.0in) and 2 big size cylinder samples (Ø2.0*4.85in) were cast. The composition of Group 1 (G1) geopolymer cement mixture is shown in Table 2.2. Sodium hydroxide pellets were mixed with distilled and deionized water to
prepare an alkaline solution about one or two hours in advance (it mainly depends on the size of the container, the stirring velocity and the size of the stirrer) in order to let it cool down to the room temperature of 22°C. Then, the class F fly ash was added and blended with the alkaline solution (NaOH solution), and the mixed solution was stirred about 90 minutes before it was cast in the prepared plastic cylinders. The water/cement ratio was calculated as a ratio of the total mass of water to the total mass of fly ash and the sodium hydroxide. The water/cement ratio plays an important role for the workability of the fly ash cement.

Table 2.2 The composition of Group 1 (G1) geopolymer cement mixture.

<table>
<thead>
<tr>
<th></th>
<th>G1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/Al</td>
<td>2.15</td>
</tr>
<tr>
<td>Si/Na</td>
<td>1.0</td>
</tr>
<tr>
<td>Water/Cement (FA+NaOH)</td>
<td>0.5</td>
</tr>
<tr>
<td>Class F fly ash</td>
<td>100g</td>
</tr>
<tr>
<td>NaOH (g)</td>
<td>19.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>59.5g</td>
</tr>
</tbody>
</table>

2.2.2.2 NaOH and Na₂SiO₃ Activated Fly Ash Geopolymer Cement Samples (G2)
For the Group 2 (G2) geopolymer cement samples, the sodium hydroxide pellets were mixed with sodium silicate solution to prepare an alkaline solution one day in advance in order to let it cool down to the room temperature of 22°C. It is also to make sure there is enough time for the dissolution of Na₂SiO₃ to generate small reactive silica and alumina (Al³⁺, Si⁴⁺) by alkali. Hence, in the reorientation process, the large molar ratio of the dissolved precursor ions can be easily transported and condensate into
monomers accompanied with a high rate of geopolymerization in the directly followed process (Davidovitts, 2013). In the alkali-activated solution, the molar concentration of OH\(^{-}\) and Na\(^{+}\) are 10.8M and 20.0M, respectively.

Two things must be paid attention to during the process. (1) The sodium hydroxide pellets should be added slowly to the sodium silicate solution to prevent the spalling of NaOH to the air and for safety purpose. Some water will evaporate due to the heat released from the dissolution process. Even if the plastic cylinders are sealed quickly, the water loss still exists, which reduces the water/ash ratio to some extent. So the sodium hydroxide pellets should be added by several steps with careful stirring. (2) It is not suggested to make too much alkaline solution at one time because it is difficult for all the sodium hydroxide pellets to dissolve in a short time and the generated heat during the dissolution is large.

As the sodium hydroxide pellets dissolved in the sodium silicate solution with stirring, a transparent alkali solution was achieved. Then, the transparent solution became white and hardened one day later. It should be noted that plastic containers, instead of glass beakers, are highly recommended to contain the solution during the process. It was witnessed that the glass beakers broke after the hardened solution being heated and stirred again, which may be due to that the glass reacts with the alkali solution, or the variation of the temperature.

The class F fly ash was blended with the cooled down alkaline solution (the mixed solution of NaOH and Na\(_2\)SiO\(_3\)) by three or four steps with stirring for several minutes before the mixtures were cast in the plastic cylinders. The composition of the geopolymer cement mixtures (G2) is shown in Table 2.3 along with the curing methods adopted.
Table 2.3 Geopolymer mixture combinations of Group 2 (G2) samples

<table>
<thead>
<tr>
<th>Mixture no.</th>
<th>Si/Al</th>
<th>Na/Si</th>
<th>W/FA</th>
<th>Curing regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2-No.1</td>
<td>2.50</td>
<td>1.0</td>
<td>0.30</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.2</td>
<td>2.50</td>
<td>1.5</td>
<td>0.30</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.3</td>
<td>2.50</td>
<td>1.0</td>
<td>0.35</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.4</td>
<td>2.50</td>
<td>1.0</td>
<td>0.40</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.5</td>
<td>3.00</td>
<td>1.5</td>
<td>0.74</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.6</td>
<td>3.00</td>
<td>1.5</td>
<td>0.74</td>
<td>22°C(3h), 60°C(7h)</td>
</tr>
<tr>
<td>G2-No.7</td>
<td>3.00</td>
<td>1.5</td>
<td>0.74</td>
<td>22°C(24h), 60°C(7h)</td>
</tr>
<tr>
<td>G2-No.8</td>
<td>2.50</td>
<td>1.5</td>
<td>0.35</td>
<td>22°C</td>
</tr>
<tr>
<td>G2-No.9</td>
<td>2.50</td>
<td>1.0</td>
<td>0.30</td>
<td>22°C water curing(60days)</td>
</tr>
<tr>
<td>G2-No.1*</td>
<td>2.50</td>
<td>1.0</td>
<td>0.30</td>
<td>60°C(24h)</td>
</tr>
<tr>
<td>G2-No.2*</td>
<td>2.50</td>
<td>1.5</td>
<td>0.30</td>
<td>60°C(24h)</td>
</tr>
<tr>
<td>G2-No.3*</td>
<td>2.50</td>
<td>1.0</td>
<td>0.35</td>
<td>60°C(24h)</td>
</tr>
<tr>
<td>G2-No.4*</td>
<td>2.50</td>
<td>1.0</td>
<td>0.40</td>
<td>60°C(24h)</td>
</tr>
<tr>
<td>G2-No.5*</td>
<td>3.00</td>
<td>1.5</td>
<td>0.74</td>
<td>60°C(24h)</td>
</tr>
</tbody>
</table>

Note: W/FA refers to the ratio of water/fly ash. * refers to a different curing method adopted as compared with the ones without the *.

2.2.2.3 KOH and Na$_2$SiO$_3$ Activated Fly Ash Geopolymer Cement Samples (G3)

In preparing the KOH and Na$_2$SiO$_3$ Activated Fly Ash Geopolymer Cement Samples, the potassium hydroxide (KOH) pellets were added to sodium silicate solution by several steps with careful stirring in plastic containers. The alkaline solution should be prepared one day in advance to let it cool down to the room temperature of 22°C. For this alkali-activated solution, the molar concentration of OH$^-$ is 6.2M. Then, the class F fly ash was
blended with the alkaline solution (the mixed solution of KOH and Na$_2$SiO$_3$) by three or four steps. The mixed solution was stirred for several minutes manually before it was cast in plastic cylinders, the same procedure as for preparing the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples. The composition of Group 3 (G3) geopolymer cement mixtures is shown in Table 2.4 with several curing regimes in order to avoid the water loss during the cement curing. No. 1 was cured at the room temperature (~22°C) with a plastic wrap preservative film for 60 days. No. 2 was cured by the normal curing method, which is in ambient environment at the room temperature with wet cloth covered for 60 days. No.3, No.4, and No.5 were cured in water at room temperature for 7 days, 60 days, and 90 days, respectively.

Table 2.4 Geopolymer mixture combinations of Group 3 (G3)

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Si/Al</th>
<th>Si/M (Na, K)</th>
<th>W/FA</th>
<th>Na$_2$SiO$_3$/KOH</th>
<th>Curing regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>G3-No.1</td>
<td>2.83</td>
<td>1.81</td>
<td>0.34</td>
<td>1.8</td>
<td>22°C for 60 days</td>
</tr>
<tr>
<td>G3-No.2</td>
<td>2.83</td>
<td>1.81</td>
<td>0.34</td>
<td>1.8</td>
<td>22°C wet cloth curing for 60 days</td>
</tr>
<tr>
<td>G3-No.3</td>
<td>2.83</td>
<td>1.81</td>
<td>0.34</td>
<td>1.8</td>
<td>22°C water curing for 7 days</td>
</tr>
<tr>
<td>G3-No.4</td>
<td>2.83</td>
<td>1.81</td>
<td>0.34</td>
<td>1.8</td>
<td>22°C water curing for 60 days</td>
</tr>
<tr>
<td>G3-No.5</td>
<td>2.83</td>
<td>1.81</td>
<td>0.34</td>
<td>1.8</td>
<td>22°C water curing for 90 days</td>
</tr>
</tbody>
</table>

2.2.3 Geopolymer Synthesis and Characterization

To examine whether the samples were cured completely or not, several methods can be adopted: (1) Test the compressive strength after 14 days, 21 days, 28 days, 35 days to investigate the changes of the compressive strength. Most researchers used this method;
however, it takes more time and effort. (2) Test the weight changes of the samples to check whether the water still evaporates from the inside of the samples. In the current study, the second method was used, which is more convenient and takes less time and effort.

For the heating methods, the cylinder samples were exposed to 500°C and 800°C with the heating curve shown in Figure 2.3. For the setup of the temperature in the furnace, a heating rate of 10°C/min was adopted, and then the temperature was maintained for 60 min. After that, the temperature inside the furnace was left to cool down to the room temperature at a pace of -40°C/min (natural cooling down method: NC). For some samples, were put into water immediately after exposing to 500°C and 800°C for 1 hour (Water cooling down method: WC). Meanwhile, the unheated samples were left undisturbed at the room temperature of 22°C.

![Figure 2.3 The heating curve in different temperatures](image-url)
The unconfined compressive strength of the cured and heated geopolymer cylindrical specimens were measured using an automated GeoTAC loading frame (Trautwein Soil Testing Equipment, Inc., USA) with load limit of 2000Ib, and a strain limit of 15% at a fixed strain rate of 0.5%/min (ASTM C39 and C39M), as shown in Figure 2.4. In order to obtain flat and parallel surfaces of the two ends of each sample, sand papers were used to polish each sample at the two ends. Then, a very thin layer of lubricant coating was used for both ends of each sample so as to reduce the friction effects and the possible shear stress, which was developed during the test between the sample ends and the contacting surfaces of the test frame.

Figure 2.4 The unconfined compressive strength test

The compositions of the class F fly ash raw materials and completely cured NaOH activated geopolymer cement were characterized by the X-ray diffraction (XRD) analysis
based on a Bruker/Siemens D5000 automated X-ray powder diffractometer. The scanned materials were grinded into fine powders with particle sizes $\leq 38 \, \mu m$ for most silicate minerals in a McCrone micronizing mill (McCrone Accessories and Components) (He, J. et al. 2012).

2.3 Results and Discussion
2.3.1 NaOH Activated Fly Ash Based Geopolymer Cement (G1)

2.3.1.1 General Observations

For NaOH activated fly ash based geopolymer cement (G1), a number of 35 small size cylinder samples ($\phi 0.75 \times 2.0 \, in$) and 2 big size cylinder samples ($\phi 2.0 \times 4.85 \, in$) were casted (Figure 2.5). After the casting, some transparent solution permeated from the bottom of all the plastic cylinder molds, which indicated that a smaller water/cement ratio should be chosen for this kind of class F fly ash materials. The samples were sealed for another 60 hours at the room temperature of $22^\circ C$, and de-molded 12 days later. As the whole sample exposed to the air, crystal needles grew out (as shown in Fig. 2.6), which may be due to the excess of the sodium hydroxide solution, i.e. the water/cement ratio is higher to some extent for this kind of class F fly ash.

![Molded samples (G1)](image)

(a) Demolding  (b) Cling film sealing

Figure 2.5 Molded samples (G1)
Figure 2.6 The crystal needles on the samples during curing (G1)

All the samples cracked after 60 days (Figure 2.7) and the weight of the samples continued decreasing. The compressive strength of the samples was very low and the fire resistant performance of these samples was very poor, which indicated that the fly ash and alkaline solution did not act very well and the geopolymerization rate was very small. The main reason might be attributed to the high water/cement ratio.
2.3.1.2 Weight Change

The weight change of 9 selected samples (2 big size samples and 7 small size samples) was measured and partial of the results are shown in Table 2.5. All the test results of the 9 samples are plotted as shown in Figure 2.8, and Figure 2.9.

Table 2.5 The weight change of the selected 9 samples

<table>
<thead>
<tr>
<th>s#</th>
<th>25days</th>
<th>26days</th>
<th>27days</th>
<th>28days</th>
<th>31days</th>
<th>33days</th>
<th>34days</th>
<th>35days</th>
<th>38days</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>210.42</td>
<td>209.97</td>
<td>208.97</td>
<td>208.62</td>
<td>207.76</td>
<td>207.42</td>
<td>206.98</td>
<td>205.98</td>
<td>198.78</td>
</tr>
<tr>
<td>s2</td>
<td>214.57</td>
<td>214.27</td>
<td>213.87</td>
<td>213.55</td>
<td>212.54</td>
<td>212.13</td>
<td>211.77</td>
<td>210.75</td>
<td>203.27</td>
</tr>
<tr>
<td>s3</td>
<td>24.63</td>
<td>24.62</td>
<td>24.55</td>
<td>24.55</td>
<td>24.27</td>
<td>24.34</td>
<td>23.89</td>
<td>24.00</td>
<td>23.02</td>
</tr>
<tr>
<td>s4</td>
<td>25.65</td>
<td>25.62</td>
<td>25.67</td>
<td>25.59</td>
<td>25.28</td>
<td>25.23</td>
<td>24.81</td>
<td>24.58</td>
<td>23.87</td>
</tr>
<tr>
<td>s5</td>
<td>23.78</td>
<td>23.79</td>
<td>23.82</td>
<td>23.72</td>
<td>23.74</td>
<td>23.76</td>
<td>23.40</td>
<td>23.34</td>
<td>22.78</td>
</tr>
<tr>
<td>s6</td>
<td>23.97</td>
<td>23.97</td>
<td>23.98</td>
<td>23.91</td>
<td>23.73</td>
<td>23.72</td>
<td>23.59</td>
<td>23.34</td>
<td>22.29</td>
</tr>
<tr>
<td>s7</td>
<td>24.28</td>
<td>24.29</td>
<td>24.31</td>
<td>24.20</td>
<td>24.07</td>
<td>24.05</td>
<td>23.59</td>
<td>23.52</td>
<td>22.48</td>
</tr>
<tr>
<td>s8</td>
<td>25.25</td>
<td>25.27</td>
<td>25.29</td>
<td>25.28</td>
<td>24.79</td>
<td>24.80</td>
<td>24.40</td>
<td>24.62</td>
<td>23.6</td>
</tr>
<tr>
<td>s9</td>
<td>25.3</td>
<td>25.32</td>
<td>25.35</td>
<td>25.29</td>
<td>25.13</td>
<td>24.97</td>
<td>24.67</td>
<td>24.47</td>
<td>23.58</td>
</tr>
</tbody>
</table>

Note: s# refers to the number of the selected specimen. The error of measurement can be ±0.25g.
It is observed in Figure 2.8 and Figure 2.9 that the average weight loss rate between 25 days and 38 days of big size samples (s1 and s2) and small size samples (s3-s9) is 5.4% and 6.5%, respectively, while for the average weight loss rate between 25 days and 61 days of big size samples (s1 and s2) and small size samples (s3-s9) is 12.7% and 11.9%, respectively. Therefore, the short term weight loss for the big size samples (s1 and s2) is smaller than those for the small size samples (s3-s9), while the long term weight loss is the opposite. The long term weight loss without sealing (s1 and s2) is larger than that with sealing (s3-s9), indicating that the sealing is a good method to prevent the water loss.
2.3.1.3 Compressive Strength

The compressive strength of the geopolymer samples without the heating procedure was measured after 28 days of curing. The failure patterns are shown in Figure 2.10 and the test results of 3 samples (s3-s5) are shown in Figure 2.11 and Table 2.6. The ultimate stress is the broken stress, and the ultimate strain is the strain when the sample reaches the ultimate stress.

![Figure 2.10 Failure patterns of Group 1 samples](image)

![Figure 2.11 The axial stress (MPa)-axial strain (%) curve of the geopolymer cement samples after 28 days.](image)
<table>
<thead>
<tr>
<th>specimen#</th>
<th>Diameter (inch)</th>
<th>Height (inch)</th>
<th>Ultimate Stress (MPa)</th>
<th>Ultimate Strain (%)</th>
<th>Elastic Modulus(MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s3</td>
<td>0.75</td>
<td>1.91</td>
<td>4.6</td>
<td>2.66</td>
<td>234</td>
</tr>
<tr>
<td>s4</td>
<td>0.75</td>
<td>1.87</td>
<td>5.1</td>
<td>1.70</td>
<td>314</td>
</tr>
<tr>
<td>s5</td>
<td>0.75</td>
<td>1.92</td>
<td>4.4</td>
<td>1.73</td>
<td>314</td>
</tr>
</tbody>
</table>

It is shown in the Figure 2.11 that the typical compressive strength of the Group 1 geopolymer cement are less than 5.5MPa, which indicated that the geopolymerization rate for Group 1 was very small. The elastic modulus of specimen 3 was only 234MPa and it was only 314MPa for specimens 4 and 5, far less than the elastic modulus of ordinary Portland cement concrete, 22000MPa.

Several reasons may contribute to this phenomenon: (1) the water/cement ratio is very large, which directly reduced the compressive strength of the geopolymer concrete similar to that for the ordinary Portland cement concrete; (2) the silicate in the class F fly ash raw material may exist mostly as crystal phase which did not dissolve in the solution, resulting in a low Si/Al ratio in the geopolymerization. However, this reason was excluded by the XRD characterization of the class F fly ash raw materials from Figure 2.1 that the fly ash is mainly amorphous with little crystalline inclusions of quartz; (3) only hydroxide alkali-activator cannot form good geopolymer, which directly lead to the low geopolymerization.

To improve the compressive strength, low water/cement ratios should be considered, with the addition of silicate (this is the main reason that sodium silicate was added in the
later tests for G2 and G3 samples), and some additives which will help the crystal phase silicate in class F fly ash raw material to dissolve easily.

2.3.1.4 Thermal Properties

After exposed to the elevated temperature, the color of the geopolymer samples became slight lighting. Macro-cracks can be observed on the surface of the samples after 800°C heating, as shown in Figure 2.12. The thermal test results for three selected samples are shown in Table 2.7, which shows that the high water/cement ratio contributes mostly to the large deformation and weight loss for G1 samples.

Kong et al. (2007) reported that a slight lighting of color and macro-cracks in the order of 0.1 to 0.2 mm were found in the metakaolin based geopolymer with the solids-to-liquids ratio of 0.8. However, the fly ash geopolymer paste with the solids-to-liquids ratio of 3.0 did not have any cracks on the surface after high temperature exposure, which indicated that the solids-to-liquids ratio (or the opposite water/cement ratio) influences the thermal properties and compressive strength of geopolymer cement significantly.

Figure 2.12 Group 1 samples before and after heating (800°C).
Table 2.7 Thermal extraction of Group 1 geopolymer cement samples

<table>
<thead>
<tr>
<th>specimen#</th>
<th>Diameter decrease (%)</th>
<th>Height decrease (%)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s3</td>
<td>1.7</td>
<td>1.6</td>
<td>17.2</td>
</tr>
<tr>
<td>s4</td>
<td>3.0</td>
<td>1.3</td>
<td>17.5</td>
</tr>
<tr>
<td>s5</td>
<td>1.0</td>
<td>1.8</td>
<td>14.7</td>
</tr>
</tbody>
</table>

2.3.1.5 X-Ray Diffraction (XRD) Analysis

Figure 2.13 shows the comparison of the XRD patterns between the class F fly ash and the NaOH activated fly ash-based geopolymer.

![XRD patterns comparison](image)

Figure 2.13 XRD patterns of fly ash raw material and geopolymer sample (G1) (Q=quartz, K= Kaolinite).

The XRD pattern of the fly ash shows a huge broad hump between 6-36° 2θ with a few sharp peaks, indicating that there are a large number of calcined silica and alumina and a small number of crystalline phases such as quartz (SiO₂), and Kaolinite (Al₂Si₂O₅(OH)₄). As for the geopolymer end products, the broad hump (2θ) indicates that there is amorphous geopolymer matrix formed. A broad hump between 18-36° 2θ is the
characteristic reflection of amorphous geopolymers (Li and Liu 2007; Guo et al. 2010). For the geopolymer sample, there exists a broad hump between 8-16° 2θ, which is almost the same as that of the fly ash, showing a low degree of geopolymerization and low geopolymer binder in the NaOH activated geopolymer cement samples. This observation may be used to explain why the NaOH activated fly ash-based geopolymer cement possesses low compressive strength and stiffness. In addition, this also explains why the NaOH activated fly ash-based geopolymer cement is weak and has poor thermo-mechanical properties.

2.3.2 NaOH and Na₂SiO₃ Activated Fly Ash Geopolymer Cement (G2)

2.3.2.1 General Observations

For each mixture combination of G2 as shown in Table 2.3, 5 duplicate specimens were cast to ensure reproducibility, as shown in Figure 2.14. From Figure 2.14, it can be seen that the organic epoxy like geopolymer adhesive were formed, which proved that sodium silicate improves the degree of geopolymerization with an appropriate ratio of Si/Al.

It was found that some water precipitated from the samples of G2-No.2 and G2-No.8 (Na/Si=1.5) mixtures 2 days later after the casting, as shown in Fig. 2.15, which will be
further discussed in the bleed water effect section later. The bottom molds were taken away 6 days later.

![Figure 2.15 The water precipitation of the G2-No.2 samples](image)

After 14 days, all the samples were demolded except the water precipitated samples of G2-No.2 and G2-No.8 mixtures, as well as the samples of G2-No.5 mixture. The water/ash ratio (0.74) for the samples of G2-No.5 mixture is relatively high. As such, some crystals grew out of the bottom surface of the samples of G2-No.5 mixture, which makes the demolding not available at this time.

After 17 days, the samples G2-No.2 and G2-No.5 mixtures expanded, especially the samples of G2-No.5 mixture, which may be due to its high water/ash ratio (0.74). The G2-No.5 samples shrank on both ends, but expanded in the middle of the cylinder, and they were broken with lots of macro-cracks. The G2-No.6~7 samples also had macro-
cracks on the bottom, expanded and cracked, similar as observed for G2-No.5 samples which have the same water/ash ratio.

All the samples of G2-No.1*-5* cracked after 24 hours of 60°C heat curing in the oven. There was some water vapor in the cling film sealed on the top of the samples 4 days later. The reasons are analyzed in the following: (1) the samples may not be sealed well, and the water inside of the samples evaporated quickly in the heat curing; (2) the water may not act with the fly ash and alkali-activators completely before the heat curing. More time are needed to let the samples stay alone for a while. It is known that different curing methods have different effects on the compressive strength of the geopolymer cement. Further studies about the effects of different heat curing methods on geopolymerization are needed.

2.3.2.2 Weight Change

The weight change of selected samples of G2-No.1-3 and G2-No.5 mixtures were measured with the data listed in Table 2.8 and plotted in Figure 2.16. From Table 2.8, the weight change of the samples of G2-No.5 was larger than that for the samples of G2-No.1 and G2-No.3, which was probably due to the higher water/ash ratio (0.74) adopted for samples of G2-No.5. As the water precipitation cannot be avoided during the curing process, it tends to be that lower compressive strength is accompanied with more water precipitation. In addition, a range of the water/ash ratio from 0.3 to 0.35 was tested to be a good range for appropriate operability of the mixture. The G2-No.5 samples cracked finally maybe due to the high water/ash ratio.

Although the water precipitation lasted for a long time for the G2-No.2 samples, it is noted that the weight of these samples increased 0.3g. This may be due to the production of Na$_2$CO$_3$ by CO$_2$ and additional NaOH caused by the large molar ratio of Na/Si (1.5).
Table 2.8 The weight change of the G2-No.1-3, and G2-No.5 samples.

<table>
<thead>
<tr>
<th>No.</th>
<th>16days</th>
<th>18days</th>
<th>20days</th>
<th>24days</th>
<th>26days</th>
<th>34days</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>30.5</td>
<td>30.5</td>
<td>30.5</td>
<td>30.4</td>
<td>30.4</td>
<td>30.1</td>
<td>-0.4</td>
</tr>
<tr>
<td>1.2</td>
<td>30.8</td>
<td>30.8</td>
<td>30.7</td>
<td>30.6</td>
<td>30.6</td>
<td>30.5</td>
<td>-0.3</td>
</tr>
<tr>
<td>2.1</td>
<td>29.7</td>
<td>29.7</td>
<td>29.9</td>
<td>29.9</td>
<td>29.9</td>
<td>30.0</td>
<td>+0.3</td>
</tr>
<tr>
<td>2.2</td>
<td>31.5</td>
<td>31.5</td>
<td>31.7</td>
<td>31.8</td>
<td>31.8</td>
<td>31.8</td>
<td>+0.3</td>
</tr>
<tr>
<td>2.3</td>
<td>30.6</td>
<td>30.6</td>
<td>30.8</td>
<td>30.8</td>
<td>30.8</td>
<td>30.9</td>
<td>+0.3</td>
</tr>
<tr>
<td>3.1</td>
<td>29.7</td>
<td>29.7</td>
<td>29.6</td>
<td>29.4</td>
<td>29.4</td>
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<td>-0.3</td>
</tr>
<tr>
<td>3.2</td>
<td>30.9</td>
<td>31.0</td>
<td>30.9</td>
<td>30.8</td>
<td>30.8</td>
<td>30.7</td>
<td>-0.2</td>
</tr>
<tr>
<td>3.3</td>
<td>29.5</td>
<td>29.4</td>
<td>29.4</td>
<td>29.3</td>
<td>29.3</td>
<td>29.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>5.1</td>
<td>26.9</td>
<td>26.8</td>
<td>26.7</td>
<td>26.2</td>
<td>26.2</td>
<td>Cracked</td>
<td>-0.7</td>
</tr>
<tr>
<td>5.2</td>
<td>28.6</td>
<td>28.5</td>
<td>28.2</td>
<td>27.9</td>
<td>27.8</td>
<td>Cracked</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

Note: No.2.3 means the third sample for the mixture of No.2; + means increased; -means decreased.

Figure 2.16 The weight change of G2-No.1-3, and G2-No.5 samples
2.3.2.3 Compressive Strength

The compressive strength test curves of the G2 samples are plotted as shown in Figure 2.17 with the mechanical values listed in Table 2.9. Since the samples of G2-No.7 all cracked, their results are not available.

![Figure 2.17 The compressive strength of G2-No.1~9 samples](image)

<table>
<thead>
<tr>
<th>Nos.</th>
<th>Ultimate stress (MPa)</th>
<th>Elastic modulus (MPa)</th>
<th>Ultimate strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2-No.1</td>
<td>28.2</td>
<td>1490</td>
<td>2.11</td>
</tr>
<tr>
<td>G2-No.2</td>
<td>18.6</td>
<td>910</td>
<td>2.10</td>
</tr>
<tr>
<td>G2-No.3</td>
<td>29.5</td>
<td>1630</td>
<td>2.60</td>
</tr>
<tr>
<td>G2-No.4</td>
<td>19.5</td>
<td>1250</td>
<td>1.74</td>
</tr>
<tr>
<td>G2-No.5</td>
<td>6.4</td>
<td>290</td>
<td>2.69</td>
</tr>
<tr>
<td>G2-No.6</td>
<td>6.4</td>
<td>230</td>
<td>2.80</td>
</tr>
<tr>
<td>G2-No.8</td>
<td>19.7</td>
<td>1060</td>
<td>2.00</td>
</tr>
<tr>
<td>G2-No.9</td>
<td>26.1</td>
<td>1160</td>
<td>2.63</td>
</tr>
</tbody>
</table>
Since the GeoTAC loading frame has a load limit of 2000lb, the actual compressive strength for the G2-No.1 mixture samples is larger than 28.2 MPa. Compared to the G2-No.1 mixture samples, the compressive strength of the G2-No.2 mixture samples is lower, indicating that the molar ratio of Na/Si around 1.0 is preferable than 1.5. The unsmoothness for the compressive strength test curves of the G2-No.3 may be due to the two ends of the samples are not paralleled very well. As such, it is extremely important to have parallel surfaces in the test in order to avoid partial failure. The compressive strength for samples of G2-No.5-7 are very low due to its high water/ash ratio. There is only one difference between the mixture combinations of G2-No.2 and G2-No.8 that the water/ash ratio for G2-No.8 is 0.35, instead of 0.30. The compressive strength and the elastic modulus of G2-No.8 are 19.7 MPa and 1060 MPa, respectively, relatively larger than those of the G2-No.2. The compressive strength of G2-No.9 samples is 26.1MPa, which is a little smaller than that of the G2-No.1 samples, indicating that the natural curing method may be better than the water curing method.

2.3.2.4 Thermal Properties

To investigate the thermal effects on the geopolymerization, selected samples of G2-No.1 and 2 mixtures were exposed to the 500°C (1 hour) heating. The compressive strength of the samples with and without the heating are compared as shown in Figure 2.18 (a) and (b).

The compressive strength and elastic modulus of G2-No.1 before the heating are 28.8MPa and 1490MPa, respectively; the values are 19.9MPa and 1330MPa, respectively, after the 500°C (1 hour) heating. While the compressive strength and elastic modulus of G2-No.2 before the heating are 18.6 MPa and 910MPa, respectively; the values are 2.7MPa and 50MPa, respectively, after the 500°C (1 hour) heating. The
strength and elastic modulus of G2-No.2 mixture after the 500°C (1 hour) heating decreased largely because of the water bleeding effect.

2.3.2.5 Bleed Water Effect

As discussed in the general observations, some water precipitated at the top of the G2-No.2 and G2-No.8 samples two days later and the phenomena were recorded with the photos taken at different dates for the samples of G2-No.2, as shown in Figure 2.19. The water precipitation continued after the whole samples were exposed to the air (14 days).
The bleed water phenomena can also be observed through the failure patterns of the samples. As shown in Figure 2.20 and 2.21, the failure patterns of G2-No.1 and G2-No.2 were shown, respectively. It is noted that while the geopolymer cement of G2-No.1 samples are dense and the surfaces (the end surfaces and the broken face) are smooth, the geopolymer cement of G2-No.2 samples are friable and the surfaces are uneven, and lots of pores can be seen. Although the samples of G2-No.1 and No.2 have the same water/ash ratios, the bleed water effect plays a significant role in reducing the compressive strength of the geopolymer cement. At the same time, the G2-No.2 samples with water precipitation have a lower compressive strength after 500°C (1 hour) heating as compared with those of the G2-No.1 samples under the same conditions, as can be observed in Figure 2.18.

![Figure 2.20 Failure patterns of G2-No.1 samples without water precipitation](image)

As discussed above, the main reason may be attributed to the high molar ratio of the sodium/silicate (1.5). Due to the high molar ratio of the sodium/silicate, some alkaline solution may precipitate and \( \text{Na}_2\text{CO}_3 \) is produced by \( \text{CO}_2 \) and the precipitated NaOH. The
Na$_2$CO$_3$ is harmful to the development of the compressive strength for the geopolymer cement. As such, further studies are needed in order to investigate the mechanism of the water precipitation of geopolymer cement.

![Figure 2.21 Failure patterns of G2-No.2 samples with water precipitation](image)

2.3.3 KOH and Na$_2$SiO$_3$ Activated Fly Ash Geopolymer Cement (G3)

For this group of samples, only one composition of the mixture combinations was considered for the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement, and the tested compressive strength and heat resistance were witnessed with much better features than those for the G1 and G2 specimens. More variables will be considered and further analyzed in chapter 3.

2.3.3.1 General Observations

It was witnessed that with the appropriate composition of the Group 3 (G3), very good geopolymer cement was produced with the adhesive character similar like the organic epoxy, which was observed from Figure 2.22. The geopolymer precursor became hardened with an early strength half an hour later. As for G3-No.1, no water precipitation phenomenon was observed.
The failure patterns of G3-No.1 sample after 500°C heating and G3-No.2 samples before 500°C heating are shown in Figure 2.23 and Figure 2.24, respectively, which indicated that the curing process of the samples of G3-No.1~2 developed well. The failure patterns of G3-No.5 samples are shown in Figure 2.25 with smooth crack surfaces, indicating a high compressive strength could be achieved as expected.

Figure 2.23 Failure pattern of G3-No.1 sample (Natural curing for 60 days) after 500°C heating.
Figure 2.24 Failure pattern of G3-No.2 samples (wet cloth curing for 60 days) before 500°C heating

Figure 2.25 Failure patterns of G3-No.5 samples (water curing for 90 days)
2.3.3.2 Effects of Curing Periods

The compressive strength of the samples of G3-NO.3-5, which were under a curing period of 7 days, 60 days and 90 days, respectively, are 11.4MPa, 16.6MPa, 23.1MPa, respectively, as shown in Figure 2.26. As for the water curing samples, the compressive strength develops with the increase of the curing period. The experiments done by Davidovits (2013) on the pyramid-like stones show that the mechanical properties of geopolymer develop along with time, and the extent and rate of the geopolymerization improve due to the age followed by the zeolite-type structure finally. It is also found that the elastic moduli are 720MPa, 1070MPa and 1140MPa, respectively, for the samples of G3-No.3–5 and it can be predicted that the elastic modulus may keep stable after a curing period of 60 days.

![Figure 2.26 The compressive strength considering different curing periods](image)

2.3.3.3 Thermal properties

After a natural curing period of 60 days, the samples of G3-No.1 were exposed to the 500°C (1hour) heating and the compressive strength of the samples with different cooling methods are shown in Figure 2.27. From this figure, there is not much difference between
these two kinds of cooling methods. The compressive strength after the 500°C (1hour) heating is still as high as 25.4MPa. It is predicted that the KOH and Na₂SiO₃ activated geopolymer cement possesses good heat resistant performance.

Figure 2.27 The compressive strength of samples with different cooling methods after the 500°C (1hour) heating
Note: NC-natural cooling; WC-water cooling.

Figure 2.28 The compressive strength of G3-No. 4 samples
Note: N3-Stand for 3 days after water cooling (WC)
The compressive strength of G3-No.4 samples are shown in Figure 2.28. As compared with the results of G3-No.1 samples, the water curing method may be not preferable with a negative effect on the development of the compressive strength of the geopolymer cement. For the results as shown in Figure 2.28, the compressive strength of the samples stand for 3 days after water cooling is relatively higher than that of the samples just with water cooling after the 500°C (1hour) heating. It is interpreted that the compressive strength of the geopolymer cement may recover a little in normal environment after sudden water cooling.

### 2.4 Conclusions

Based on the observations of the three groups of geopolymer samples, the following summaries are identified and concluded:

1. The Na$_2$SiO$_3$ is necessary for the development of geopolymer cement. The NaOH activated fly ash geopolymer cement has very low compressive strength, implying the geopolymerization is very low for using the NaOH only.

2. The curing method plays a very significant role for the properties of the geopolymer. The natural curing method with just the plastic film covered is better than the wet cloth covered natural curing method and the water curing method. The heating curing method without sealing will lead to a quicker evaporation of water and then cause macrocraks on the surface of the samples. Heat curing with good sealing to prevent the quick water evaporation during the curing in order to avoid cracks occurring on the surfaces of the samples will be further studied and used.

3. The water precipitation phenomenon was observed for the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples, where Na$_2$CO$_3$ was produced by CO$_2$ and additional NaOH due to a large molar ratio of Na/Si (1.5). Hence, it is better to take the
molar ratio of Na/Si as 1.0 to avoid the water precipitation. The water/ash ratio is preferred to be located between 0.30 and 0.35. However, as an emerging topic in geopolymer cement, the water precipitation effects should be further studied.

4. The compressive strength develops with the increase of the curing period. The high compressive strength was accompanied with brittle failure patterns.

5. The KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement is expected to have a higher compressive strength than the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement, as pointed out by many researchers. As the observations are based on limited samples, more studies are needed to further investigate the characteristics of the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement. Hence, more samples were prepared to further study the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement, especially the thermo-mechanical properties under the high temperature heating. This will be discussed in Chapter 3.
CHAPTER 3 THERMO-MECHANICAL PROPERTIES OF KOH AND Na₂SiO₃ ACTIVATED FLY ASH-BASED GEPOLYMER CEMENT

3.1. Introduction

This chapter presents a further study on the thermo-mechanical properties of class F fly ash based geopolymer materials prepared using KOH and Na₂SiO₃ alkaline activators with different curing and cooling methods. The mechanical properties, including the compressive strength, shrinkage, weight loss, and chemical composition, are investigated utilizing several key tools, such as X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive X-ray Spectroscopy (EDXS) measurements. The effects of the water/ash ratio, curing methods, cooling methods, and sealing degree on the compressive strength and thermal properties of the geopolymer products are studied and analyzed in details.

3.2 Materials and Experimental Methods

3.2.1 Materials

A low calcium Class F fly ash supplied by Boral Material Technologies, Inc. (Monticello, Texas, USA) is used as the raw material for geopolymer synthesis. Based on its chemical composition (Table 2.1 in Chapter 2), the Si/Al molar ratio in this class F fly ash itself is 2.154, with a specific gravity of 2.46. A sodium silicate solution consisting of 9.07 wt.% Na₂O and 29.35 wt.% SiO₂ (Aqua Solutions Inc, USA) and a potassium hydroxide (88% purity quotient, Sigma-Aldrich Co., USA) are selected as the alkali activators. This fly ash is mainly amorphous with little crystalline inclusions of quartz (Figure 2.1) and the particle size distribution (PSD) curve of the fly ash determined by the ASTM standard test method combining both sieving and hydrometer analyses (ASTM 2010) shows that the median particle size (D₅₀) is 22 µm and this fly ash contains 20% sand-sized (>75 µm) coarse particles (Figure 2.2).
3.2.2 Sample Preparation

The KOH pellets are first mixed with the sodium silicate solution with a molarity of 6.66 mol/L to prepare an alkaline solution about one day in advance to ensure it to cool down to the room temperature (~22°C). The fly ash raw materials without any further processing is then blended with the alkaline solution made from KOH and Na₂SiO₃ solution followed by the manual stirring for several minutes before it is cast in plastic cylinders (3/4 inches in diameter, 2 inches in length). The geopolymer design mix is listed in Table 3.1, in which the water/ash ratio is the weight of the total water to that of the fly ash. This parameter affects the workability of the fly ash based geopolymer cement. Even though all the cases consider include the 6% crystal SiO₂ (Quartz) in the fly ash, the real active Si/Al ratio is still lower than the Si/Al ratio calculated according to the composition of the fly ash and alkali activation (KOH and Na₂SiO₃) due to that there may exist unreacted fly ash grains wrapped in the geopolymeric matrix.

<table>
<thead>
<tr>
<th>Mixture No.</th>
<th>Water/ash</th>
<th>Na₂O(SiO₂)₃/KOH</th>
<th>Curing regime</th>
<th>Si/Al (mol)</th>
<th>Si/M (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.2</td>
<td>1.6</td>
<td>22°C (24h)--80°C (24h)</td>
<td>2.40</td>
<td>3.60</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>1.6</td>
<td>22°C (24h)--80°C (24h)</td>
<td>2.50</td>
<td>3.09</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>1.6</td>
<td>22°C (24h)--80°C (24h)</td>
<td>2.59</td>
<td>2.74</td>
</tr>
<tr>
<td>4</td>
<td>0.35</td>
<td>1.6</td>
<td>22°C (24h)--80°C (24h)</td>
<td>2.69</td>
<td>2.47</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>1.6</td>
<td>22°C (24h)--80°C (20h)</td>
<td>2.78</td>
<td>2.27</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>1.6</td>
<td>22°C (24h)--80°C (20h)</td>
<td>2.50</td>
<td>3.09</td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>1.6</td>
<td>22°C (24h)--60°C (20h)</td>
<td>2.50</td>
<td>3.09</td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
<td>1.6</td>
<td>60°C (24h)</td>
<td>2.50</td>
<td>3.09</td>
</tr>
<tr>
<td>9</td>
<td>0.2</td>
<td>1.6</td>
<td>80°C (24h)</td>
<td>2.40</td>
<td>3.60</td>
</tr>
<tr>
<td>10</td>
<td>0.2</td>
<td>1.6</td>
<td>22°C (24h)--80°C (20h)</td>
<td>2.40</td>
<td>3.60</td>
</tr>
</tbody>
</table>

Note: All the cases were considered 6% crystal SiO₂ (Quartz) in the fly ash; M=(Na, K).

The heat curing method developed by Bakharev (2005) is used for the mixtures of Nos. 1-4 in Table 3.1: the samples are initially cured for 24 hours at the room temperature 22°C, then cured at 80°C for another 24 hours, and finally cooled down to the room
temperature inside the furnace. To investigate the influence of the heating duration, samples of mixture Nos. 5-6 and No. 10 are heated to 80°C for 20 hours instead of 24 hours after the 24 hours curing in the ambient environment (room temperature). With the same initial curing method at the room temperature of 24 hours, a curing temperature of 60°C with 20 hours curing is set for the No.7 samples. To examine whether it is good to put the samples in the ambient environment for 24 hours before the heat curing, mixtures No.8 and No.9 are heat cured directly for 24 hours with the temperature of 60°C and 80°C, respectively, right after they are cast. Afterwards, all the samples of Nos.1-10 are sealed at the room temperature with caps to prevent the potential rapid water evaporation before they are tested. For each mixture, at least 3 samples are prepared.

3.2.3 Geopolymer Synthesis and Characterization

The selected geopolymer specimens are exposed to the 500°C and 800°C heating with the same heating regime as shown in Figure 2.3 (Chapter 2). The thermal expansion/shrinkage coefficient of the selected samples is also measured. The diameter and length of the cylinder samples are measured at three sections each time for each sample by electrical Vernier calipers before and after the heating test.

The unconfined compressive strength of the cured (without the 500°C and 800°C heating) and heated geopolymer cylindrical specimens are measured using a closed loop uniaxial test systems with an axial force capacity of 150kN at a constant strain rate of 0.02 in/min (Figure 3.1). The two ends of all the samples are cut to be in parallel and normal to the cylinder length by the mechanical center. The length of all the geopolymer cement samples is between 1.6~1.9 inches, about 2.0~2.5 times of the diameter (0.775 inches), which meets the requirements of ASTM standard. Then, a very thin layer of lubricant coating is applied at both ends of each sample so as to reduce the friction effects.
and the possible shear stress, which is developed during the test between the sample ends and the contacting surfaces of the test frame.

Figure 3.1 The unconfined compressive strength test

To better understand the rate and extent of the synthesis process of the geopolymer products, the microstructural and chemical composition analysis are conducted through the XRD, SEM and EDXS methods. For each type of the geopolymer mixture, the fractured pieces from the unconfined compressive testes are selected for further analysis by the SEM and EDXS. The raw materials and the failed geopolymer end products are grinded into fine powders with particle sizes ≤38 μm in a McCrone micronizing mill (McCrone Accessories and Components) for the XRD analysis (He et al. 2012). The fractured surfaces of the selected pieces are paid more attention than the external surfaces for the SEM and EDXS analysis because the external surfaces may have different microstructures when the samples are exposed to the air during the curing process (He et al. 2012). All the selected pieces are coated with platinum before the SEM and EDXS examination.
3.3 Results and Discussion

3.3.1 General Observation of Geopolymer Cement

The failure patterns of the Nos.1~4 samples without the heat treatment (the 500°C and 800°C heating) are like the failure patterns of the stone in the compression tests, which indicates that the compressive strength of these samples are very high, as shown in Figure 3.2. The fractured surfaces are very smooth-going without irregular interlocking patterns. It is noteworthy that some discrete pores are observed in the fractured surfaces and hence more pores can be found inside the bulky failed bodies. Two possible reasons are accounting for this: (1) the pores are firstly dominated by the water and then left after the water evaporation; (2) the air bubbles may be introduced during the manual stirring or pouring into the plastic cylinders (He et al. 2012). The existing pores definitely have detrimental influence on the mechanical properties. Special processing technologies are proposed to remove the air using vacuum or suppress the air bubbles using the high pressure for the de-airing treatment (Zivica et al. 2011).

![Figure 3.2 The failure patterns of the Nos.1~4 samples before heating.](image)

Figure 3.3 shows the failure patterns of the samples of No.3 mixture before and after the heating, as well as the No.3c samples (not completely sealed) after the 500°C heating. It can be observed from Figure 3.3 that the structure of the samples of No.3 mixture after the 500°C heating is weaker and the structure of the No.3c samples after the 500°C heating seems much weaker (the broken surfaces present powdery characteristics), which
indicates that the geopolymer products have much less compressive strength after the high temperature heating and the sealing degree also affects the thermo-mechanical properties of the geopolymer cement since the samples of No.3c are not completely sealed when curing.

![Images of samples before and after heating]

Figure 3.3 The failure patterns of the No.3 and No.3c samples before and after heating

For all the heated geopolymer cement samples (exposure to 500°C or 800°C), no spalling phenomenon is observed using either the natural cooling down method or the water cooling down method (cooled down by the water suddenly right after exposed to
500°C or 800°C). After exposed to the 500°C heating, the external color of the geopolymer cement cylinders becomes slightly lighter. Macro-cracks are observed on the surfaces of the samples of No.5, No. 6, No.7, and No.8 mixture. There are one or two cracks on No.5 and No.6 specimens, and the width of the cracks is very small. Compared to samples of No.6, there is no crack on No.2 ones, which means that the curing regime 22°C (24h)--80°C (24h) is better than 22°C (24h)--80°C (20h). Compared with the samples of No.5 and No.6, there are many cracks observed on the surfaces of No.7 and No.8 samples (Figure 3.4). It is further found that the 60°C heat curing method (No.8) is not enough for geopolymerization and results in more cracks, while the 80°C heat curing (No.9) method is much better.

![Figure 3.4 The samples before and after 500°C, and 800°C heating.](image)

After exposed to the 800°C heating, the samples of No. 1 mixture expand largely in both the length and the diameter directions, as shown in Figure 3.4. It is interesting to find that the color of the external surfaces of the samples varies a lot after the high temperature exposure. There is no crack found on the surfaces of the heated samples. It can be inferred that the crystallization structures of the No.1 samples change largely after the 800°C heating, which would be confirmed by the SEM-EDXS analyses discussed later.
3.3.2 Factors Affecting the Thermo-mechanical Properties of Geopolymer Cement

3.3.2.1 Effects of the Curing Methods

There are many studies about the influence and mechanism of the heat curing on the compressive strength of the fly ash based geopolymer (Davidovits 2011; Jiang et al. 1992; Duxson et al. 2007; Bakharev 2005). Jiang et al. (1992) explained the reason for the need of the heat treatment is that the activation of fly ash is an endothermic reaction so that the heat curing is very important for the geopolymerization synthesis of the fly ash based geopolymer cement. Hardjito et al. (2004) studied the compressive strength of the fly ash based geopolymer cement with the curing temperature ranging from 30°C to 90 °C and concluded that the compressive strength of cement increases when the curing temperature increases. It is also proven that a longer heat curing time improves the degree of geopolymerization and hence resulted in a higher compressive strength. However, the increase in the compressive strength beyond 24 hours heat curing is not significant. Therefore, the heat-curing time is better to be set as less than 24 hours in the practical applications. Long pre-curing process at the room temperature before the heat treatment is also beneficial for the strength development of the fly ash based geopolymer cement. Bakharev (2005) proved that the compressive strength is significantly higher if the geopolymer cement samples are stored 24 hours at the room temperature before the heat curing.

The tested results are listed in Table 3.2 with some missing data owing to that: (1) some specimens are not well cut and hence disregarded; (2) some samples have cracks after exposed to the high temperature treatment. Based on the available results, it is found that the heat curing improves the compressive strength and the strength after exposed to 500°C heating of the geopolymer cement samples. Taking the samples with the same
water/ash ratio of 0.35 as an example, the strength after the 500°C heating and the strength reduction rate of the geopolymer cement with the heat curing method (No. 4) are 46.6 MPa and 47.9%, respectively. While for the samples with the normal curing method and water curing method (G3 samples in Chapter 2), the counterparts are 23.6 MPa, 62.6%, and 20.2MPa and 57.7%, respectively. Hence, it can be concluded that the heat curing method can develop higher strength cement than the normal curing and water curing methods. For the samples with the water/ash ratio of 0.20, the samples with the heat curing method (24 hours at the room temperature and then cured at 80°C for another 24 hours, called 22°C (24h)--80°C (24h) hereafter) also have much better compressive strength than the samples with the other two different curing methods. As such, it is proven that the heat curing is beneficial to the development of the compressive strength of the geopolymer products and hence the heat performance is enhanced. This observation has also been documented by many researchers (Davidovits 2011; Jiang et al. 1992; Duxson et al. 2007; Bakharev 2005).

<table>
<thead>
<tr>
<th>Curing methods</th>
<th>Normal curing (G3)</th>
<th>Water curing (G3)</th>
<th>22°C (24h) -- 80°C (24h) (No. 4)</th>
<th>22°C (24h) -- 80°C (24h) (No. 1)</th>
<th>22°C (24h) -- 80°C (20h) (No. 10)</th>
<th>80°C (24h) (No. 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive Strength before heated (MPa)</td>
<td>63.1</td>
<td>47.8</td>
<td>89.4</td>
<td>113.8</td>
<td>--</td>
<td>50.6</td>
</tr>
<tr>
<td>Compressive Strength after 500°C heated (MPa)</td>
<td>23.6</td>
<td>20.2</td>
<td>46.6</td>
<td>95.9</td>
<td>47.6</td>
<td>--</td>
</tr>
<tr>
<td>Reduction rate %</td>
<td>62.6%</td>
<td>57.7%</td>
<td>47.9%</td>
<td>15.7%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Normal curing refers to the curing with the wet cloth covered.
The water curing method is proven to be beneficial in the Portland cement curing. However, the compressive strength and strength after the 500°C heating of the geopolymer cement under the water curing are lower than those under the normal curing with the wet cloth covered as shown in Table 3.2. Thus, the water curing method is not favorable for the geopolymer cement.

3.3.2.2 Effects of the Water/Ash Ratio

To investigate the effects of different water/ash ratios on the mechanical properties of the geopolymer products, the mixtures of No.1 to No. 4 with the same curing regime (22°C (24h)--80°C (24h)) are examined and the tested results are plotted in Figure 3.5 and listed in Table 3.3. As shown in Figure 3.5, the compressive strength of the tested specimens is very high. All of them are larger than 80 MPa and the highest one even reaches up to 110 MPa. The examined geopolymer samples all display brittle failure features. The elastic modulus for the water/ash ratio of 0.25 and 0.3 are very close with each other, and they are higher than that with the water/ash ratio of 0.2 and 0.35.

![Figure 3.5 Effect of water/ash ratio on compressive strength](image-url)
From Table 3.3, it generally shows that the lower the water/ash ratio, the higher the compressive strength is. The water/ash ratio affects the volume of pores and the porosity in the matrix which directly influences the strength of the geopolymer concrete (Kong et al. 2008b). The compressive strength of the geopolymer cement with the water/ash ratio of 0.20 is the highest, 113.8MPa. However, the compressive strength of the geopolymer cement with the water/ash ratio of 0.25 and 0.3 are very close, and it seems that 0.3 is the optimum water/ash ratio if the fluidity and workability of geopolymer cement are taken into consideration. This can be further explained by the role of water in the development of geopolymer cement.

<table>
<thead>
<tr>
<th>Water/ash ratio</th>
<th>0.2 (No. 1)</th>
<th>0.25(No. 2)</th>
<th>0.3(No. 3)</th>
<th>0.35(No. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength before heated (MPa)</td>
<td>113.8</td>
<td>103.5</td>
<td>102.2</td>
<td>83.4</td>
</tr>
<tr>
<td>Compressive strength after 500°C heated (MPa)</td>
<td>95.9</td>
<td>62.7</td>
<td>65.4</td>
<td>46.6</td>
</tr>
<tr>
<td>Reduction rate %</td>
<td>15.7%</td>
<td>39.4%</td>
<td>36.0%</td>
<td>44.1%</td>
</tr>
</tbody>
</table>

In the synthesis of the geopolymer products, it is generalized that three essential steps can be summarized from the complex process consisting of a series of dissolution, reorientation, and solidification reactions. At first, the amorphous phases from the raw materials dissolve in the alkali solutions in order to generate the reactive species of silica and alumina. Then, the active ions (Al\text{3+}, \text{Si4+}) transport and condensate into monomers. Finally, the amorphous or semi-crystalline aluminosilicate polymers are formed through further polycondensations (He et al. 2012). During the first step, enough water can make the dissolution of the raw materials much easily in order to generate more reactive species. In the second step, an appropriate amount of water ensures the active ions and
the alkali-activation to transport smoothly. However, in the actual setting process (the third step), the redundant water will precipitate from the geopolymer slurry or paste.

The added water remains outside of the geopolymeric network, acting as a lubricating element (Davidovitts, 2011). Although the mechanism of the polymerization is yet to be fully understood, a critical feature is that water is presented only to facilitate the workability and it does not become a part of the resulting geopolymer structure. In other words, water is not involved in the chemical reaction and instead it is expelled during the curing and the subsequent drying.

It is well accepted that the addition of water decreases the compressive strength. However, water plays an important role in the dissolution and transportation process, indicating that the water influences the first two essential steps of the geopolymerization. There must be a proper range of the water/ash ratio that an optimum compressive strength of geopolymer cement can be warranted. The lower the water/ash ratio, the less fluidity is. Thus, consider workability of the geopolymer slurry and the mechanical properties of the end products together, it seems that the optimum water/ash ratio is around 0.3 for the fly ash based geopolymer cement, the same as that for the ordinary Portland cement.

Table 3.3 also shows the compressive strength after the 500°C heating for the class F fly ash-based geopolymer cement prepared with various water/ash ratios ranging from 0.2 to 0.35. The curing regime for these samples is the same as those without the 500°C heating. All the samples after the high temperature treatment are naturally cooled down to the room temperature in the furnace before the compressive tests. The compressive strength of the final geopolymer cement after the 500°C heating varies according to the water/ash ratios. Generally speaking, a higher water/ash ratio results in a lower strength.
after the 500°C heating (Except the water/ash ratio of 0.3). The compressive strength reduction rates for different mixtures before and after the 500°C heating are different according to the different water/ash ratios. The compressive strength reduction rate of the geopolymer cement with the water/ash ratio of 0.2 is 15.7%, while the reduction rate of the geopolymer cement with the water/ash ratio of 0.35 is 44.1%. It means that the abundant water decreased greatly the residual compressive strength of the geopolymer cement. An increase of water results in an increase of the pore pressure by the steam pressure under high temperatures. If the vaporized water cannot escape fast enough, the increasing internal pore pressure in the geopolymer matrix will cause cracks, thus reduce the compressive strength (Shorter GW et al. 1961; Zhao et al. 2011).

The strength of the geopolymer matrix after the 500°C heating with the water/ash ratio of 0.3 is higher than the strength for the water/ash ratio of 0.25, which indicates that the water/ash ratio of 0.3 may be the optimal mixture ratio. The pore proportion, pore size, and pore distribution and connectivity in the geopolymer matrix will influence the strength after the high temperature heating. The test results indicate that the cement with the water/ash ratio of 0.3 behaves better heat resistant performance when compared to that with the water/ash ratio of 0.25. The reason may be that it has the better characterization of the pore proportion, pore size, and pore distribution and connectivity so that the vaporized water stream can escape easier and cause less damage to the structure. This can be also expressed and proven by the SEM micro analysis.

From the Differential Thermal Analysis (DTA) and Thermal Gravimetric Analysis (TGA) curves, Davidovits proved that more than 70% of the reaction water (almost the added water) is physically bonded water and evaporates before 100°C (Davidovits, 2011).
In fact, during the 80°C heat curing, the loss of this physically bonded water determines the microporosity of the geopolymer cement (Davidovits, 1988). That maybe one of the reason why the strength of the geopolymer cement strength after the 500°C heating with the water/ash ratio of 0.3 is a little higher than that of the geopolymer cement with 0.25 water/ash ratio.

3.3.2.3 Effect of Sealing Degree

Open curing conditions produce high porosity and low compressive strength solid bodies (Izquierdo et al. 2010). The open air conditions allow the water to evaporate freely, which reduces the availability of the water for geopolymer matrix to grow. The porosity after the open curing conditions is probably not homogeneously distributed in the sample. It is observed in the tests that the pores and cracks are primarily concentrated near the uncovered surface due to the air exposure. The compressive strength decreases largely after being cured in the open conditions. Therefore, the degree of sealing (from sealed completely to open curing conditions) also affects the compressive strength of the geopolymer cement.

The sealing degree (whether sealing completely or not) also affects the heat resistant performance of the geopolymer cement. Table 3.4 shows the related results of the different sealing methods for mixtures of No. 3 and No. 4. All the geopolymer cement samples showed in this table are cured with the curing regime of 22°C (24h)–80°C (24h), and then they are naturally cooled down in the oven after the 500°C heat exposure. The original compressive strength (without the 500°C heating) of the geopolymer cement samples with the water/ash ratio of 0.3 and 0.35 are 102.2MPa, and 83.4MPa, respectively (Table 3.3). From the results shown in Table 3.4, the strength of the geopolymer cement after the 500°C heating not completely sealed is lower than that of
the geopolymer cement sealed completely for the two different water/ash ratios of 0.3 and 0.35. The test results verify that open curing condition is not good for the geopolymerization process, as documented by the previous studies (Izquierdo et al. 2010).

Table 3.4 Effect of sealing degree on compressive strength

<table>
<thead>
<tr>
<th>Sealing methods</th>
<th>water/ash=0.3 (No. 3)</th>
<th>water/ash=0.35 (No. 4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Strength after 500°C heated</td>
<td>reduction rate</td>
</tr>
<tr>
<td>sealed completely</td>
<td>65.4MPa</td>
<td>36.0%</td>
</tr>
<tr>
<td>not completely sealed</td>
<td>50.3MPa</td>
<td>50.8%</td>
</tr>
</tbody>
</table>

3.3.2.4 Effect of Cooling Methods on Thermal Properties

Two different cooling methods are adopted in this part, the natural cooling down method and the water cooling down method. For the water cooling down method, the samples are immersed into the room temperature water right after the high temperature heating in 500°C. For the samples with the 800°C heating, only the natural cooling down method is considered. After all the samples are cooled down to the room temperature by the saturation in the water for 5 minutes and by the natural cooling down method, they are put into zipped bags for preventing quick water evaporation until the compression tests are conducted.

The stress-strain curves of the selected No. 1 samples are shown in Figure 3.6. From Figure 3.6, the compressive strength and the elastic modulus for the two cooling down methods after the high temperature heating are obvious smaller than the corresponding ones without the high temperature heating treatment. It is also observed in Figure 3.6 that the mechanical properties for the samples with the natural cooling down method are much better than those with the water cooling down method. Comparatively, much strength loss occurs when the geopolymer samples are exposed to the high temperature
heating in 800°C. The reason for this will be further discussed in the following parts (3.3.3-3.3.7).

Figure 3.6 Compressive strength of No.1 samples with and without the high temperature heating
Note: NC refers to the natural cooling down method; W refers to the water cooling down method.

The compressive strength before and after the 500°C heating are listed in Table 3.5. From the table, it shows that the strength after the 500°C heating of the geopolymer cement cooled down by water is obviously lower (79.8 MPa for the water/ash ratio of 0.2, and 49.3 MPa for the water/ash ratio of 0.25) than that of the geopolymer cement with the natural cooling down method (95.9 MPa for the water/ash ratio of 0.2, and 62.7 MPa for the water/ash ratio of 0.25). The reduction rate is calculated based on the compressive strength without the heating treatment. While the strength loss for the water cooling down method is 29.9% and 52.4% for the water/ash ratio of 0.2 and 0.25, respectively, the corresponding values for the natural cooling down method are 15.7% and 39.4%, respectively. The probable reason for the difference between the reduction rates of the
compressive strength can be explained that the outside part (external surfaces) of the geopolymer cement is suddenly cooled down by the water, shrinks largely and then results in uneven contraction. The uneven contraction leads to a large number of cracks which decreases the compressive strength of the geopolymer cement samples.

Table 3.5 Effect of cooling methods on residual compressive strength (MPa)

<table>
<thead>
<tr>
<th></th>
<th>water/ash=0.2</th>
<th>reduction rate %</th>
<th>water/ash=0.25</th>
<th>reduction rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original strength</td>
<td>113.8 MPa</td>
<td>--</td>
<td>103.5 MPa</td>
<td>--</td>
</tr>
<tr>
<td>Natural cooling down</td>
<td>95.9 MPa</td>
<td>15.7%</td>
<td>62.7 MPa</td>
<td>39.4%</td>
</tr>
<tr>
<td>Water cooling down</td>
<td>79.8 MPa</td>
<td>29.9%</td>
<td>49.3 MPa</td>
<td>52.4%</td>
</tr>
</tbody>
</table>

It is interesting to notice that there is no spalling of the geopolymer samples even cooled suddenly by water after the high temperature heating. This is different with the Portland cement concrete which has a high risk of spalling if cooled down by water suddenly after the high temperature heating. The reason may be that the geopolymer binder is more adhesive and it is amorphous to semi-crystalline shaped microstructures, hence the induced strength loss due to the shrinkage for the geopolymer cement is not as critical as that for the Portland concrete. Plus, the residual compressive strength is still competitive, 79.8 MPa for the geopolymer cement with the water/ash ratio of 0.2.

3.3.3 Weight Loss after Elevated Temperature

The weight loss is mainly caused by the water loss. French scientist Joseph Davidovits proved that the added water does not act in the geopolymerization and remains outside of the geopolymer network just as lubricating element (Davidovits, 2011). It is generally considered that three types of water exist in the hardened geopolymer products: physically bonded water, chemically bonded water and hydroxyl groups OH. The physical bonded water and chemically bonded water evaporate between 20°C to 100°C, and between100°C to 300°C, respectively. When the temperature reaches above
300°C, the dehydroxylation of OH groups happens with the subsequent polycondensation into siloxo bond Si-O-Si, linking neighboring geopolymeric micelles. It is proven that more than 70% of the reaction water is physically bonded water, which evaporates before 100°C without causing any internal stress and remarkable shrinkage. However, many micro pores will be produced owing to the empty space left by the water evaporation. The remaining 30% water, chemically bonded water and hydroxyl groups OH, accounting for up to 90% of the total shrinkage when the samples are heated from 20°C to 500°C (Davidovits, 1988).

It is further verified by Perera and his team at ANSTO in Australia that the water presents after the curing of the geopolymer cement as three types: “free” water, interstitial water, and OH groups. The “free” water mainly exists in the intergranular regions with a thin external film. About 60% of the starting water is lost after heating to 150°C. While after exposed to 300°C, almost all the remaining interstitial water is lost. The OH groups constitute a quite low ratio of the starting water. (Davidovits, 2013)

The weight loss of geopolymer cement samples according to different water/ash ratio under the curing regimes of 22°C (24h)--80°C (24h), 22°C (24h)--80°C (20h) and 80°C (24h) is shown in Table 3.6. All the samples are cooled down naturally in the oven by the elevated temperature exposure. From Table 3.6, it is obvious that the weight loss increases with the increase of the water/ash ratio since the weight loss is represented mainly by the water loss of the samples. The weight loss of geopolymer paste samples with the water/ash ratio of 0.2 is 14.2% between 22°C and 500°C heating and only 0.5% between 500°C and 800°C, which means that the weight loss mainly occurs before the 500°C heating. It is interesting to note that the chemical bonded water and OH groups
formed in the geopolymer cement with the 22°C (24h)--80°C (24h) curing regime (i.e., 0.5% for No. 1) is more than that of the geopolymer cement with the 80°C (24h) heat curing regime (i.e., 1% for No. 9), indicating that 24 hours curing at the normal temperature (22°C) before the heat curing (80°C) is better for the geopolymerization process and hence induces higher compressive strength geopolymer cement.

Table 3.6 Weight loss for different mixtures after heating

<table>
<thead>
<tr>
<th>Curing methods</th>
<th>22°C (24h)--80°C (24h)</th>
<th>22°C (24h)--80°C (20h)</th>
<th>80°C (24h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture No.</td>
<td>No.1</td>
<td>No.2</td>
<td>No.3</td>
</tr>
<tr>
<td>Water/ash ratio</td>
<td>0.2</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>Original weight (g)</td>
<td>30.3</td>
<td>28.2</td>
<td>28.4</td>
</tr>
<tr>
<td>Weight after 500°C heating (g)</td>
<td>26.0</td>
<td>23.7</td>
<td>23.3</td>
</tr>
<tr>
<td>Weight after 800°C heating (g)</td>
<td>25.8</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Weight loss after 500°C</td>
<td>14.2%</td>
<td>16.0%</td>
<td>18.0%</td>
</tr>
<tr>
<td>Weight loss after 800°C</td>
<td>14.7%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Weight loss 500°C-800°C</td>
<td>0.5%</td>
<td>0.6%</td>
<td>--</td>
</tr>
</tbody>
</table>

3.3.4 Thermal Contraction/Expansion

As shown in Figure 3.4, the geopolymer cement samples contract after exposed to the 500°C heating and expanded after exposed to 800°C using the natural cooling down method (cooled down naturally in the oven after the 500°C or 800°C heating). While Figure 3.4 mainly shows the results related to the topic of thermal contraction/expansion of the No. 1 mixture, more results are listed in Table 3.7. The length of all the samples before and after the elevated temperature exposure is measured by the Vernier caliper. The contraction/expansion rate of the geopolymer cement samples for different water/ash ratios is calculated based on the original length before the high temperature exposure.
The geopolymer samples with the water/ash ratio of 0.2 shrink 2.0% between 22°C and 500°C, and expand 9.4% between 22°C and 800°C. For the geopolymer specimens with the water/ash ratio of 0.4, the contraction rate is 3.4% and the expansion rate is 25.2%. The higher the water/ash ratio, the more deformation of the geopolymer paste is. As such, the thermal shrinkage/expansion of geopolymer cement is highly affected by the water/ash ratio.

Table 3.7 The contraction/expansion rate of geopolymer cement according to different water/ash ratios

<table>
<thead>
<tr>
<th>Water/ash ratio</th>
<th>0.2 (No.1)</th>
<th>0.25 (No.2)</th>
<th>0.3 (No.3)</th>
<th>0.35 (No.4)</th>
<th>0.4 (No.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500°C</td>
<td>2.0%</td>
<td>2.6%</td>
<td>3.1%</td>
<td>3.6%</td>
<td>3.4%</td>
</tr>
<tr>
<td>800°C</td>
<td>-9.4%</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>-25.2%</td>
</tr>
<tr>
<td>500°C–800°C</td>
<td>-11.4%</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>-28.6%</td>
</tr>
</tbody>
</table>

Note: Positive represent contraction and negative represent expansion.

The main reason for the shrinkage when the samples are exposed to the 500°C heating may be caused by the loss of the chemically bonded water and hydroxyl groups OH. For the thermal expansion problem, it may be due to the change of the microstructures for the geopolymer binders when the samples are exposed to as high as the 800°C heating. This will be further verified by the SEM analysis as discussed later.

Different cooling methods also influence the thermal contraction and the results for the mixtures of No.1 and No.2 are listed in Table 3.8. From the table, the contraction of the geopolymer cement samples cooled down by water after the 500°C exposure is higher than those cooled down naturally.

Table 3.8 The contraction rate of geopolymer cement according to different cooling down methods

<table>
<thead>
<tr>
<th>Cooling methods</th>
<th>Water/Ash=0.2 (No.1)</th>
<th>Water/Ash=0.25 (No.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Cooling</td>
<td>2.0%</td>
<td>2.6%</td>
</tr>
<tr>
<td>Water Cooling</td>
<td>2.6%</td>
<td>3.1%</td>
</tr>
</tbody>
</table>

63
3.3.5 Density and Softening Temperature

It is concluded by Davidovits (2011) that the thermal insulating values are a function of the density, which means that a good thermal conductivity requires low density material. This conclusion is addressed based on the samples with the same compressive strength. The value of the apparent density of the geopolymer cement (without fillers or any constraint) is a very important factor. Davidovits (2011) also concluded that geopolymer has a low apparent density due to its microporous structure. Figure 3.7 shows that the apparent density increases with the ratio of Si/Al (i.e., the densification of the geopolymeric structure). Figure 3.7 also shows the softening temperature points of the geopolymers. Geopolymers have several dehydroxylation and crystallization phases before melting. One phase is that the geopolymer matrix softens and induces recrystallization (or ceramisation) at a certain temperature (Davidovits, 2011). This softening temperature point is important for high temperature geopolymer applications and it is lower than the melting point.

![Figure 3.7 Apparent density (left) and softening temperature (right) for pure matrix without fillers (Davidovits 1991)](image-url)
Table 3.8 The density for the geopolymer cements with different water/ash ratios

<table>
<thead>
<tr>
<th>Water/Ash</th>
<th>0.2</th>
<th>0.25</th>
<th>0.3</th>
<th>0.35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>2.05</td>
<td>2.02</td>
<td>1.96</td>
<td>1.91</td>
</tr>
</tbody>
</table>

From Tables 2.5 and 2.8 in last chapter, the average densities of the G1 and G2 geopolymer samples are 1.6g/cm³ and 1.8g/cm³, respectively. However, it is found that the heat resistant performance of G1 samples was worse than that of the G2 samples because G1 samples did not form good geopolymer cement. In this chapter, the average density for the geopolymer cement is around 2.0 g/cm³, as listed in Table 3.8. The apparent density is usually higher than the normal density. According to Figure 3.7, and 3.8, the softening temperature for the geopolymer cement samples discussed in this chapter is between 500°C and 800°C. This is verified by the test results that the geopolymer cement expand or soften or recrystallize between 500°C and 800°C.

3.3.6 X-Ray Diffraction (XRD) Analysis

Figure 3.8 compares the XRD patterns of the class F fly ash and the No. 1 geopolymer samples before and after the heating (500°C, and 800°C). Two different cooling methods (natural cooling down method and water cooling down method) are adopted for the samples after exposed to the 500°C heating. The XRD patterns of the fly ash shows a huge broad hump between 8-18° 2θ with a few sharp peaks indicated as quartz (SiO₂). It is interpreted that the amorphous phases, calcined silica and alumina, constitute the major part of this raw material. As for the geopolymer end products, the broad hump indicates that there is amorphous geopolymer matrix formed. A broad hump between 18-36° 2θ is the characteristic reflection of amorphous geopolymers (Li and Liu 2007; Guo et al. 2010). More discernable XRD patterns are shown in Figure 3.8 (b), in which a huge and broad hump from amorphous phases is clearly observed at 8-38° 2θ,
along with a few sharp peaks identified as crystalline quartz, suggesting a very high degree of geopolymerization in the KOH and Na₂SiO₃ activated geopolymer cement samples. This observation explains why the KOH and Na₂SiO₃ activated fly ash-based geopolymer cement possess higher compressive strength, stiffness, and thermal properties. Furthermore, a few sharp peaks are also observed in the geopolymer products, indicating that these crystalline phases probably present as the inactive fillers in the geopolymer synthesis (Zhang et al. 2004; Zhang et al. 2010).

![XRD patterns of fly ash, No.1 samples before and after heating.](image)

Figure 3.8 XRD patterns of fly ash, No.1 samples before and after heating. (Q=quartz, NC=natural cooling down, W=water cooling down)
It can be seen from Figure 3.8 (b) that the heating affects the XRD patterns of geopolymer samples. The XRD patterns of the geopolymer sample of No.1. 800°C. NC (natural cooling down after the 800°C heating for 1 hour) have two huge and broad humps at 8-18° and 18-38° 2θ, respectively, indicating the presence of the amorphous phases as well as more pronounced damage. The second broad hump is the same like other geopolymer samples of No.1 which indicates the amorphous geopolymer matrix. The first broad hump is like the fly ash raw material, which indicates that the heating will damage the formed amorphous geopolymer matrix and change back to the fly ash raw materials, such as amorphous silica and alumina. It is reasonable that the patterns of No.1.500.W and No.1.500.NC are between the patterns of No.1.800°C.NC and No.1 geopolymer samples.

3.3.7 Characterization of Microstructure (SEM-EDXS)

3.3.7.1 SEM-EDXS of Class F Fly Ash

Figure 3.9 shows the micromorphological features of the class F fly ash raw material. The Class F fly ash particles are mainly microspheres with sizes from 1 to 20µm, which verifies the Particle Size Distribution (PSD) analyses (D50=22 µm, Figure 2.3). The knowledge of the micromorphology of the class F fly ash raw material can help to identify those nonreactive and unreacted phases present in the geopolymer cement samples, which will be discussed later. EDXS chemical analyses of the ball indicated by A (Figure 3.9 (b)) and the whole area of picture (b) are shown in Figure 3.9 (c) and (d), respectively. From Figure 3.9 (c), it can be seen that the ball contains more Al than Si, and also some O, Ca, Mg, and Fe, which matches the compositions of SiO₂, Al₂O₃, CaO, and Fe₂O₃ in the class F fly ash in Table 2.1. The SEM-EDXS analyses of the class F fly ash confirm the above compositional analyses by XRD (Figure 3.8).
Figure 3.9 SEM micrographs and EDXS analyses of the class F fly ash raw material: (a) and (b), fly ash; (c) EDXS spectrum of a ball indicated by A in (b); and (d) EDXS spectrum of the whole area of (b).
3.3.7.2 SEM-EDX of No.1, No.2, No.3, No.4, and No.5 Geopolymer Samples

Figure 3.10 shows the microstructure of the No. 1 geopolymer samples. Micropores and microcracks can be clearly observed on the fractured surface (Figure 3.10 (a)), as well as in the manifested views in the same figure. The porous microstructure leads to a good fire resistant performance, as discussed above. Some fly ash particles present as nonactive fillers between the geopolymer binders (Figure 3.10 (f)), which is further supported by the EDXS spectrum analysis in Figure 3.11. Due to many unreacted fly ash balls, the real Si/Al ratio for the whole geopolymer samples seems unfeasible to obtain yet. The dense and bulky base (Figure 3.10 (d)) is gel-like substances and can be characterized as geopolymer binders. The semi-spherical surface maybe the interface of the geopolymer binder and the fly ash ball, where many needle or stripe-shaped particles are formed (Figure 3.10 (e)). The reason for the presence of many needle-shaped particles may be due to the high concentration or abundant alkali solution surrounded the fly ash ball in the geopolymer paste: the unreacted alkali precipitated after the tests and formed the needle or stripe-shaped particles. This inference can be verified by the neo-formed particles on the surface of the fly ash ball as shown in Figure 3.10 (f).

Based on the analysis of the microstructure of the sample of No. 1, the as-received geopolymer products consist of many features: voids, pores, micro cracks, fly ash balls, dense and bulky geopolymer binders. It is considered as a hybrid mix but rather pure geopolymers. The porous microstructure proves that it is of a good fire resistant performance. The neo-formed needle or stripe-shaped particles indicate that the current geopolymer products may have the capability for the future growth of the compressive strength in the extended curing.
The microstructure of the sample No.1 showing the presence of micropores and microcracks, a fractured fly ash particle (e), fly ash ball (f), and some neoformed substances (e.g., needle-shaped particles (e), and bulky gel-like geopolymer matrix (f))
Figure 3.11 shows the selected EDXS results for the No. 1 geopolymer samples based on the SEM analysis in Figure 3.10. Figure 3.11 (a) shows the EDXS spectrum obtained from the whole area in Figure 3.10 (a).

Figure 3.11 EDXS analyses of selected areas from Figure 3.10, the sample No.1: (a) the spectrum of the whole area in Figure 3.10 (a); (b) and (c) the spectrum of the Areas A and B in Figures 3.11(d) and (e), respectively; (d) the spectrum of the Area C in Figure 3.10 (f).
In addition to the major elements (Na, K, Al, O, Si), constituting the geopolymer binders, the elements of Ca and Fe are also present. It is observed that the whole area contains more Si than Al, while the fly ash big ball which contains more Al than Si did not act in the geopolymerization. In addition, the Mg element is not shown in the spectrum of the whole area, which may be due to its tiny concentration or it is covered by the peaks of other elements. From the spectrum of the areas of A and B, indicated in Figure 3.10 (d) and (e), the bulky and gel-like area can be confirmed as the pure geopolymer binder. The EDXS spectrum obtained from the ball indicated in Figure 3.10 (f) further proves that the big fly ash ball is unreacted in the synthesis process but with some unreacted alkali on the surface of the ball (element K in the spectrum).

Figure 3.12 shows the SEM micrographs of the geopolymer samples of Nos. 2~5, and Figure 3.13 shows the EDXS analysis for the selected areas from Figure 3.12. Generally speaking, unreacted fly ash balls present in all the images for all the different water/ash ratios and Si/Al ratios. All the geopolymer final products are continuous, bulky and dense geopolymer matrix with discrete pores and cracks. Two possible reasons are accounting for the cracks: (1) the major parts of the cracks are caused by the loading during the unconfined compressive tests; (2) some cracks are caused by the uneven internal stress or shrinkage due to the water evaporation during the curing. It is observed that more pores are presented for the samples with the higher water/ash ratio, which may be due to that a possible larger volume of water gathered in one place and left a larger void after the water evaporation for such a higher water/ash ratio. The pores and cracks definitely have detrimental influences on the geopolymer products.
Figure 3.12 The comparison of microstructures of the samples of Nos.2~5: (a) and (b), No.2; (c) and (d), No. 3; (e) and (f), No. 4; (g) and (h), No. 5
Figure 3.13 EDXS analyses of selected areas from the Figure 3.12
It is noteworthy that many semi-spherical concavities left on the fractured surfaces for all the selected pieces of the geopolymer products. The reason may be that the physically bounded water exists between the geopolymer binders and the fillers (unreacted big fly ash balls) like a film. After the loss of the water, the voids around the fly ash ball will appear. Hence, the fractured surface tends to pass through these voids and presents many semi-spherical concavities. However, the reacted portion of the fly ash balls may be bonded on the continuous base.

In Figure 3.12 (b), a particular attention is paid to a small ball as indicated by A. Further EDXS analysis of this small ball shows that it is a reacted fly ash ball with the major elements of Na (K), O, Al and Si, which constitute the major parts of the geopolymer cement. The areas indicated by B in Figure 3.12 (d) refer to a semi-spherical concavity and a discrete aggregate with smooth and round-shaped surface. The EDXS spectrum shows that the areas indicated by B are well formed geopolymer binders. The areas of C in Figure 3.12 (f) show the geopolymer binders with complex and cloudy shapes, as well as the areas of D in Figure 3.12 (h). These complex shaped materials are characterized as with the same elements as the pure geopolymers, while they have much lower compressive strength as compared with that of the pure geopolymers.

Based on the observations of the microstructures for the samples of Nos.1~5 (Figure 3.10~3.13), it is concluded that: (1) the geopolymers for the samples prepared with different water/ash ratios are not pure geopolymers but rather with some impurities and discrete pores and cracks of various sizes; (2) for the geopolymer products of No. 1 (water/ash=0.2; Si/Al=2.38), the fractured surfaces seem very continuous without any complex shapes of geopolymer binders. While for the samples of Nos. 4 and 5 with
higher ratios of water/ash and Si/Al, the microstructure surfaces present cloudy and complex shaped geopolymer binders on the bulky base, which have negative influence on the compressive strength of the geopolymers as discussed in Figure 3.5; (3) micro pores can be observed for all the examined geopolymer samples regarding to the different water/ash ratios adopted. Considering the workability of the geopolymer slurry, the optimum water /ash ratio can be taken as 0.3.

3.3.7.3 SEM-EDX analysis of No.1.500°C-NC, No.1.500°C-W, No.3.500°C-NC, and No.1.800°C-NC Geopolymer Samples

Figure 3.14 compares the SEM microstructures of the geopolymer samples of No.1 with two different cooling down methods after the 500°C heating. The EDXS spectrums of the selected interested areas are also shown in Figure 3.14. Similar as the samples without the high temperature heating, the failure surfaces of the samples with the 500°C heating have pores, cracks, voids, unreacted fly ash balls and semi-spherical concavities left by the fly ash balls. Based on the EDXS spectrum analysis shown in Figure 3.14 (e) and (f), geopolymer binders are well conserved after the high temperature heating, hence a relatively high compressive strength is still presented as discussed before.

From this figure, it is observed that the fractured surfaces of the No.1.500°C-NC samples are very smooth, while lots of power-shaped, irregular and small particles are pronounced on the fractured surfaces of the No.1.500°C-W samples (Figure 3.14 (c)), indicating that the water cooling down method causes negative effects on some vulnerable areas where the geopolymer binders are not connected well. However, smooth failure surfaces are still witnessed for the No.1.500°C-W samples (Figure 3.14 (d)), which contributes to the high residual compressive strength of the No.1.500°C-W samples.
Figure 3.14 SEM micrographs and EDXS analyses for the samples of No. 1.500°C-NC and No. 1.500°C-W: (a) and (b), No. 1.500°C–NC; (c) and (d), No. 1.500°C-W; (e) EDXS spectrum of area A indicated in (b); and (f) EDXS spectrum of area B indicated in (c).
Figure 3.15 shows the SEM micrographs of the interested failure pieces of No.3.500°C-NC samples, and Figure 3.16 shows the selected EDXS spectrum for the interested areas indicated in Figure 3.15.

Figure 3.15 The microstructure of the sample No.3.500°C-NC.
Figure 3.16 EDXS analyses of selected areas from the Figure 3.15: (a) EDXS spectrum for area A indicated in Figure 3.15 (c); (b) EDXS spectrum for area B indicated in Figure 3.15 (c); (c) EDXS spectrum for area C indicated in Figure 3.15 (e); and (d) EDXS spectrum for area D indicated in Figure 3.15 (f).
Compared with the microstructures of the No.1.500°C-NC samples, some distinguishable narrow and long strips or zones are recognized in Figure 3.15 (a) and (b). Further investigation by the EDXS spectrum analysis of several interested areas indicated by B and C in Figure 3.15 (c) and (e) shows that the narrow strips are mainly Si and SiO$_2$. The leather or strip-shaped precipitated materials indicated by D in Figure 3.15 (f) are consisted by alumina and silicate and this is verified by the EDXS spectrum analysis as shown in Figure 3.16 (d).

The understanding for the presence of the silicate strips is not clear yet, while its influence on the mechanical properties of the geopolymer end products are very clear. From the analysis of the data listed in Table 3.3, the reduction rate of the compressive strength for the No. 3 samples after the 500°C heating is 36%, while it is 15.7% for the No. 1 samples under the same conditions. However, further studies are needed to warrant a full understanding of the presence of the silicate strips.

Figure 3.17 shows the detailed images of the No.1.800°C-NC samples and several interested areas are further investigated by the EDXS spectrums. From the micrographs shown in Figure 3.17 (a)~(d), the microstructure after the 800°C heating (No.1.800°C-NC) becomes loose, porous and honeycomb-shaped patterns as compared with the samples without the heating treatment and the samples with the heating treatment, such as the No.1, No.1.500°C-NC, and No.1.500°C-WC samples. This micro-level change is reflected on the macro-level that the samples expanded 9.4% based on the samples without the high temperature treatment, as shown in Table 3.7. The expanded structures result in the notably much lower compressive strength (only 12 MPa) which was shown in Figure 3.6.
Figure 3.17 The microstructure of the sample No.1.800°C-NC.

The continuous and shell-like area indicated by A in Figure 3.17 (d) shows the existence of the geopolymer binder, as confirmed by the EDXS spectrum in Figure 3.18.
(a). It is noted that several reacted fly ash balls stick on the porous geopolymer base (Figure 3.17 (d), Figure 3.18 (b)).

![Diagram showing EDXS analyses of selected areas from Figure 3.17: (a) EDXS spectrum for area A indicated in Figure 3.17 (d); (b) EDXS spectrum for area B indicated in Figure 3.17 (d); and (c) EDXS spectrum for area C indicated in Figure 3.17 (f).](image)

Some neo-formed needle shaped materials extrude or grow on the geopolymer base and they are identified as the new generated geopolymers by the EDXS analysis (Figure 3.18 (c)), which indicates that the formation of the final geopolymer products can last for a long duration. While the verified elements from the EDXS spectrum analysis for the No.1.800°C-NC samples are the same as those for the examined geopolymers without the
high temperature heating, the mechanical properties are significantly affected by the porous and loose microstructures. The main reason may be that the evaporation of the chemically bonded water and hydroxyl groups OH produces many micro pores and hence deteriorates the mechanical behavior under the compression tests.

3.4 Conclusions

In this chapter, an experimental study regarding the thermo-mechanical properties of a geopolymer cement prepared using the class F fly ash and KOH and Na$_2$SiO$_3$ alkaline activators under different silicate/hydroxide ratios is conducted and presented. Based on the experimental results, XRD and SEM-EDXS analyses, the following conclusions can be drawn.

1. The failure patterns of the geopolymer cement samples without the heat treatment (the 500$^\circ$C and 800$^\circ$C heating) are like the failure patterns of the stone in the compression tests. The compressive strength of the geopolymer cement samples cured at appropriate conditions with the water/ash ratio is 0.2 even reaches up to 110 MPa. It is competitive with the high-strength concrete used in the high-rise buildings.

2. The strength of the geopolymer cement samples with a water/ash ratio of 0.2 after the 500$^\circ$C exposure is still as high as 96 MPa. The shrinkage in the longitudinal direction of the geopolymer cement sample with a water/ash ratio of 0.2 is 2.0% after the 500$^\circ$C heating, but the expansion reaches 9.4% after the 800$^\circ$C heating, while after the 800$^\circ$C exposure, it is 12MPa, which verifies that the softening temperature for the geopolymer cement samples discussed in this chapter is between 500$^\circ$C and 800$^\circ$C.

3. The heat curing method can develop higher strength cement than the normal curing and water curing methods. The samples with the heat curing method (24 hours at the room temperature and then cured at 80$^\circ$C for another 24 hours) have very good
compressive strength. Open curing condition (without sealing or sealed not completely) is not good for the geopolymerization process.

4. The water/ash ratio of 0.3 may be the optimal mixture ratio if the fluidity and workability of geopolymer cement are taken into consideration.

5. For all the heated geopolymer cement samples (exposure to 500°C or 800°C), no spalling phenomenon was observed using either the natural cooling down method or the water cooling down method.

6. According to the compositional and microstructural analyses, the as-received geopolymer products consist of many features: voids, pores, micro cracks, fly ash balls, dense and bulky geopolymer binders. It is considered as a hybrid mix but rather pure geopolymers. The porous microstructure proves that it is with a good fire resistant performance.
CHAPTER 4 CONCLUSIONS

Alkali-activators play an important role in the geopolymerization, which determines the mechanical and thermal properties of geopolymer cements. First, three groups of geopolymer cements are discussed, which are activated by NaOH activator, NaOH and Na$_2$SiO$_3$ mixed activators, and KOH and Na$_2$SiO$_3$ mixed activators. Then, a further study on the thermo-mechanical properties of the class F fly ash based geopolymer materials prepared using KOH and Na$_2$SiO$_3$ alkaline activators with different curing and cooling methods are presented. The effects of the water/ash ratio, curing methods, cooling methods, and sealing degree on the compressive strength and thermal properties of the geopolymer products are investigated and analyzed in details. Based on the experimental results, XRD and SEM-EDXS analyses, the following conclusions can be drawn.

1. The Na$_2$SiO$_3$ is necessary for the development of geopolymer cement. The NaOH activated fly ash geopolymer cement has very low compressive strength, implying the geopolymerization is very low for using the NaOH only. The compressive strength of NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement is around 30 MPa. The compressive strength of the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples cured at appropriate conditions with the water/ash ratios 0.2 even reaches up to 110 MPa.

2. The strength of the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples with a water/ash ratio of 0.2 after the 500°C exposure is still as high as 96 MPa, while after the 800°C exposure, it is 12 MPa, which verifies that the softening temperature for the geopolymer cement samples discussed in chapter 3 is between 500°C and 800°C.
3. The heat curing method can develop higher strength cement than the normal curing and water curing methods. The KOH and Na$_2$SiO$_3$ activated fly ash geopolymer samples with the heat curing method (24 hours at the room temperature and then cured at 80°C for another 24 hours) have very good compressive strength. Open curing condition (without sealing or sealed not completely) is not good for the geopolymerization process.

4. The water/ash ratio of 0.3 may be the optimal mixture ratio if the fluidity and workability of geopolymer cement are taken into consideration.

5. For all the heated geopolymer cement samples (exposure to 500°C or 800°C), no spalling phenomenon was observed using either the natural cooling down method or the water cooling down method.

6. According to the compositional and microstructural analyses, the as-received geopolymer products consist of many features: voids, pores, micro cracks, fly ash balls, dense and bulky geopolymer binders. It is considered as a hybrid mix but rather pure geopolymers. The porous microstructure proves that it is with a good fire resistant performance.

7. The water precipitation phenomenon was observed for the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement samples, where Na$_2$CO$_3$ was produced by CO$_2$ and additional NaOH due to a large molar ratio of Na/Si (1.5). Hence, it is better to take the molar ratio of Na/Si as 1.0 to avoid the water precipitation. The water/ash ratio is preferred to be located between 0.30 and 0.35. However, as an emerging topic in geopolymer cement, the water precipitation effects should be further studied.

In this study, good fly ash based geopolymer cement is formed, which can be used in many applications. Two possible applications are as:
1. For the NaOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement, the compressive strength is around 30 MPa in the ambient environment and the setting time is around 30 minutes. First, this geopolymer cement can be used to form a new geopolymer concrete by adding coarse and fine aggregates and sands. Second, this geopolymer cement can be used for concrete recycling with its excellent bonding capacity and this will result in great economic and environmental benefits and will finally promote sustainable development of communities.

2. For the KOH and Na$_2$SiO$_3$ activated fly ash geopolymer cement, the compressive strength and strength after 500°C exposure is as high as 110 MPa, and 96 MPa, respectively. This high performance geopolymer cement can be used in the high rise buildings and bridges as alternative structural materials. Further, it also can be used in heat or fire resistant applications.
REFERENCES


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Lloyd, N., and Rangan, V. (2009). “GeopolymerConcrete—Sustainable Cementless Concrete.” *ACI Special Publication SP-261, 10th ACI International Conference on Recent Advances in Concrete Technology and Sustainability Issues*. American Concrete Institute, Farmington Hills, MI.


VITA

Fenghong Fan was born and raised in Chenzhou, China. Fenghong Fan received her Bachelor of Science in Civil Engineering from Hunan University in 2007 and Master of Science in Bridge Engineering at Hunan University in 2010. She began attending Louisiana State University in August of 2010, under the guidance of Dr. Steve C.S. Cai, to pursue her master’s degree. She expects to receive her master’s degree in May 2015.