

**Faculty of Engineering and Computing  
Department of Civil Engineering**

**Studies on Fly Ash-Based Geopolymer Concrete**

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## ABSTRACT

The use of Portland cement in concrete construction is under critical review due to high amount of carbon dioxide gas released to the atmosphere during the production of cement. In recent years, attempts to increase the utilization of fly ash to partially replace the use of Portland cement in concrete are gathering momentum. Most of this by-product material is currently dumped in landfills, creating a threat to the environment.

Geopolymer concrete is a 'new' material that does not need the presence of Portland cement as a binder. Instead, the source of materials such as fly ash, that are rich in Silicon (Si) and Aluminium (Al), are activated by alkaline liquids to produce the binder. Hence concrete with no Portland cement.

This thesis reports the details of development of the process of making fly ash-based geopolymer concrete. Due to the lack of knowledge and know-how of making of fly ash-based geopolymer concrete in the published literature, this study adopted a rigorous trial and error process to develop the technology of making, and to identify the salient parameters affecting the properties of fresh and hardened concrete. As far as possible, the technology that is currently in use to manufacture and testing of ordinary Portland cement concrete were used.

Fly ash was chosen as the basic material to be activated by the geopolymerization process to be the concrete binder, to totally replace the use of Portland cement. The binder is the only difference to the ordinary Portland cement concrete. To activate the Silicon and Aluminium content in fly ash, a combination of sodium hydroxide solution and sodium silicate solution was used.

Manufacturing process comprising material preparation, mixing, placing, compaction and curing is reported in the thesis. Napthalene-based superplasticiser was found to be

useful to improve the workability of fresh fly ash-based geopolymer concrete, as well as the addition of extra water. The main parameters affecting the compressive strength of hardened fly ash-based geopolymer concrete are the curing temperature and curing time, the molar  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  ratio, and mixing time.

Fresh fly ash-based geopolymer concrete has been able to remain workable up to at least 120 minutes without any sign of setting and without any degradation in the compressive strength. Providing a rest period for fresh concrete after casting before the start of curing up to five days increased the compressive strength of hardened concrete.

The elastic properties of hardened fly ash-based geopolymer concrete, i.e. the modulus of elasticity, the Poisson's ratio, and the indirect tensile strength, are similar to those of ordinary Portland cement concrete. The stress-strain relations of fly ash-based geopolymer concrete fit well with the expression developed for ordinary Portland cement concrete.

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The tests to measure the stress-strain curves of geopolymer concrete in compression were undertaken at the laboratory of School of Civil and Environmental Engineering at the University of New South Wales in Sydney with the help of Professor Stephen Foster. His help is gratefully acknowledged.

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## LIST OF PUBLICATIONS

The following publications were produced using the results reported in this thesis:

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- Hardjito, D.**, Wallah, S. E. & Rangan, B. V., 2002b, 'Study on Engineering Properties of Fly Ash-Based Geopolymer Concrete', *Journal of the Australasian Ceramic Society*, vol. 38, no. 1, pp. 44-47.
- Hardjito, D.**, Wallah, S. E. & Rangan, B. V., 2002c, 'The Influence of Curing Time and NaOH-Water Ratio on the Compressive Strength of Fly Ash-Based Geopolymer Concrete', in *Austceram 2002 International Conference*, eds. I. M. Low & D. N. Phillips, Perth, Western Australia, pp. 35-36.
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- Hardjito, D.**, Wallah, S. E., Sumajouw, D. M. J. & Rangan, B. V., 2003a, 'Geopolymer Concrete: Turn Waste Into Environmentally Friendly Concrete', in *International Conference on Recent Trends in Concrete Technology and Structures (INCONTEST)*, I, eds. D. L. V. Babu, R. Gettu & R. Krishnamoorthy, KCT, Coimbatore, India, pp. 129-140.
- Hardjito, D.**, Wallah, S. E., Sumajouw, D. M. J. & Rangan, B. V., 2003b, 'Properties of Fly Ash-Based Geopolymer Concrete: Influence of Mixture Composition and Curing Temperature', in *The Ninth East Asia-Pasific Conference on Structural Engineering and Construction (EASEC-9)*, Bali, Indonesia.
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- Hardjito, D.,** Wallah, S. E., Sumajouw, D. M. J. & Rangan, B. V., 2004c, 'Properties of Geopolymer Concrete with Fly Ash as Source Material: Effect of Mixture Composition', in V. M. Malhotra, (ed.) *Recent Advances in Concrete Technology*, vol. ACI SP 222-8, Las Vegas, USA, pp. 109-118.
- Hardjito, D.,** Wallah, S. E., Sumajouw, D. M. J. & Rangan, B. V., 2004d, 'The Stress-Strain Behaviour of Fly Ash-Based Geopolymer Concrete', in *Development in Mechanics of Structures & Materials*, vol. 2, Eds. A.J. Deeks and Hong Hao, A.A. Balkema Publishers - The Netherlands, pp. 831-834.
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# 1. INTRODUCTION

## 1.1 GENERAL

After wood, concrete is the most often used material by the community. Concrete is conventionally produced by using the ordinary Portland cement (OPC) as the primary binder. The environmental issues associated with the production of OPC are well known. The amount of the carbon dioxide released during the manufacture of OPC due to the calcination of limestone and combustion of fossil fuel is in the order of one ton for every ton of OPC produced. In addition, the amount of energy required to produce OPC is only next to steel and aluminium.

On the other side, the abundance and availability of fly ash worldwide create opportunity to utilise this by-product of burning coal, as partial replacement or as performance enhancer for OPC. Fly ash in itself does not possess the binding properties, except for the high calcium or ASTM Class C fly ash. However, in the presence of water and in ambient temperature, fly ash reacts with the calcium hydroxide during the hydration process of OPC to form the calcium silicate hydrate (C-S-H) gel. This pozzolanic action happens when fly ash is added to OPC as a partial replacement or as an admixture. The development and application of high volume fly ash concrete, which enabled the replacement of OPC up to 60-65% by mass (Malhotra 2002; Malhotra and Mehta 2002), can be regarded as a landmark in this attempt.

In another scheme, pozzolans such as blast furnace slag and fly ash may be activated using alkaline liquids to form a binder and hence totally replace the use of OPC in concrete. In this scheme, the alkalinity of the activator can be low to mild or high. In the first case, with low to medium alkalinity of the activator, the main contents to be activated are silicon and calcium in the by-product material such as blast furnace slag. The main binder produced is a C-S-H gel, as the result of a hydration process. In the later case, the main constituents to be activated with high alkaline solution are

mostly the silicon and the aluminium present in the by-product material such as low calcium (ASTM Class F) fly ash (Palomo, Grutzeck et al. 1999). The binder produced in this case is due to polymerisation. Davidovits (1999) in 1978 named the later as Geopolymers, and stated that these binders can be produced by a polymeric synthesis of the alkali activated material from geological origin or by-product materials such as fly ash and rice husk ash.

In 2001, when the research reported in this thesis began, several research publications were available regarding geopolymer pastes and geopolymer coating materials (Davidovits 1991; Davidovits 1994; Davidovits, Davidovits et al. 1994; Balaguru, Kurtz et al. 1997; van Jaarsveld, van Deventer et al. 1997; Balaguru 1998; van Jaarsveld, van Deventer et al. 1998; Davidovits 1999; Kurtz, Balaguru et al. 1999; Palomo, Grutzeck et al. 1999; Barbosa, MacKenzie et al. 2000). However, not a great deal was known regarding using the geopolymer technology to make fly ash-based geopolymer concrete.

The research reported in this thesis was dedicated to investigate the process of making fly ash-based geopolymer concrete and the short-term engineering properties of the fresh and hardened concrete.

## **1.2 FLY ASH-BASED GEOPOLYMER CONCRETE**

In this work, fly ash-based geopolymer is used as the binder, instead of Portland or any other hydraulic cement paste, to produce concrete. The fly ash-based geopolymer paste binds the loose coarse aggregates, fine aggregates and other un-reacted materials together to form the geopolymer concrete, with or without the presence of admixtures. The manufacture of geopolymer concrete is carried out using the usual concrete technology methods.

As in the OPC concrete, the aggregates occupy the largest volume, i.e. about 75-80 % by mass, in geopolymer concrete. The silicon and the aluminium in the low calcium (ASTM Class F) fly ash are activated by a combination of sodium hydroxide and sodium silicate solutions to form the geopolymer paste that binds the aggregates and other un-reacted materials.

### **1.3 AIMS OF THE RESEARCH**

As mentioned earlier, most of the published research on geopolymers studied the behaviour of pastes with various types of source materials. The present study deals with the manufacture of low calcium (ASTM Class F) fly ash-based geopolymer concrete, the parameters influencing the mixture proportioning, and the short-term engineering properties in the fresh and hardened states. The research reported in this thesis is the first stage of a research project on fly ash-based geopolymer concrete currently in progress in the Faculty of Engineering and Computing at Curtin University of Technology, Perth, Australia.

The aims of the research are:

1. To develop a mixture proportioning process of making fly ash-based geopolymer concrete.
2. To identify and study the effect of salient parameters that affects the properties of fly ash-based geopolymer concrete.
3. To study the short-term engineering properties of fresh and hardened fly ash-based geopolymer concrete.

### **1.4 SCOPE OF WORK**

The research utilized low calcium (ASTM Class F) fly ash as the base material for making geopolymer concrete. The fly ash was obtained from only one source, because the main focus of this study was the short-term behaviour and the engineering properties of fly ash-based geopolymer concrete. As far as possible, the technology and the equipment currently used to manufacture OPC concrete were also used to make the geopolymer concrete.

The concrete properties studied included the compressive and indirect tensile strengths, the elastic constants, the stress-strain relationship in compression, and the workability of fresh concrete.



## **1.5 THESIS ARRANGEMENT**

The remainder of the thesis is arranged as follow: Chapter 2 describes the need to find alternatives to make concrete more environmentally friendly, and the availability and the potential use of low calcium (ASTM Class F) fly ash. This chapter also provides a brief literature review of geopolymer technology.

Chapter 3 describes the experimental program carried out to develop the mixture proportions, the mixing process, and the curing regime of geopolymer concrete. The tests performed to study the behaviour and the short term engineering properties of the fresh concrete and the hardened concrete are also described.

Chapter 4 presents and discusses the test results. Chapter 5 states the summary and the conclusions of this study, followed by a set of recommendations for future work. The thesis ends with a Reference List and several Appendices.

## **2. LITERATURE REVIEW**

This chapter presents a background to the needs on the development of a fly ash-based geopolymer technology. The available published literature on geopolymer technology is also briefly reviewed.

### **2.1 CONCRETE AND ENVIRONMENT**

The trading of carbon dioxide (CO<sub>2</sub>) emissions is a critical factor for the industries, including the cement industries, as the greenhouse effect created by the emissions is considered to produce an increase in the global temperature that may result in climate changes. The ‘tradeable emissions’ refers to the economic mechanisms that are expected to help the countries worldwide to meet the emission reduction targets established by the 1997 Kyoto Protocol. Speculation has arisen that one ton of emissions can have a trading value about US\$10 (Malhotra 1999; Malhotra 2004).

The climate change is attributed to not only the global warming, but also to the paradoxical global dimming due to the pollution in the atmosphere. Global dimming is associated with the reduction of the amount of sunlight reaching the earth due to pollution particles in the air blocking the sunlight. With the effort to reduce the air pollution that has been taken into implementation, the effect of global dimming may be reduced, however it will increase the effect of global warming (Fortune 2005). In this view, the global warming phenomenon should be considered more seriously, and any action to reduce the effect should be given more attention and effort.

The production of cement is increasing about 3% annually (McCaffrey 2002). The production of one ton of cement liberates about one ton of CO<sub>2</sub> to the atmosphere, as the result of de-carbonation of limestone in the kiln during manufacturing of cement and the combustion of fossil fuels (Roy 1999).

The contribution of Portland cement production worldwide to the greenhouse gas emission is estimated to be about 1.35 billion tons annually or about 7% of the total greenhouse gas emissions to the earth's atmosphere (Malhotra 2002). Cement is also among the most energy-intensive construction materials, after aluminium and steel. Furthermore, it has been reported that the durability of ordinary Portland cement (OPC) concrete is under examination, as many concrete structures, especially those built in corrosive environments, start to deteriorate after 20 to 30 years, even though they have been designed for more than 50 years of service life (Mehta and Burrows 2001).

The concrete industry has recognized these issues. For example, the U.S. Concrete Industry has developed plans to address these issues in 'Vision 2030: A Vision for the U.S. Concrete Industry'. The document states that *'concrete technologists are faced with the challenge of leading future development in a way that protects environmental quality while projecting concrete as a construction material of choice. Public concern will be responsibly addressed regarding climate change resulting from the increased concentration of global warming gases.* In this document, strategies to retain concrete as a construction material of choice for infrastructure development, and at the same time to make it an environmentally friendly material for the future have been outlined (Mehta 2001; Plenge 2001).

In order to produce environmentally friendly concrete, Mehta (2002) suggested the use of fewer natural resources, less energy, and minimise carbon dioxide emissions. He categorised these short-term efforts as *'industrial ecology'*. The long-term goal of reducing the impact of unwanted by-products of industry can be attained by lowering the rate of material consumption. Likewise, McCaffrey (2002) suggested three alternatives to reduce the amount of carbon dioxide (CO<sub>2</sub>) emissions by the cement industries, i.e. to decrease the amount of calcined material in cement, to decrease the amount of cement in concrete, and to decrease the number of buildings using cement.

## **2.2 FLY ASH**

According to the American Concrete Institute (ACI) Committee 116R, fly ash is defined as *'the finely divided residue that results from the combustion of ground or*

*powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system' (ACI Committee 232 2004). Fly ash is removed from the combustion gases by the dust collection system, either mechanically or by using electrostatic precipitators, before they are discharged to the atmosphere. Fly ash particles are typically spherical, finer than Portland cement and lime, ranging in diameter from less than 1  $\mu\text{m}$  to no more than 150  $\mu\text{m}$ .*

The types and relative amounts of incombustible matter in the coal determine the chemical composition of fly ash. The chemical composition is mainly composed of the oxides of silicon ( $\text{SiO}_2$ ), aluminium ( $\text{Al}_2\text{O}_3$ ), iron ( $\text{Fe}_2\text{O}_3$ ), and calcium ( $\text{CaO}$ ), whereas magnesium, potassium, sodium, titanium, and sulphur are also present in a lesser amount. The major influence on the fly ash chemical composition comes from the type of coal. The combustion of sub-bituminous coal contains more calcium and less iron than fly ash from bituminous coal. The physical and chemical characteristics depend on the combustion methods, coal source and particle shape. The chemical compositions of various fly ashes show a wide range, indicating that there is a wide variations in the coal used in power plants all over the world (Malhotra and Ramezani pour 1994).

Fly ash that results from burning sub-bituminous coals is referred as ASTM Class C fly ash or high calcium fly ash, as it typically contains more than 20 percent of  $\text{CaO}$ . On the other hand, fly ash from the bituminous and anthracite coals is referred as ASTM Class F fly ash or low calcium fly ash. It consists of mainly an aluminosilicate glass, and has less than 10 percent of  $\text{CaO}$ . The colour of fly ash can be tan to dark grey, depending upon the chemical and mineral constituents (Malhotra and Ramezani pour 1994; ACAA 2003). The typical fly ash produced from Australian power stations is light to mid-grey in colour, similar to the colour of cement powder. The majority of Australian fly ash falls in the category of ASTM Class F fly ash, and contains 80 to 85% of silica and alumina (Heidrich 2002).

Aside from the chemical composition, the other characteristics of fly ash that generally considered are loss on ignition (LOI), fineness and uniformity. LOI is a measurement of unburnt carbon remaining in the ash. Fineness of fly ash mostly depends on the operating conditions of coal crushers and the grinding process of the

coal itself. Finer gradation generally results in a more reactive ash and contains less carbon.

In 2001, the annual production of fly ash in the USA was about 68 million tons. Only 32 percent of this was used in various applications, such as in concrete, structural fills, waste stabilisation/solidification etc. (ACAA 2003). Ash production in Australia in 2000 was approximated 12 million tons, with some 5.5 million tons have been utilised (Heidrich 2002). Worldwide, the estimated annual production of coal ash in 1998 was more than 390 million tons. The main contributors for this amount were China and India. Only about 14 percent of this fly ash was utilized, while the rest was disposed in landfills (Malhotra 1999). By the year 2010, the amount of fly ash produced worldwide is estimated to be about 780 million tons annually (Malhotra 2002). The utilization of fly ash, especially in concrete production, has significant environmental benefits, viz, improved concrete durability, reduced use of energy, diminished greenhouse gas production, reduced amount of fly ash that must be disposed in landfills, and saving of the other natural resources and materials (ACAA 2003).

### **2.3 THE USE OF FLY ASH IN CONCRETE**

One of the efforts to produce more environmentally friendly concrete is to reduce the use of OPC by partially replacing the amount of cement in concrete with by-products materials such as fly ash. As a cement replacement, fly ash plays the role of an artificial pozzolan, where its silicon dioxide content reacts with the calcium hydroxide from the cement hydration process to form the calcium silicate hydrate (C-S-H) gel. The spherical shape of fly ash often helps to improve the workability of the fresh concrete, while its small particle size also plays as filler of voids in the concrete, hence to produce dense and durable concrete. Generally, the effective amount of cement that can be replaced by fly ash is not more than 30% (Neville 2000).

An important achievement in the use of fly ash in concrete is the development of high volume fly ash (HVFA) concrete that successfully replaces the use of OPC in concrete up to 60% and yet possesses excellent mechanical properties with enhanced

durability performance. HVFA concrete has been proved to be more durable and resource-efficient than the OPC concrete (Malhotra 2002). The HVFA technology has been put into practice, for example the construction of roads in India, which implemented 50% OPC replacement by the fly ash (Desai 2004).

Activation of fly ash with alkaline solutions enables this by-product material to be a cement-like construction material. In this case, concrete binder can be produced without using any OPC; in other words, the role of OPC can be totally replaced by the activated fly ash. Palomo et al (1999) described two different models of the activation of fly ash or other by-product materials. For the first model, the silicon and the calcium in the material is activated by a low to mild concentration of alkaline solution. The main product of the reaction is believed to be a calcium silicate hydrate (C-S-H) that results from the hydration process. On the contrary, the material used in the second model contains mostly silicon and aluminium, and is activated by a highly alkaline solution. The chemical process in this case is polymerisation.

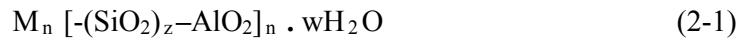
A well known example of the first model is the activation of blast furnace slag, that has a long history in the former Soviet Union, Scandinavia and Eastern Europe (Roy 1999). On the other hand, studies on the second model are limited (Palomo, Grutzeck et al. 1999). Many aspects of the material characteristics and reaction mechanisms are still not clear. For the second model, Davidovits (1999) coined the term Geopolymer in 1978 to describe the alkali activated material from geological origin or by-product materials such as fly ash and rice husk ash. Davidovits (1994) also revealed the fact that very few scientific literatures on geopolymer material available was caused by the patent oriented schemes of research works. Only from the late 1990s scientific information were becoming available in the published literature.

## **2.4 GEOPOLYMERS**

Polymer is a class of materials made from large molecules that are composed of a large number of repeating units (monomers). The molecular structure of the unit that makes up the large molecules controls the properties of the material. The non-crystalline or amorphous state is the state when the regularity of atomic packing is

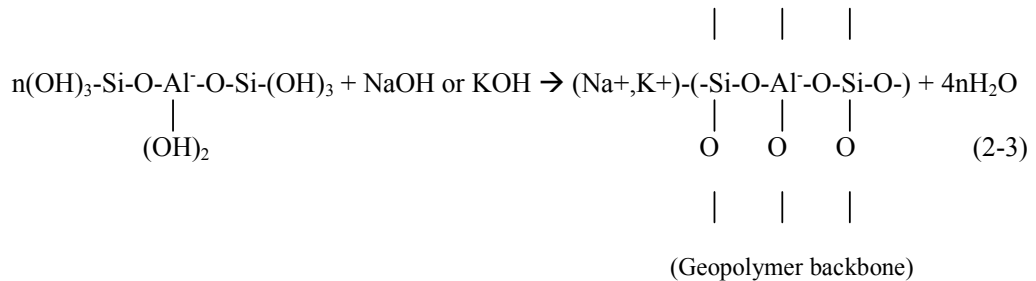
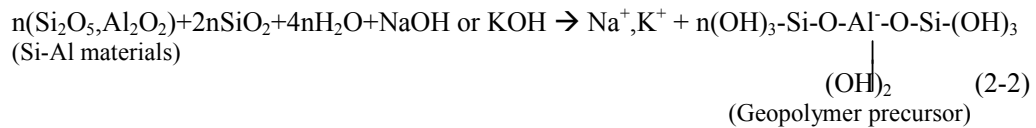
completely absent. The most familiar kind of an amorphous solid is glass (Young, Mindness et al. 1998).

Geopolymers are a member of the family of inorganic polymers, and are a chain structures formed on a backbone of Al and Si ions. The chemical composition of this geopolymer material is similar to natural zeolitic materials, but they have amorphous microstructure instead of crystalline (Palomo, Grutzeck et al. 1999; Xu and van Deventer 2000). The polymerisation process involves a substantially fast chemical reaction under highly alkaline condition on Si-Al minerals, that results in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds, as follows (Davidovits 1999):



Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol – indicates the presence of a bond, n is the degree of polycondensation or polymerisation; z is 1,2,3, or higher, up to 32.

The schematic formation of geopolymer material can be shown as described by Equations (2-2) and (2-3) (van Jaarsveld, van Deventer et al. 1997; Davidovits 1999). These formations indicate that all materials containing mostly Silicon (Si) and Aluminium (Al) can be processed to make the geopolymer material.



To date, the exact mechanism of setting and hardening of the geopolymer material is not clear, as well as its reaction kinetics. However, most proposed mechanisms consist of the following (Davidovits 1999; Xu and van Deventer 2000):

- Dissolution of Si and Al atoms from the source material through the action of hydroxide ions.
- Transportation or orientation or condensation of precursor ions into monomers.
- Setting or polycondensation/polymerisation of monomers into polymeric structures.

However, these three steps can overlap with each other and occur almost simultaneously, thus making it difficult to isolate and examine each of them separately (Palomo, Grutzeck et al. 1999).

A geopolymer can take one of the three basic forms (Davidovits 1999), i.e:

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

Sialate is an abbreviation of silicon-oxo-aluminate.

Davidovits (1999) proposed the possible applications of the geopolymer material depending on the molar ratio of Si to Al, as given in Table 2.1.



**Table 2.1: Applications of Geopolymer Material**

Si/Al	Application
1	Bricks, ceramics, fire protection
2	Low CO <sub>2</sub> cements, concrete, radioactive & toxic waste encapsulation
3	Heat resistance composites, foundry equipments, fibre glass composites
>3	Sealants for industry
20<Si/Al<35	Fire resistance and heat resistance fibre composites

### **2.4.1 Constituents of Geopolymer**

#### **2.4.1.1 Source Materials**

Any material that contains mostly Silicon (Si) and Aluminium (Al) in amorphous form is a possible source material for the manufacture of geopolymer. Several minerals and industrial by-product materials have been investigated in the past. Metakaolin or calcined kaolin (Davidovits 1999; Barbosa, MacKenzie et al. 2000; Teixeira-Pinto, Fernandes et al. 2002), ASTM Class F fly ash (Palomo, Grutzeck et al. 1999; Swanepoel and Strydom 2002), natural Al-Si minerals (Xu and van Deventer 2000), combination of calcined mineral and non calcined materials (Xu and van Deventer 2002), combination of fly ash and metakaolin (Swanepoel and Strydom 2002; van Jaarsveld, van Deventer et al. 2002), and combination of granulated blast furnace slag and metakaolin (Cheng and Chiu 2003) were investigated as source materials.

Metakaolin is preferred by the niche geopolymer product developers due to its high rate of dissolution in the reactant solution, easier control on the Si/Al ratio and the white colour (Gourley 2003). However, for making concrete in a mass production state, metakaolin is very expensive.

Low calcium (ASTM Class F) fly ash is preferred as a source material than high calcium (ASTM Class C) fly ash. The presence of calcium in high amount may interfere with the polymerisation process and alter the microstructure (Gourley 2003).

Davidovits (1999) calcined kaolin clay for 6 hours at 750°C. He termed this metakaolin as KANDOXI (**KA**olinite, **Nac**rite, **Dickite OXI**de), and used it to make geopolymers. For the purpose of making geopolymer concrete, he suggested that the molar ratio of Si-to-Al of the material should be about 2.0 (Table 2.1).

On the nature of the source material, it was stated that the calcined source materials, such as fly ash, slag, calcined kaolin, demonstrated a higher final compressive strength when compared to those made using non-calcined materials, for instance kaolin clay, mine tailings, and naturally occurring minerals (Barbosa, MacKenzie et al. 2000). However, Xu and van Deventer (Xu and van Deventer 2002) found that using a combination of calcined (e.g. fly ash) and non-calcined material (e.g. kaolinite or kaolin clay and albite) resulted in significant improvement in compressive strength and reduction in reaction time.

Natural Al-Si minerals have shown the potential to be the source materials for geopolymerisation, although quantitative prediction on the suitability of the specific mineral as the source material is still not available, due to the complexity of the reaction mechanisms involved (Xu and van Deventer 2000). Among the by-product materials, only fly ash and slag have been proved to be the potential source materials for making geopolymers. Fly ash is considered to be advantageous due to its high reactivity that comes from its finer particle size than slag. Moreover, low calcium fly ash is more desirable than slag for geopolymer feedstock material.

The suitability of various types of fly ash to be geopolymer source material has been studied by Fernández-Jiménez and Palomo (2003). These researchers claimed that to produce optimal binding properties, the low-calcium fly ash should have the percentage of unburned material (LOI) less than 5%, Fe<sub>2</sub>O<sub>3</sub> content should not exceed 10%, low CaO content, the content of reactive silica should be between 40-

50%, and 80-90% of particles should be smaller than 45  $\mu\text{m}$ . On the contrary, van Jaarsveld et al (2003) found that fly ash with higher amount of CaO produced higher geopolymer compressive strength, due to the formation of calcium aluminate hydrate and other calcium compounds, especially in the early ages. The other characteristics that influenced the suitability of fly ash to be a source material for geopolymers are the particle size, amorphous content, as well as morphology and the origin of fly ash.

#### **2.4.1.2 Alkaline Activators**

The most common alkaline activator used in geopolymerisation is a combination of sodium hydroxide (NaOH) or potassium hydroxide (KOH) and sodium silicate or potassium silicate (Davidovits 1999; Palomo, Grutzeck et al. 1999; Barbosa, MacKenzie et al. 2000; Xu and van Deventer 2000; Swanepoel and Strydom 2002; Xu and van Deventer 2002). The use of a single alkaline activator has been reported (Palomo, Grutzeck et al. 1999; Teixeira-Pinto, Fernandes et al. 2002),

Palomo et al (1999) concluded that the type of activator plays an important role in the polymerisation process. Reactions occur at a high rate when the alkaline activator contains soluble silicate, either sodium or potassium silicate, compared to the use of only alkaline hydroxides. Xu and van Deventer (2000) confirmed that the addition of sodium silicate solution to the sodium hydroxide solution as the alkaline activator enhanced the reaction between the source material and the solution. Furthermore, after a study of the geopolymerisation of sixteen natural Al-Si minerals, they found that generally the NaOH solution caused a higher extent of dissolution of minerals than the KOH solution.

#### **2.4.2 Mixtures Proportions**

Most of the reported works on geopolymer material to date were related to the properties of geopolymer paste or mortar, measured by using small size specimens. In addition, the complete details of the mixture compositions of the geopolymer paste were not reported.

Palomo et al (1999) studied the geopolymerisation of ASTM Class F fly ash (molar Si/Al=1.81) using four different activator solutions with the solution-to-fly ash ratio by mass of 0.25 to 0.30. The molar SiO<sub>2</sub>/K<sub>2</sub>O or SiO<sub>2</sub>/Na<sub>2</sub>O of the solutions was in the range of 0.63 to 1.23. The specimens were 10x10x60 mm in size. The best compressive strength obtained was more than 60 MPa for mixtures that used a combination of sodium hydroxide and sodium silicate activator solution, after curing the specimens for 24 hours at 65°C. Xu and van Deventer (2000) reported that the proportion of alkaline solution to alumino-silicate powder by mass should be approximately 0.33 to allow the geopolymeric reactions to occur. Alkaline solutions formed a thick gel instantaneously upon mixing with the alumino-silicate powder. The specimen size in their study was 20x20x20 mm, and the maximum compressive strength achieved was 19 MPa after 72 hours of curing at 35°C with stilbite as the source material. On the other hand, van Jaarsveld et al (1998) reported the use of the mass ratio of the solution to the powder of about 0.39. In their work, 57% fly ash was mixed with 15% kaolin or calcined kaolin, and was activated by 3.5% sodium silicate, 20% water and 4% sodium or potassium hydroxide. In this case, they used specimen size of 50x50x50 mm. The maximum compressive strength obtained was 75 MPa for the case of using fly ash and builders' waste as the source material.

Following the earlier work of Davidovits (1982) and using calcined kaolin as source material, Barbosa et al (2000) prepared seven mixture compositions of geopolymer paste for the following range of molar oxide ratios:  $0.2 < \text{Na}_2\text{O}/\text{SiO}_2 < 0.48$ ;  $3.3 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 4.5$  and  $10 < \text{H}_2\text{O}/\text{Na}_2\text{O} < 25$ . From the tests performed on the paste specimens, they found that the optimum composition occurred when the ratio of Na<sub>2</sub>O/SiO<sub>2</sub> was 0.25, the ratio of H<sub>2</sub>O/Na<sub>2</sub>O was 10.0, and the ratio of SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was 3.3. Mixtures with high water content, i.e. H<sub>2</sub>O/Na<sub>2</sub>O = 25, developed very low compressive strengths, and thus underlying the importance of water content in polymerisation. There was no information regarding the size of the specimens, while the moulds used were of a thin polyethylene film.

### **2.4.3 Fresh Geopolymers and Manufacturing Process**

Only limited information on the behaviour of the fresh geopolymers has been reported. Using metakaolin as the source material, Teixeira Pinto et al (2002) found

that the fresh geopolymer mortar became very stiff and dry while mixing, and exhibited high viscosity and cohesive nature. They suggested that the forced mixer type should be used in mixing the geopolymer materials, instead of the gravity type mixer. An increase in the mixing time increased the temperature of the fresh geopolymers, and hence reduced the workability. To improve the workability, they suggested the use of admixtures to reduce the viscosity and cohesion.

While Teixeira Pinto et al (2002) concluded that Vicat needle apparatus is not appropriate to measure the setting time of fresh geopolymer concrete, Cheng and Chiu (2003) reported the only information available to date on the quantitative measure of the setting time of geopolymer material using the Vicat needle. For the fresh geopolymer paste based on metakaolin and ground blast furnace slag, they measured the setting time of the geopolymer material both at room and elevated temperature. In the elevated temperature, the measurement was done in the oven. They found that the initial setting time was very short for geopolymers cured at 60°C, in the range of 15 to 45 minutes.

(Barbosa, MacKenzie et al. 1999) measured the viscosity of fresh metakaolin-based geopolymer paste, and reported that the viscosity of the geopolymer paste increased with time.

Most of the manufacturing process of making geopolymer paste involved dry mixing of the source materials, followed by adding the alkaline solution and then further mixing for another specified period of time (van Jaarsveld, van Deventer et al. 1998; Swanepoel and Strydom 2002; Teixeira-Pinto, Fernandes et al. 2002).

However, Cheng and Chiu (2003) reported the mixing of the KOH and metakaolin first for ten minutes. Sodium silicate and ground blast furnace slag were then added, followed by a further mixing for another five minutes. The paste samples were then cast in 50x50x50 mm cube moulds and vibrated for five minutes.

For curing, a wide range of temperatures and curing periods were used, ranging from room temperature to about 90°C, and from 1 hour to more than 24 hours. Geopolymers produced by using metakaolin have been reported to set at ambient

temperature in a short time (Davidovits 1999). However, curing temperature and curing time have been reported to play important roles in determining the properties of the geopolymer materials made from by-product materials such as fly ash. Palomo et al (1999) stated that increase in curing temperature accelerated the activation of fly ash, and resulted in higher compressive strength.

Barbosa et al (2000) elaborated the process of manufacturing geopolymers by allowing the fresh mixtures to mature in room temperature for 60 minutes, followed by curing at 65°C for 90 minutes, and then drying at 65°C.

#### **2.4.4 Factors Affecting the Properties of Geopolymers**

Several factors have been identified as important parameters affecting the properties of geopolymers. Palomo et al (1999) concluded that the curing temperature was a reaction accelerator in fly ash-based geopolymers, and significantly affected the mechanical strength, together with the curing time and the type of alkaline activator. Higher curing temperature and longer curing time were proved to result in higher compressive strength. Alkaline activator that contained soluble silicates was proved to increase the rate of reaction compared to alkaline solutions that contained only hydroxide.

Van Jaarsveld et al (2002) concluded that the water content, and the curing and calcining condition of kaolin clay affected the properties of geopolymers. However, they also stated that curing at too high temperature caused cracking and a negative effect on the properties of the material. Finally, they suggested the use of mild curing to improve the physical properties of the material. In another report, van Jaarsveld et al (2003) stated that the source materials determine the properties of geopolymers, especially the CaO content, and the water-to-fly ash ratio.

Based on a statistical study of the effect of parameters on the polymerisation process of metakaolin-based geopolymers, Barbosa et al (1999; 2000) reported the importance of the molar composition of the oxides present in the mixture and the water content. They also confirmed that the cured geopolymers showed an amorphous microstructure and exhibited low bulk densities between 1.3 and 1.9.

Based on the study of geopolymerisation of sixteen natural Si-Al minerals, Xu and van Deventer (2000) reported that factors such as the percentage of CaO, K<sub>2</sub>O, and the molar Si-to-Al ratio in the source material, the type of alkali activator, the extent of dissolution of Si, and the molar Si-to-Al ratio in solution significantly influenced the compressive strength of geopolymers.

#### **2.4.5 Geopolymer Concrete Products**

Palomo et al (2004) reported the manufacture of fly ash-based geopolymer concrete railway sleepers. They found that the geopolymer concrete structural members could easily be produced using the existing current concrete technology without any significant changes. The engineering performances of the products were excellent, and the drying shrinkage was small.

Earlier, Balaguru et al (1997; 1999) reported the use of geopolymer composites layers to strengthen concrete structures as well as geopolymer coating to protect the transportation infrastructures. They reported that geopolymer composites have been successfully applied to strengthen reinforced concrete beams. The performance of geopolymers was better than the organic polymer in terms of fire resistance, durability under ultra violet light, and did not involve any toxic.

### **3. EXPERIMENTAL PROGRAM**

#### **3.1 INTRODUCTION**

This chapter presents the details of development of the process of making fly ash-based geopolymer concrete. In 2001, very little knowledge and know-how of making of fly ash-based geopolymer concrete were available in the published literature. Due to this lack of information, the study began based on limited available literature on geopolymer pastes and mortars.

The published papers on geopolymers available at that time mostly reported the use of metakaolin or calcined kaolin as source material of geopolymer paste. Moreover, most of the information available was part of the patent literature or commercially oriented research, and many details were kept undisclosed.

Therefore, the present study adopted a rigorous trial and error process in order to develop the fly ash-based geopolymer concrete technology. The focus of the study was to identify the salient parameters that influence the mixture properties and the properties of fly ash-based geopolymer concrete.

As far as possible, the technology that is currently in use to manufacture and test ordinary Portland cement (OPC) was used. The aim of this action was to ease the promotion of this 'new' material later on to the concrete industry.

In order to simplify the development process, the compressive strength was selected as the benchmark parameter. This is not unusual because compressive strength has an intrinsic importance in the structural design of concrete structures (Neville 2000).

Although geopolymer concrete can be made using various source materials, the present study used only low calcium (ASTM Class F) fly ash. Also, as in the case of OPC, the aggregates occupy 75-80 % of the total mass of concrete. In order to



minimize the effect of the properties of the aggregates on the properties of fly ash-based geopolymer, the study used aggregates from only one source.

## **3.2 MATERIALS**

### **3.2.1 Fly Ash**

In the present experimental work, low calcium, Class F (American Society for Testing and Materials 2001) dry fly ash obtained from the silos of Collie Power Station, Western Australia, was used as the base material. Three different batches of fly ash were used; the first batch was obtained in the middle of 2001, the second batch arrived in the middle of 2003, and the last batch was obtained in 2004. The chemical compositions of the fly ash from all batches, as determined by X-Ray Fluorescence (XRF) analysis, are given in Table 3.1. The XRF analysis was carried out by the Department of Applied Chemistry, Curtin University of Technology, Perth, Australia.

It can be seen from Table 3.1, that the three batches of fly ash contained a very low percentage of carbon as indicated by the low Loss on Ignition (LOI) values. In all three batches, the molar Si-to-Al ratio was about 2, and the calcium oxide content was very low. The iron oxide ( $\text{Fe}_2\text{O}_3$ ) contents from all batches are relatively high, especially in the fly ash from Batch II. The colour of the fly ash from Batch II was therefore darker than the ashes from the other two Batches.

The particle size distributions of the fly ashes are given in Figures 3.1, 3.2 and 3.3. Both graph A and graph B show the particle size distribution of the fly ash. In these Figures, graph A shows the particle size distribution in percentage by volume in interval, while graph B shows the particle size distribution in percentage by volume passing size or cumulative. For fly ash from Batch I, 80% of the particles were smaller than 55  $\mu\text{m}$ , and the Specific Surface Area was 1.29  $\text{m}^2/\text{cc}$ . For Batch II, 80% of the particles were smaller than 39  $\mu\text{m}$ , and the Specific Surface Area was 1.94  $\text{m}^2/\text{cc}$ . For fly ash from Batch III, 80% of the particles were smaller than 46  $\mu\text{m}$ , and the Specific Surface Area was 1.52  $\text{m}^2/\text{cc}$ . The particle size distribution tests

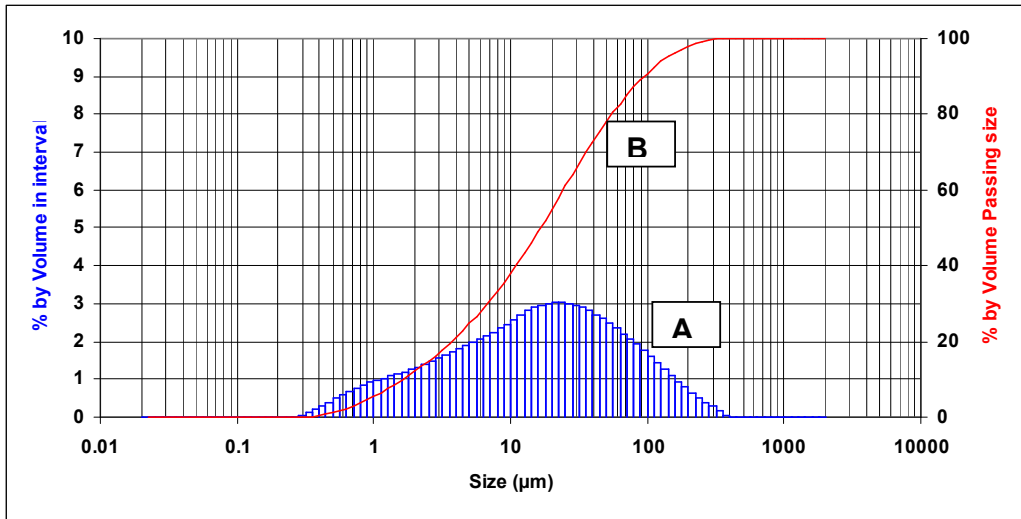
were performed using the Malvern Instruments Mastersizer MS2000, and were carried out by CSIRO Minerals, Waterford, Australia.

The Scanning Electron Microscopy (SEM) image of fly ash from Batch I is shown in Figure 3.4. As can be seen, the particle shapes of the fly ash were generally spherical.

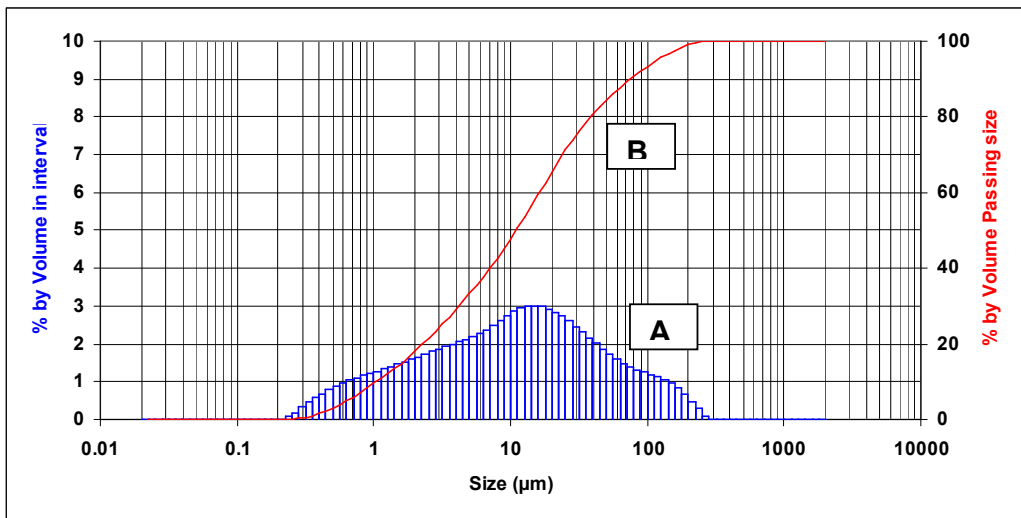
The fly ash from Batch I was used in Mixtures 1 to 4 and 13 to 15, the fly ash from Batch III was used in the mixture 5 to 8 and 22, while other Mixtures utilised the fly ash from Batch II.

**Table 3.1: Composition of Fly Ash as Determined by XRF (mass %)**

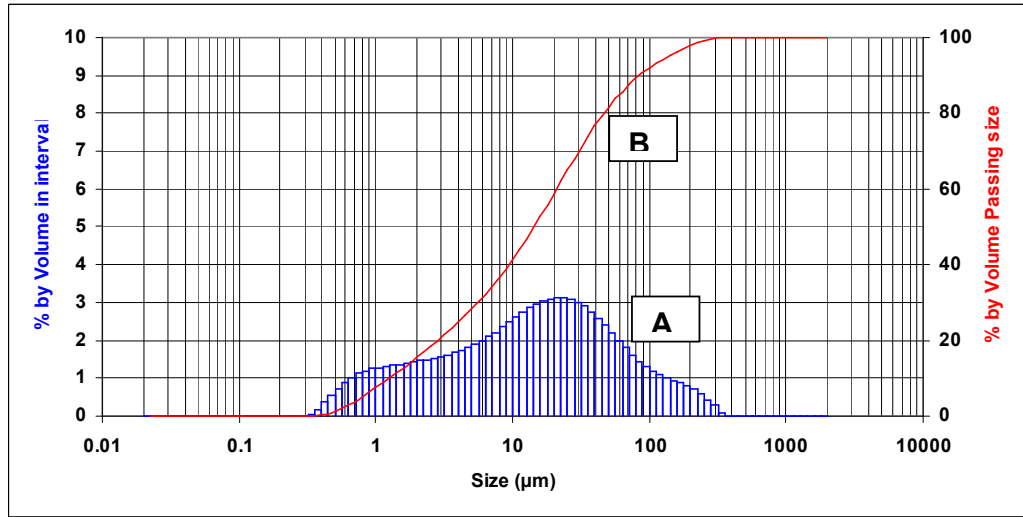
<b>Oxides</b>	<b>Batch I</b>	<b>Batch II</b>	<b>Batch III</b>
SiO <sub>2</sub>	53.36	47.80	48.00
Al <sub>2</sub> O <sub>3</sub>	26.49	24.40	29.00
Fe <sub>2</sub> O <sub>3</sub>	10.86	17.40	12.70
CaO	1.34	2.42	1.78
Na <sub>2</sub> O	0.37	0.31	0.39
K <sub>2</sub> O	0.80	0.55	0.55
TiO <sub>2</sub>	1.47	1.328	1.67
MgO	0.77	1.19	0.89
P <sub>2</sub> O <sub>5</sub>	1.43	2.00	1.69
SO <sub>3</sub>	1.70	0.29	0.50
ZrO <sub>2</sub>	-	-	0.06
Cr	-	0.01	0.016
MnO	-	0.12	0.06
LOI	1.39	1.10	1.61



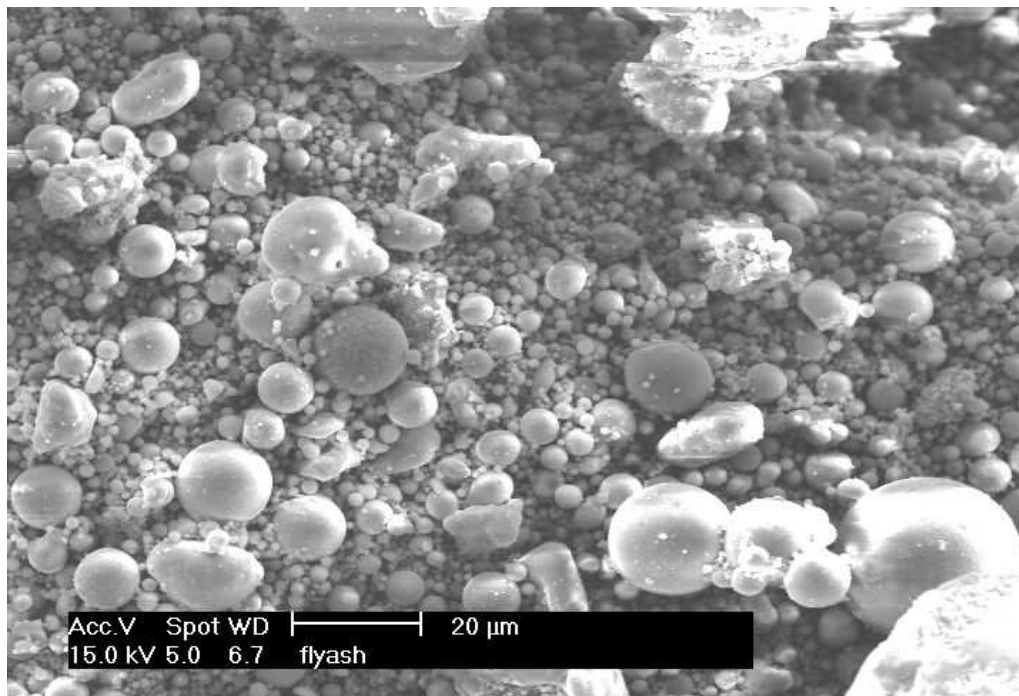
**Figure 3.1: Particle Size Distribution of Fly Ash from Batch I**



**Figure 3.2: Particle Size Distribution of Fly Ash from Batch II**



**Figure 3.3: Particle Size Distribution of Fly Ash from Batch III**



**Figure 3.4: SEM Image of Fly Ash from Batch I**

### 3.2.2 Alkaline Activators

To activate the fly ash, a combination of sodium hydroxide solution and sodium silicate solution was chosen as the alkaline activator. Sodium-based activators were

chosen because they were cheaper than Potassium-based activators. The sodium hydroxide used was either a technical grade sodium hydroxide in flakes form (3 mm), with a specific gravity of 2.130, 98% purity, and obtained from Sigma-Aldrich Pty Ltd, Australia, or a commercial grade in pellets form with 97% purity, obtained from Lomb Scientific, Australia.

The sodium hydroxide (NaOH) solution was prepared by dissolving either the flakes or the pellets in water. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, M. For instance, NaOH solution with a concentration of 8M consisted  $8 \times 40 = 320$  grams of NaOH solids (in flake or pellet form) per litre of the solution, where 40 is the molecular weight of NaOH. The mass of NaOH solids was measured as 262 grams per kg of NaOH solution of 8M concentrations. Similarly, the mass of NaOH solids per kg of the solution for other concentrations were measured as 10M: 314 grams, 12M: 361 grams, 14M: 404 grams, and 16M: 444 grams. Note that the mass of NaOH solids was only a fraction of the mass of NaOH solution, and water is the major component.

Sodium silicate solution (Vitrosol D - A53) obtained from PQ Australia was used. The chemical composition of the sodium silicate solution was  $\text{Na}_2\text{O}=14.7\%$ ,  $\text{SiO}_2=29.4\%$ , and water 55.9% by mass. The other characteristics of the sodium silicate solution were specific gravity=1.53 g/cc and viscosity at  $20^\circ\text{C}=400$  cp.

### **3.2.3 Aggregates**

Aggregates currently used by the local concrete industry in Western Australia, and supplied by BGC Concrete and Asphalt were used. Both coarse and fine aggregates were in saturated surface dry (SSD) condition, in accordance to relevant Australian Standards, AS 1141.5-2000 and AS 1141.6.1-2000 (2000; 2000). Coarse aggregates were obtained in crushed form; majority of the particles were of granite type. The fine aggregate was obtained from the sand dunes in uncrushed form.

Three different aggregate combinations were used, as given in Table 3.2, Table 3.3, and Table 3.4. All of these combinations comply with the grading requirements for

combined aggregates in accordance with the British Standard BS 882:92 (Neville 2000). The Fineness Modulus (FM) of the aggregates combination I was 5.01, while the FM of the aggregates combination II and III were 4.5 and 4.6 respectively.

**Table 3.2: Grading of Combined Aggregates I**

Sieve Size	Aggregates				Combination *)	BS 882:92
	20 mm	14 mm	7 mm	Fine		
19.00 mm	93.34	99.99	100.00	100.00	99.00	95-100
9.50 mm	3.89	17.40	99.90	100.00	69.03	
4.75 mm	0.90	2.99	20.10	100.00	37.77	35-55
2.36 mm	0.88	1.07	3.66	100.00	31.63	
1.18 mm	0.87	0.81	2.05	99.99	31.01	
600 µm	0.85	0.70	1.52	79.58	24.67	10-35
300 µm	0.75	0.59	1.08	16.53	5.57	
150 µm	0.54	0.42	0.62	1.11	0.72	0-8

\*) 15% (20 mm) + 20% (14 mm) + 35% (7 mm) + 30% (Fine)

**Table 3.3: Grading of Combined Aggregates II**

Sieve Size	Aggregates			Combination *)	BS 882:92
	10 mm	7 mm	Fine		
19.00 mm	100.00	100.00	100.00	100.00	95-100
9.50 mm	74.86	99.99	100.00	92.42	
4.75 mm	9.32	20.10	100.00	44.83	35-55
2.36 mm	3.68	3.66	100.00	37.39	
1.18 mm	2.08	2.05	100.00	36.34	
600 µm	1.47	1.52	79.60	28.83	10-35
300 µm	1.01	1.08	16.50	6.47	
150 µm	0.55	0.62	1.11	0.77	0-8

\*) 30% (10 mm) + 35% (7 mm) + 35% (Fine)

**Table 3.4: Grading of Combined Aggregates III**

Sieve Size	Aggregates		Combination *)	BS 882:92
	7 mm	Fine		
19.00 mm	100.00	100.00	100.00	95-100
9.50 mm	99.99	100.00	99.93	
4.75 mm	20.10	100.00	44.07	35-55
2.36 mm	3.66	100.00	32.56	
1.18 mm	2.05	100.00	31.43	
600 µm	1.52	79.60	24.94	10-35
300 µm	1.08	16.50	5.72	
150 µm	0.62	1.11	0.77	0-8

\*) 70% (7 mm) + 30% (Fine)

### **3.2.4 Super plasticiser**

To improve the workability of the fresh geopolymer concrete, a naphthalene sulphonate super plasticiser in liquid form, supplied by Master Builders Technologies, Perth, Australia, under the brand name of Rheobuild 1000, was used in nearly all cases.

Another type of super plasticiser, a polycarboxylic ether hyperplasticiser in liquid form, under the brand name of Glenium 27, supplied by Master Builders Technologies, Perth, Australia, was also tried. However, this type of super plasticiser was not used due to the cost.

### **3.3 PRELIMINARY LABORATORY WORK**

In the beginning, numerous trial mixtures of geopolymer concrete were manufactured, and test specimens in the form of 75x75x75 mm cubes or 100x200 mm cylinders were made. Initially, the mixing was done in a Hobart mixer. However, this was considered to be not practical in large applications. Therefore, the

mixing changed to an eighty litre capacity pan mixer with rotating drum available in the concrete laboratory for making OPC concrete. The details of the preliminary mixtures can be seen in Appendix A.

The main objectives of the preliminary laboratory work were:

- to familiarize with the making of fly ash-based geopolymer concrete;
- to understand the effect of the sequence of adding the alkaline activator to the solids constituents in the mixer;
- to observe the behaviour of the fresh fly ash-based geopolymer concrete;
- to develop the process of mixing and the curing regime; and
- to understand the basic mixture proportioning of fly ash-based geopolymer concrete.

The preliminary laboratory work revealed the following:

### **3.3.1 Mixing**

It was found that the fresh fly ash-based geopolymer concrete was dark in colour (due to the dark colour of the fly ash), and was cohesive. The amount of water in the mixture played an important role on the behaviour of fresh concrete. When the mixing time was long, mixtures with high water content bled and segregation of aggregates and the paste occurred. This phenomenon was usually followed by low compressive strength result of hardened concrete.

Communication with Davidovits (2002), suggested that it is preferable to mix the sodium silicate solution and sodium hydroxide solution before adding it to the solid constituents. He also suggested that the sodium silicate liquid obtained from the market usually is in the form of a dimer or a trimer, instead of a monomer, and mixing it together with the sodium hydroxide solution assists the polymerisation process. When this suggestion was followed, it was found that the occurrence of bleeding and segregation ceased.



The effects of water content in the mixture and the mixing time were identified as test parameters in the detailed study (see Chapter 4). From the preliminary work, it was decided to observe the following standard process of mixing in all further studies.

- Mix sodium hydroxide solution and sodium silicate solution together prior to adding to the dry materials.
- Mix all dry materials in the pan mixer for about three minutes. Add the liquid component of the mixture at the end of dry mixing, and continue the wet mixing for another four minutes.

### **3.3.2 Curing**

Geopolymer concrete specimens should be wrapped during curing at elevated temperatures in a dry environment (in the oven) to prevent excessive evaporation. Unlike the small geopolymer paste specimens, which can easily be wrapped by placing a lid on the mould, a suitable method was needed for large size geopolymer concrete specimens. Extensive trials revealed wrapping of concrete specimens by using vacuum bagging film is effective for temperatures up to 100°C for several days of curing. To tighten the film to the concrete moulds, a quick lock seal (Figure 3.5) or a twist tie wire (Figure 3.6) was utilized. The latter was used in all further experimental work due to its simplicity and economics.

Preliminary tests also revealed that fly ash-based geopolymer concrete did not set immediately at room temperature. When the room temperature was less than 30°C, the setting did not occur at least for 24 hours. Also, the handling time is a more appropriate parameter (rather than setting time used in the case of OPC concrete) for fly ash-based geopolymer concrete.



**Figure 3.5: Wrapping of Concrete Specimens before Curing (1)**



**Figure 3.6: Wrapping Concrete Specimens Before Curing (2)**

### 3.4 MIXTURE PROPORTION

Based on the limited past research on geopolymer pastes available in the literature (Chapter 2) and the experience gained during the preliminary experimental work (Section 3.3), the following ranges were selected for the constituents of the mixtures used in further studies described in Chapter 4.

- Low calcium (ASTM Class F) fly ash as given in Section 3.2.1.
- Alkaline activators as given in Section 3.2.2.
  - Ratio of sodium silicate solution-to-sodium hydroxide solution, by mass, of 0.4 to 2.5. This ratio was fixed at 2.5 for most of the mixtures because the sodium silicate solution is considerably cheaper than the sodium hydroxide solution.
  - Molarity of sodium hydroxide (NaOH) solution in the range of 8M to 16M.
  - Ratio of activator solution-to-fly ash, by mass, in the range of 0.3 and 0.40.
- Coarse and fine aggregates as given in Section 3.2.3, of approximately 75% to 80%, of the entire mixture by mass. This value is similar to that used in OPC concrete.
- Super plasticiser, as given in Section 3.2.4, in the range of 0% to 2% of fly ash, by mass.
- Extra water, when added, in mass.

### 3.5 MIXING, CASTING AND CURING

For mixing, rotating pan mixer of 80 litres capacity with fixed blades was used (Fig. 3.7). The aggregates were prepared in saturated surface dry condition, and were kept in plastic buckets with lid (Figure 3.8).



**Figure 3.7: Pan Mixer Used for Manufacturing Geopolymer Concrete**



**Figure 3.8: Dry Materials for Making Geopolymer Concrete**



**Figure 3.9: Addition of Liquid Component**



**Figure 3.10: Fresh Fly Ash Geopolymer Concrete Ready for Placing**

The solids constituents of the fly ash-based geopolymer concrete, i.e. the aggregates and the fly ash, were dry mixed in the pan mixer for about three minutes. The liquid part of the mixtures, i.e. the sodium silicate solution, the sodium hydroxide solution, added water (if any), and the super plasticiser (if any), were premixed then added to the solids (Figure 3.9). The wet mixing usually continued for another four minutes.

The fresh fly ash-based geopolymer concrete was dark in colour and shiny in appearance (Figure 3.10). The mixtures were usually very cohesive. The workability of the fresh concrete was measured by means of the conventional slump test (Figure 3.11).

Compaction of fresh concrete in the cylinder steel moulds was achieved by applying sixty manual strokes per layer in three equal layers (Figure 3.12), followed by compaction on a vibration table for ten seconds. After casting, the specimens were covered using vacuum bagging film.



**Figure 3.11: Slump Measurement of Fresh Concrete**



**Figure 3.12: Compaction into Moulds**



**Figure 3.13: Steam Boiler and Controls**



**Figure 3.14: Specimens in Steam Curing Chamber**



**Figure 3.15: Steam Curing in Progress**



Curing at elevated temperatures was done in two different ways, i.e. dry curing in the laboratory oven or steam curing in a chamber. A boiler was used to generate the steam at a specified temperature (Figure 3.13). Figures 3.14 and 3.15 show curing process in the steam curing chamber.

### **3.6 COMPRESSIVE AND TENSILE STRENGTH TESTS**

The compressive and tensile strength tests on hardened fly ash-based geopolymer concrete were performed on a 2000 kN capacity Farnell hydraulic testing machine in accordance to the relevant Australian Standards (1999; 2000). Five 100x200 mm concrete cylinders were tested for every compressive strength test. Three 150x300 mm concrete cylinders were tested for each tensile splitting strength test. The results given in the various Figures and Tables are the mean of these values.

## **4. EXPERIMENTAL RESULTS AND DISCUSSION**

### **4.1 INTRODUCTION**

In this Chapter, the experimental results are presented and discussed. Each of the compressive strength test data points plotted in various graphs or stated in various Tables corresponds to the mean value of the compressive strengths of five test concrete cylinders in a series. The standard deviations are plotted on the test data points as the error bar.

In Section 4.2 of the Chapter, the effects of various salient parameters on the compressive strength of fly ash-based geopolymer concrete are discussed. The parameters considered are as follows:

1. Ratio of activator liquid-to-fly ash, by mass
2. Concentration of sodium hydroxide (NaOH) solution, in Molar
3. Ratio of sodium silicate solution-to-sodium hydroxide solution, by mass
4. Curing temperature
5. Curing time
6. Handling time
7. Addition of super plasticiser
8. Rest period prior to curing
9. Water content of mixture
10. Dry curing versus steam curing
11. Mixing Time
12. Age of concrete

In all cases, low calcium (ASTM Class F) fly ash from Batch I, Batch II or Batch III (Section 3.2.1) was used. The mass of aggregates (Section 3.2.3) was approximately 75 to 80 percent of the mass of the entire mixture.

Section 4.3 of the Chapter presents the measured elastic constants, while Section 4.4 describes the stress-strain relations in compression for different grades of fly ash-based geopolymer concrete. Section 4.5 and 4.6 report the indirect tensile strength and the density of the fly ash-based geopolymer concrete respectively.

Temperature history during curing at elevated temperature was measured, and the results are reported in Section 4.7. The Chapter ends with Section 4.8, where a mixture design process for fly ash-based geopolymer concrete is proposed.

In all, twenty-six different Mixtures were made to study the effect of various parameters. The details of these Mixtures are given in Table 4.1 and Table 4.2, and the properties of the Mixtures are presented in Tables 4.3 to 4.8.

In Tables 4.1 and 4.2, the mass of each component of a Mixture is given in terms of kg per cubic metre of concrete.

**Table 4.1: Details of Mixtures 1 to 13**

Mixture No	Aggregate					Fly Ash (kg)	NaOH Solution		Sodium Silicate (kg)	Added Water (kg)	Super-plasticiser (kg)
	20 mm (kg)	14 mm (kg)	10 mm (kg)	7 mm (kg)	Fine Sand (kg)		Mass (kg)	Molarity			
1	277	370	-	647	554	476 <sup>a)</sup>	120	8M <sup>*)</sup>	48	-	-
2	277	370	-	647	554	476 <sup>a)</sup>	48	8M <sup>*)</sup>	120	-	-
3	277	370	-	647	554	476 <sup>a)</sup>	120	14M <sup>*)</sup>	48	-	-
4	277	370	-	647	554	476 <sup>a)</sup>	48	14M <sup>*)</sup>	120	-	-
5	-	-	-	1294	554	408 <sup>c)</sup>	51.5	14M <sup>**)</sup>	103	16.5 <sup>x)</sup>	-
6	-	-	-	1294	554	408 <sup>c)</sup>	51.5	14M <sup>**)</sup>	103	16.5 <sup>x)</sup>	4.1
7	-	-	-	1294	554	408 <sup>c)</sup>	51.5	14M <sup>**)</sup>	103	16.5 <sup>x)</sup>	8.2
8	-	-	-	1294	554	408 <sup>c)</sup>	51.5	14M <sup>**)</sup>	103	16.5 <sup>x)</sup>	16.3
9	-	-	554	647	647	408 <sup>b)</sup>	41	12M <sup>**)</sup>	103	14.3 <sup>y)</sup>	6.1
10	-	-	554	647	647	408 <sup>b)</sup>	41	14M <sup>**)</sup>	103	17.6 <sup>y)</sup>	6.1
11	-	-	554	647	647	408 <sup>b)</sup>	41	12M <sup>*)</sup>	103	14.3 <sup>y)</sup>	6.1
12	-	-	554	647	647	408 <sup>b)</sup>	41	8M <sup>*)</sup>	103	-	6.1
13	277	370	-	647	554	408 <sup>a)</sup>	41	14M <sup>*)</sup>	103	-	8.2

Note:

<sup>\*)</sup> Technical Grade  
<sup>\*\*)</sup> Commercial Grade

<sup>a)</sup> Fly Ash: Batch I  
<sup>b)</sup> Fly Ash: Batch II  
<sup>c)</sup> Fly Ash: Batch III

<sup>x)</sup> Tap water  
<sup>y)</sup> Distilled water

Table 4.2: Details of Mixtures 14 to 26

Mixture No	Aggregate					Fly Ash (kg)	NaOH Solution		Sodium Silicate (kg)	Added Water (kg)	Super-plasticiser (kg)
	20 mm (kg)	14 mm (kg)	10 mm (kg)	7 mm (kg)	Fine Sand (kg)		Mass (kg)	Molarity			
14	277	370	-	647	554	408 <sup>a)</sup>	41	14M <sup>*)</sup>	103	10.7 <sup>y)</sup>	8.2
15	277	370	-	647	554	408 <sup>a)</sup>	41	14M <sup>*)</sup>	103	21.3 <sup>y)</sup>	8.2
16	-	-	554	647	647	408 <sup>b)</sup>	41	8M <sup>*)</sup>	103	-	6.1
17	-	-	554	647	647	408 <sup>b)</sup>	41	10M <sup>*)</sup>	103	7.5 <sup>y)</sup>	6.1
18	-	-	554	647	647	408 <sup>b)</sup>	41	12M <sup>*)</sup>	103	14.4 <sup>y)</sup>	6.1
19	-	-	554	647	647	408 <sup>b)</sup>	41	14M <sup>*)</sup>	103	20.7 <sup>y)</sup>	6.1
20	-	-	554	647	647	408 <sup>b)</sup>	41	16M <sup>*)</sup>	103	26.5 <sup>y)</sup>	6.1
21	-	-	554	647	647	408 <sup>b)</sup>	41	14M <sup>**)</sup>	103	20.7 <sup>y)</sup>	6.1
22	-	-	-	1294	554	408 <sup>c)</sup>	41	14M <sup>**)</sup>	103	16.5 <sup>x)</sup>	6.1
23	-	-	554	647	647	408 <sup>b)</sup>	41	14M <sup>*)</sup>	103	-	8.2
24	-	-	554	647	647	408 <sup>b)</sup>	41	8M <sup>*)</sup>	103	-	6.1
25	-	-	554	647	647	408 <sup>b)</sup>	55.4	8M <sup>*)</sup>	103	-	6.1
26	-	-	554	647	647	408 <sup>b)</sup>	55.4	8M <sup>*)</sup>	103	-	6.1

Note:

<sup>\*)</sup> Technical Grade  
<sup>\*\*)</sup> Commercial Grade

<sup>a)</sup> Fly Ash: Batch I  
<sup>b)</sup> Fly Ash: Batch II  
<sup>c)</sup> Fly Ash: Batch III

<sup>x)</sup> Tap water  
<sup>y)</sup> Distilled water

**Table 4.3: Properties of Mixtures 1 to 9**

Mixture No	Curing			Age at Test (days)	Slump (mm)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Features
	Time (hours)	Temp. (°C)	Method						
1	24	60	Oven	7	na	2365	17	0.91	-
2	4	30	Oven	7	na	2376	8	0.27	-
	4	60	Oven	7	na	2378	24	0.47	-
	4	90	Oven	7	na	2341	37	4.39	-
	24	30	Oven	7	na	2364	20	1.13	-
3	24	60	Oven	7	na	2377	57	2.51	-
	24	90	Oven	7	na	2341	66	5.46	-
	24	60	Oven	7	na	2386	48	1.62	-
	48	30	Oven	7	na	2367	49	1.6	-
4	4	60	Oven	7	na	2320	25	2.57	-
	4	90	Oven	7	na	2376	30	3.71	-
	24	30	Oven	7	na	2367	29	1.46	-
	24	60	Oven	7	na	2386	68	4.09	-
	24	90	Oven	7	na	2385	70	2.68	-
	24	60	Steam	3	39	2340	42	0.8	Superplasticiser 0%
5	24	60	Steam	3	59	2375	41	0.5	Superplasticiser 1%
6	24	60	Steam	3	80	2347	41	2.7	Superplasticiser 2%
7	24	60	Steam	3	93	2336	36	1.3	Superplasticiser 4%
9	24	60	Steam	7	209	-	40	2.9	Rest Period = 0 day
	24	60	Steam	7	209	-	41	2.1	Rest Period = 1 day
	24	60	Steam	7	209	-	48	1.9	Rest Period = 2 days
	24	60	Steam	7	209	-	50	1.2	Rest Period = 3 days
	24	60	Steam	7	209	-	49	1.8	Rest Period = 4 days

**Table 4.4: Properties of Mixtures 10 to 13**

Mixture No	Curing			Age at Test (days)	Slump (mm)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Features
	Time (hours)	Temp. (°C)	Method						
10	24	60	Steam	7	215	2298	43	1.1	Rest Period = 0 day
	24	60	Steam	7	215	2299	53	1.5	Rest Period = 1 day
	24	60	Steam	7	215	2298	56	1.3	Rest Period = 2 days
	24	60	Steam	7	215	2305	57	2.3	Rest Period = 3 days
	24	60	Steam	7	215	2306	57	1.6	Rest Period = 4 days
	24	60	Steam	7	215	2303	58	5.0	Rest Period = 5 days
11	24	60	Steam	7	225	2305	38	2.8	Rest Period = 0 day
	24	60	Steam	7	225	2309	53	2.2	Rest Period = 1 day
	24	60	Steam	7	225	2314	56	1.9	Rest Period = 2 days
	24	60	Steam	7	225	2318	59	2.5	Rest Period = 3 days
	24	60	Steam	7	225	2318	59	2.3	Rest Period = 4 days
	24	60	Steam	7	225	2314	59	3.0	Rest Period = 5 days
12	24	60	Oven	7	60	2357	63	4.2	Rest Period = 0 day
	24	60	Oven	7	60	2364	74	4.1	Rest Period = 1 day
	24	60	Oven	7	60	2363	73	2.7	Rest Period = 2 days
	24	60	Oven	7	60	2361	76	3.5	Rest Period = 3 days
	24	60	Oven	7	60	2369	75	3.2	Rest Period = 4 days
	24	60	Oven	7	60	2368	77	5.3	Rest Period = 5 days
13	24	30	Oven	7	na	2387	44	0.51	H <sub>2</sub> O/Na <sub>2</sub> O=10.00
	24	45	Oven	7	na	2377	55	1.69	
	24	60	Oven	7	na	2375	59	2.52	
	24	75	Oven	7	na	2375	65	4.81	
	24	90	Oven	7	na	2376	71	4.69	

**Table 4.5: Details of Mixtures 14 to 20**

Mixture No	Curing			Age at Test (days)	Slump (mm)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Features
	Time (hours)	Temp. (°C)	Method						
14	24	30	Oven	7	na	2338	35	1.79	H <sub>2</sub> O/Na <sub>2</sub> O=11.25
	24	45	Oven	7	na	2336	42	4.17	
	24	60	Oven	7	na	na	na	na	
	24	75	Oven	7	na	2337	60	2.04	
	24	90	Oven	7	na	2334	59	3.13	
15	24	30	Oven	7	na	2326	32	1.02	H <sub>2</sub> O/Na <sub>2</sub> O=12.50
	24	45	Oven	7	na	2322	37	0.73	
	24	60	Oven	7	na	2321	44	2.49	
	24	75	Oven	7	na	2301	44	0.63	
	24	90	Oven	7	na	2318	44	3.35	
16	24	60	Oven	7	32	2381	55	1.50	Na <sub>2</sub> O/SiO <sub>2</sub> =0.097
	24	60	Steam	7	32	2385	47	1.24	
17	24	60	Oven	7	113	2352	53	3.00	Na <sub>2</sub> O/SiO <sub>2</sub> =0.103
	24	60	Steam	7	113	2362	45	0.82	
18	24	60	Oven	7	162	2361	51	1.70	Na <sub>2</sub> O/SiO <sub>2</sub> =0.109
	24	60	Steam	7	162	2364	42	1.55	
19	24	60	Oven	7	214	2343	45	2.17	Na <sub>2</sub> O/SiO <sub>2</sub> =0.115
	24	60	Steam	7	214	2341	40	1.16	
20	24	60	Oven	7	240	2341	47	1.93	Na <sub>2</sub> O/SiO <sub>2</sub> =0.120
	24	60	Steam	7	240	2342	40	2.30	



**Table 4.6: Properties of Mixtures 21 to 26**

Mixture No	Curing			Age at Test (days)	Slump (mm)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Features
	Time (hours)	Temp. (°C)	Method						
21	24	60	Steam	21	234	2345	37	1.44	Mixing time 2 min
	24	60	Steam	21	234	2367	40	1.92	Mixing time 4 min
	24	60	Steam	21	226	2373	45	3.36	Mixing time 6 min
	24	60	Steam	21	219	2378	45	3.06	Mixing time 8 min
	24	60	Steam	21	219	2387	47	0.25	Mixing time 10 min
	24	60	Steam	21	206	2397	49	2.08	Mixing time 13 min
	24	60	Steam	21	206	2399	52	1.01	Mixing time 16 min
22 a	4	90	Steam	3	91	2331	40	0.78	Mixing time 4 min
b	4	90	Steam	3	67	2344	47	1.24	Mixing time 8 min
c	4	90	Steam	3	49	2368	56	4.28	Mixing time 16 min
23	24	90	Oven	90	46	-	89	4.45	
24	24	90	Oven	90	135	-	68	4.56	
25	24	60	Oven	90	207	-	55	1.80	
26	24	60	Steam	90	219	-	44	1.20	

**Table 4.7: Data from Additional Studies for Mixture 2 (1)**

Super-plasticiser (kg)	Curing			Age at Test (days)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Feature/s
	Time (hours)	Temp. (°C)	Method					
-	24	60	Oven	3	2404	61	5.49	Age at test 3 days
-	24	60	Oven	7	2401	58	4	Age at test 7 days
-	24	60	Oven	14	2387	64	3.65	Age at test 14 days
-	24	60	Oven	28	2373	60	5.16	Age at test 28 days
-	24	60	Oven	56	2362	61	1.95	Age at test 56 days
-	24	60	Oven	91	2362	63	3.02	Age at test 91 days
-	4	60	Oven	7	2396	25	0.46	Curing time 4 hrs
-	8	60	Oven	7	2398	31	3.67	Curing time 8 hrs
-	12	60	Oven	7	2394	41	2.31	Curing time 12 hrs
-	24	60	Oven	7	2391	61	5.52	Curing time 16 hrs
-	48	60	Oven	7	2387	72	10.03	Curing time 24 hrs
-	72	60	Oven	7	2403	77	2.7	Curing time 72 hrs
-	96	60	Oven	7	2400	82	6.2	Curing time 96 hrs
4.1	24	60	Oven	7	2379	56	1.86	Superplasticiser 1.0%, No Rest Period
6.1	24	60	Oven	7	2374	58	3.02	Superplasticiser 1.5%, No Rest Period
8.2	24	60	Oven	7	2362	57	2.33	Superplasticiser 2.0%, No Rest Period
10.2	24	60	Oven	7	2354	50	3.28	Superplasticiser 2.5%, No Rest Period
12.2	24	60	Oven	7	2364	50	0.76	Superplasticiser 3.0%, No Rest Period
14.3	24	60	Oven	7	2335	46	2.82	Superplasticiser 3.5%, No Rest Period
4.1	24	60	Oven	7	2379	56	1.86	Superplasticiser 1.0%, 1 hr Rest Period
6.1	24	60	Oven	7	2374	58	3.02	Superplasticiser 1.5%, 1 hr Rest Period
8.2	24	60	Oven	7	2362	57	2.33	Superplasticiser 2.0%, 1 hr Rest Period

**Table 4.8: Data from Additional Studies for Mixture 2 (2)**

Super-plasticiser (kg)	Curing			Age at Test (days)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Feature/s
	Time (hours)	Temp. (°C)	Method					
10.2	24	60	Oven	7	2354	50	3.28	Superplasticiser 2.5%, 1 hr Rest Period
12.2	24	60	Oven	7	2364	50	0.76	Superplasticiser 3.0%, 1 hr Rest Period
14.3	24	60	Oven	7	2335	46	2.82	Superplasticiser 3.5%, 1 hr Rest Period
6.1	24	60	Oven	7	2363	59	2.32	Handling time = 0 Mnts
6.1	24	60	Oven	7	2376	59	2.36	Handling time = 30 Mnts
6.1	24	60	Oven	7	2365	61	4.26	Handling time = 45 Mnts
6.1	24	60	Oven	7	2366	65	1.46	Handling time = 60 Mnts
6.1	24	60	Oven	7	2374	64	1.49	Handling time = 75 Mnts
6.1	24	60	Oven	7	2370	65	1.15	Handling time = 90 Mnts
6.1	24	60	Oven	7	2370	62	4.06	Handling time = 120 Mnts
6.1	24	30	Oven	7	-	35	1.22	Curing Temperature = 30 °C
6.1	24	45	Oven	7	-	41	2.11	Curing Temperature = 45 °C
6.1	24	60	Oven	7	-	63	1.17	Curing Temperature = 60 °C
6.1	24	75	Oven	7	-	64	3.42	Curing Temperature = 75 °C
6.1	24	90	Oven	7	-	63	3.75	Curing Temperature = 90 °C
6.1	6	45	Oven	7	2378	33	1.01	Curing Temperature = 45 °C
6.1	6	60	Oven	7	2386	42	1.07	Curing Temperature = 60 °C
6.1	6	75	Oven	7	2383	48	2.68	Curing Temperature = 75 °C
6.1	6	90	Oven	7	2369	51	2.73	Curing Temperature = 90 °C
4.1 <sup>1)</sup>	24	60	Oven	7	2388	61	4.08	Rest Period 1 hr
4.1 <sup>1)</sup>	24	60	Oven	7	2393	61	3.84	No Rest Period

<sup>1)</sup> Polycarboxylic ether hyperplasticiser

## 4.2 EFFECT OF SALIENT PARAMETERS

### 4.2.1 Ratio of Activator Liquid-to-Fly Ash

The ratio of activator liquid-to-fly ash, by mass, was not varied. This ratio remained approximately around 0.35.

### 4.2.2 Concentration of Sodium Hydroxide (NaOH) Solution

Mixtures 1 to 4 (Table 4.1) were made to study the effect of concentration of sodium hydroxide solution on the compressive strength of concrete. Complete details of these mixtures and their properties are given in Tables 4.1 and 4.3. The test cylinders were left at ambient conditions for about 30 minutes prior to start of dry curing in an oven. The curing time was 24 hours at various temperatures. The measured 7<sup>th</sup> day compressive strengths of test cylinders are given in Table 4.9.

**Table 4.9: Mixtures 1 to 4**

Mixture	Concentration of NaOH liquid (in Molars)	Ratio of sodium silicate to NaOH solution (by mass)	Compressive strength at 7 <sup>th</sup> day (MPa)
			Cured for 24 hours at 60°C
1	8M	0.4	17
2	8M	2.5	57
3	14M	0.4	48
4	14M	2.5	67

In Table 4.9, the difference between Mixture 1 and Mixture 3 is the concentration of NaOH solution in terms of Molar (second column). Mixture 3 with a higher concentration of NaOH solution yielded higher compressive strength than Mixture 1. A similar trend is also observed for the Mixtures 2 and 4.

### **4.2.3 Ratio of Sodium Silicate Solution-to-Sodium Hydroxide Solution**

The effect of sodium silicate solution-to-NaOH solution by mass on compressive strength of concrete can be seen by comparing the results of Mixtures 1 and 2 as well as Mixtures 3 and 4 in Table 4.9. For Mixtures 1 and 2, although the concentration of NaOH solution (in terms of Molarity) is the same, in Mixture 2 the sodium silicate solution-to-NaOH solution ratio is higher than that of Mixture 1. This change increased the compressive strength of Mixture 2. A similar trend is also observed in the results of Mixture 3 and Mixture 4; the compressive strength of Mixture 4 is higher than that of Mixture 3. The results given in Table 4.9 reveal that the interrelation of various oxides contained in the mixture composition affects the compressive strength.

Mixtures 2 and 4, with sodium silicate solution-to-NaOH solution ratio by mass of 2.5 were selected as the basic mixtures to study the effect of other parameters for two reasons. Firstly, the cost of activator liquid is economical when the ratio of sodium silicate solution-to-NaOH solution is 2.5 (rather than 0.4). Secondly, the test results were remarkably consistent when this ratio was 2.5.

### **4.2.4 Curing Temperature**

Figure 4.1 shows the effect of curing temperature on the compressive strength for Mixture 2 and Mixture 4 after dry curing the test cylinders in an oven for 24 hours. All other test variables were held constant. Higher curing temperature resulted in larger compressive strength, although an increase in the curing temperature beyond 60°C did not increase the compressive strength substantially.

Figure 4.2 presents further results. Five different curing temperatures were used, i.e. 30°C, 45°C, 60°C, 75°C, and 90°C. Curing was performed in an oven for 24 hours in the case of Mixture 2 and 4, and 6 hours for Mixture 2 only. The results shown in Table 4.8 and Figure 4.2 confirm that higher curing temperature resulted in higher compressive strength, for both 6 hours and 24 hours of curing.

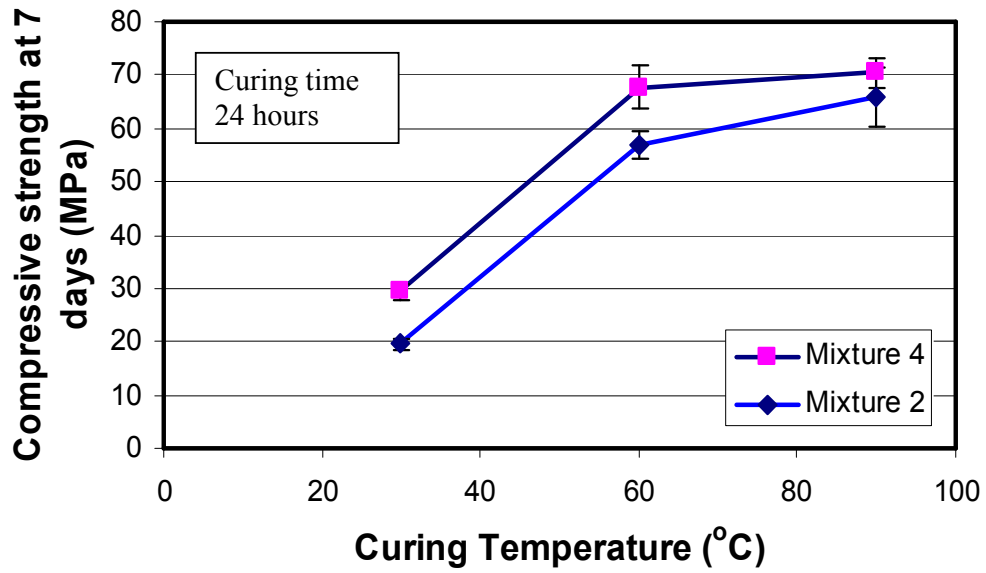


Figure 4.1: Effect of Curing Temperature on Compressive Strength (1)

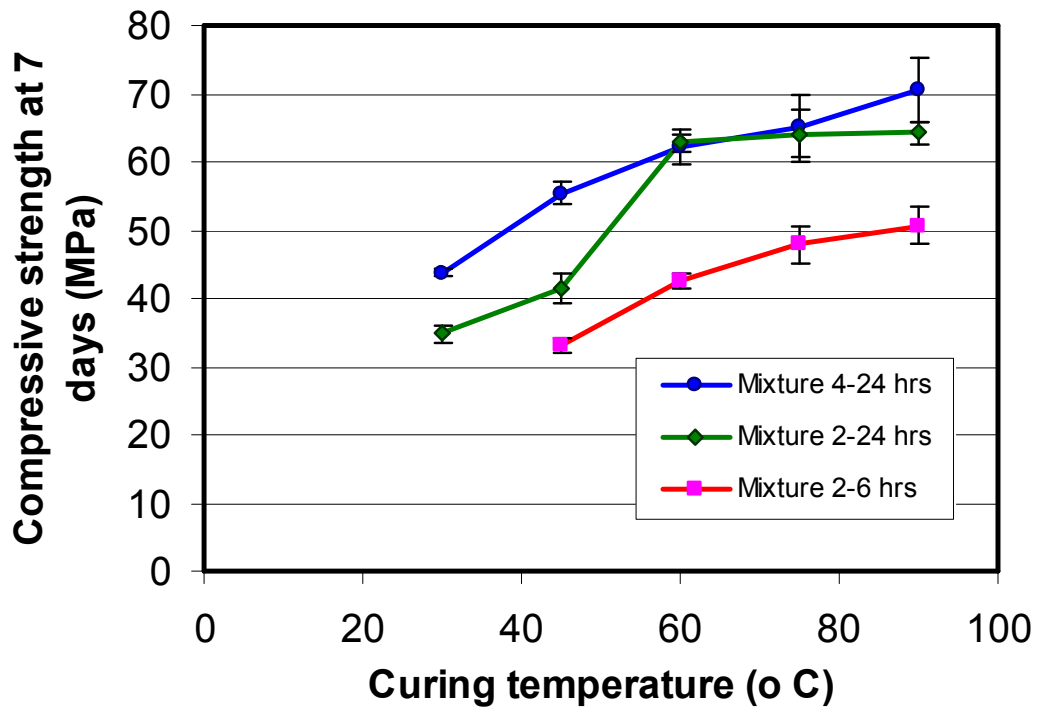
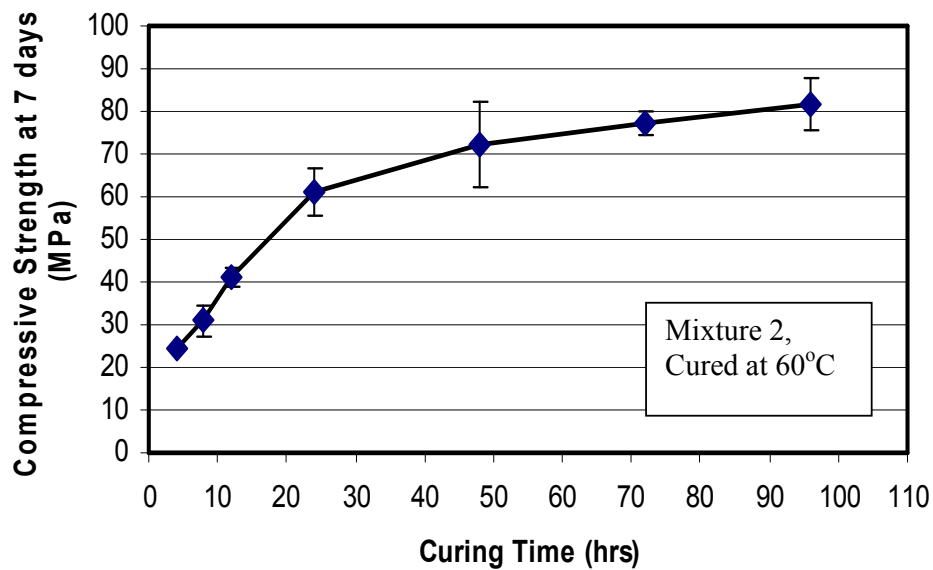


Figure 4.2: Effect of Curing Temperature on Compressive Strength (2)

#### 4.2.5 Curing Time

In order to investigate the effect of curing time, tests were prepared using Mixture 2. The test cylinders were cured for various curing periods from 4 hours to 96 hours (4 days). Table 4.7 and Figure 4.3 show the results of these tests cured at 60°C. Longer curing time improved the polymerisation process resulting in higher compressive strength. The rate of increase in strength was rapid up to 24 hours of curing time. The results indicate that longer curing time did not produce weaker material as claimed by van Jaarsveld et al (2002).



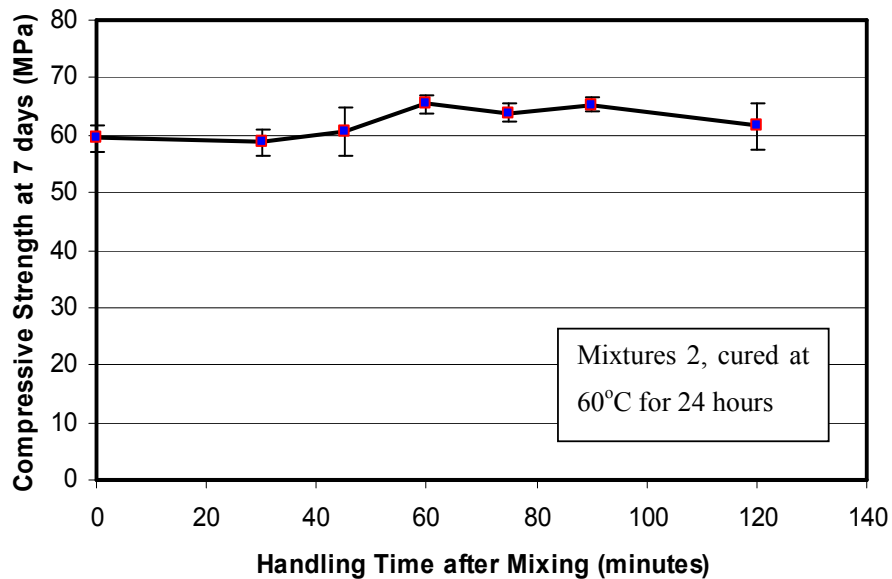
**Figure 4.3: Influence of Curing Time on Compressive Strength for Mixture 2**

#### 4.2.6 Handling Time

Due to lack of a suitable method to determine the initial setting time of geopolymer concrete, the setting time of the fresh concrete could not be measured.

In order to establish how long the fly ash-based geopolymer concrete could be handled without any degradation in compressive strength, a series of tests were performed. For these tests, Mixture 2 was used. After mixing, the geopolymer

concrete was left in the pan mixer for various periods of time ranging from 0 to 120 minutes. These periods were identified as ‘Handling Time’. At the end of the ‘handling time’, cylinder specimens were cast. The test cylinders were cured for 24 hours at 60°C. The test results are plotted in Figure 4.4. In Figure 4.4, the ‘handling time’ of zero minute mean that the test cylinders were cast immediately after mixing, whereas the handling time of, say 120 minutes, indicates that the fresh concrete was handled and placed in the moulds only after 120 minutes. The test results shown in Figure 4.4 as well as the laboratory experience showed that the fresh fly ash-based geopolymer concrete could be handled up to 120 minutes after mixing without any sign of setting and without any degradation in the compressive strength.



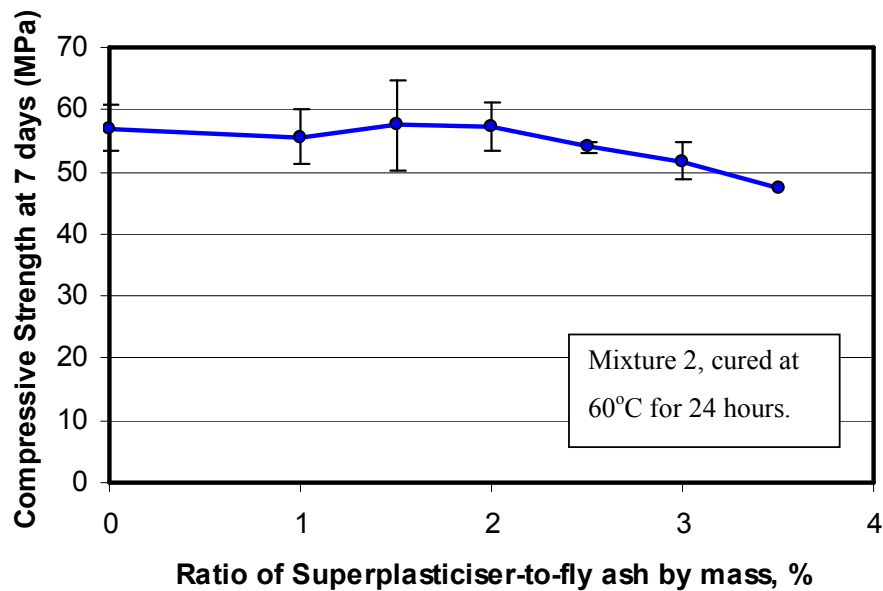
**Figure 4.4: Influence of Handling Time on Compressive Strength for Mixture 2**

#### 4.2.7 Addition of Superplasticiser

In fresh state, the geopolymer concrete has a stiff consistency. Although adequate compaction was achievable, an improvement in the workability was considered as desirable. A series of mixtures were prepared to investigate the possibility of using the new generation polycarboxylic ether hyper plasticiser. However, this type of



super plasticiser did not show any significant difference in the workability of the fresh fly ash-based geopolymer concrete.

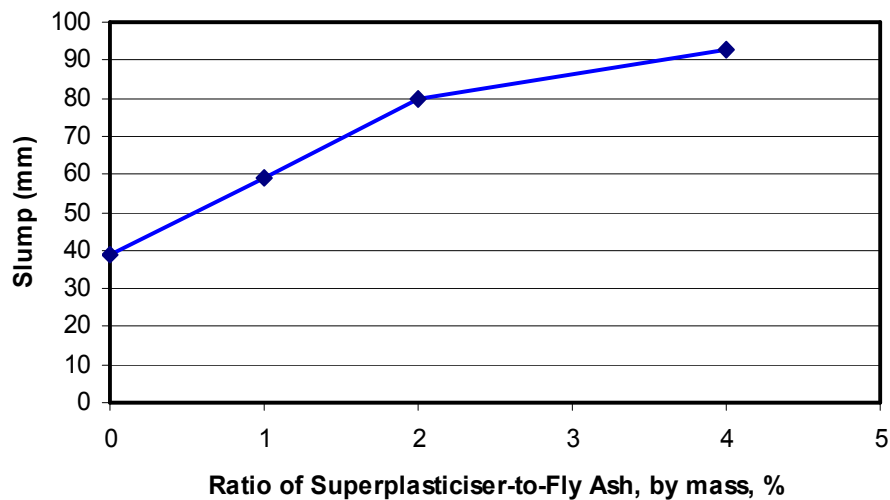


**Figure 4.5: Effect of Super plasticiser Addition on Compressive Strength**

Therefore, another series of tests were performed to study the effect of adding conventional commercially available Naphthalene Sulphonate based super plasticiser. Mixture 2 was selected for this study. The test cylinders were cured for 24 hours at 60°C in an oven. The results of these tests are given in Table 4.7, Table 4.8 and Figure 4.5. The addition of super plasticiser improved the workability of the fresh concrete but had very little effect on the compressive strength up to about two percent of this admixture to the amount of fly ash by mass. Beyond this value, there was some degradation of the compressive strength.

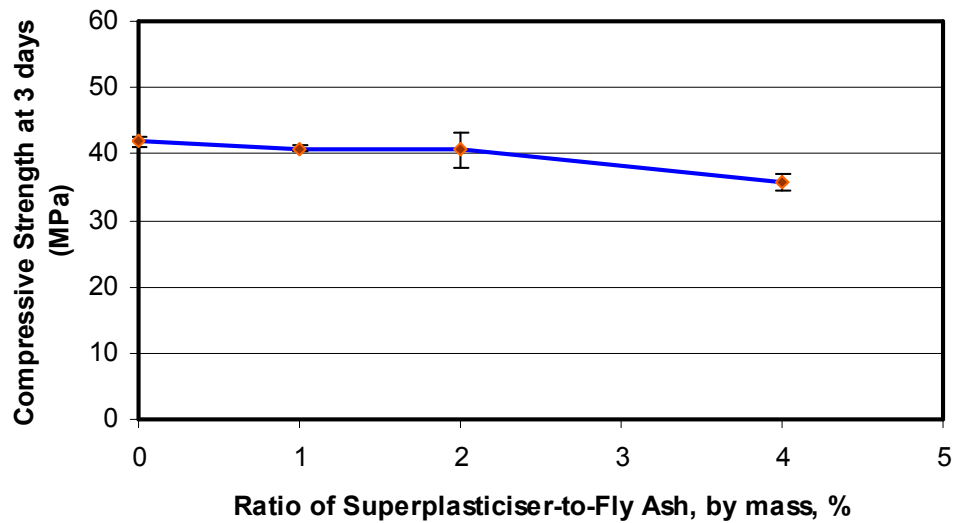
In addition, four other mixtures, i.e. Mixtures 5 to 8, were prepared. In these Mixtures, the cylinders were steam cured at 60°C for 24 hours, the maximum size of aggregates was 7 mm, and extra water was added to improve workability. Other details of these Mixtures are given in Table 4.1. The ratio of super plasticiser-to-fly ash, by mass, was the test variable.

Figure 4.6 shows that the addition of naphthalene-based super plasticiser improved the workability of the fresh fly ash-based geopolymer concrete. Figure 4.6 shows the variation of measured slump of fresh concrete with the ratio of super plasticiser-to-fly ash, by mass. The slump test was chosen to measure the workability of the fresh state concrete, as it is a simple test used extensively in practice. Slump test is useful in detecting the variations in the uniformity of a mix given for a certain mixture proportion (Neville 2000). As expected, it can be seen from Figure 4.6 that slump values increased as the content of super plasticiser in the mixtures increased.



**Figure 4.6: Effect of Superplasticiser Content on Slump of Concrete**

The variation in the compressive strength with the content of super plasticiser in the mixture is shown in Figure 4.7. These data confirm the test trend observed in Figure 4.5. The addition of naphthalene-based super plasticiser improved the workability of fresh concrete, but did not affect the compressive strength of the hardened concrete, except when the content of super plasticiser was 4% a slight reduction in compressive strength occurred.



**Figure 4.7: Effect of Super plasticiser Content on Compressive Strength**

Based on these test results, it is recommended that naphthalene sulphonate-based superplasticiser may be used to improve the workability of fresh fly ash-based geopolymer concrete. However, the content of the super plasticiser need not be more than 2% of the mass of fly ash. Beyond this amount, the addition of super plasticiser can cause a slight reduction in the compressive strength of hardened concrete; moreover, amounts greater than 2% may be uneconomical in practice.

#### **4.2.8 Rest Period Prior to Curing**

The term ‘Rest Period’ was coined to indicate the time taken from the completion of casting of test specimens to the start of curing at an elevated temperature. This may be important in certain practical applications. For instance, when fly ash-based geopolymer concrete is used in precast concrete industry, there must be sufficient time available between casting of products and sending them to the curing chamber.

In order to study the effect of Rest Period, Mixtures 9, 10, 11, 12 were made. The details of these Mixtures are given in Table 4.1. The test cylinders from Mixtures 9, 10, and 12 were left in ambient conditions for specified periods of time before the

start of curing. During this period, the test cylinders were covered to avoid the loss of moisture. The tests cylinders from Mixture 11 were placed in an oven during the Rest Period. The oven temperature on the first day was 32°C; from the second day until the end of Rest Period the temperature was increased to 40°C. This variation in the temperature simulated the hot weather condition during the Rest Period. At the end of the Rest Period, the test cylinders were steam-cured at 60°C.

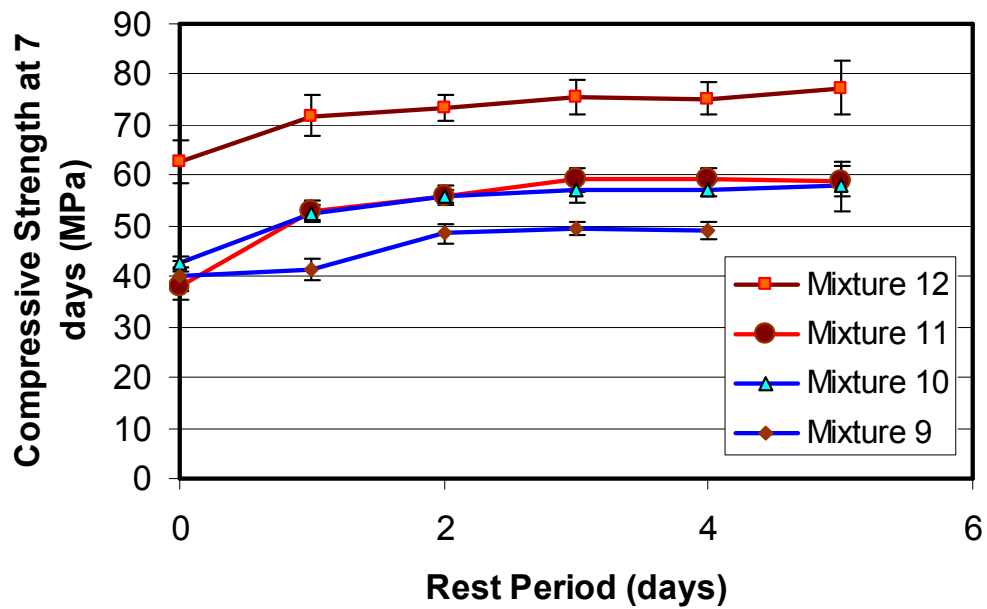
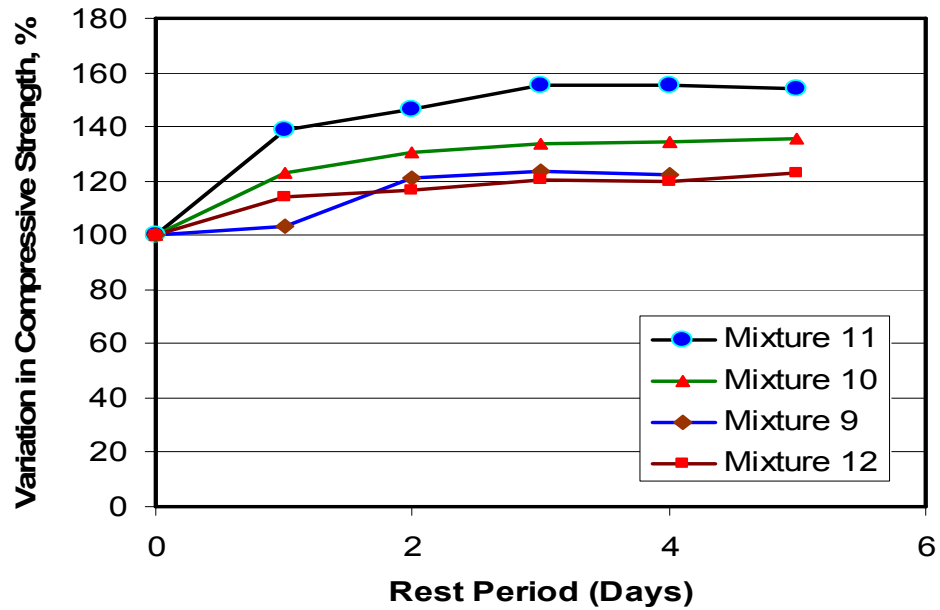


Figure 4.8: Effect of Rest Period on Compressive Strength



**Figure 4.9: Effect of Rest Period on Variation in Compressive Strength (in percentage of the compressive strength with no Rest Period)**

The test results are plotted in Figures 4.8 and 4.9. It can be seen that all the specimens from Mixtures 9 to 12 gained strength after the Rest Period. The strength gain was maximum when the Rest Period was three days; beyond that very little further strength gain was attained. The extent of strength gain was significant, in the range of 20 to 50 percent (Figure 4.9) of the compressive strength of specimens with no Rest Period. In the case of specimens from Mixture 11, the maximum strength gain was more than 50 percent.

The exact reason for this strength gain is not clear. However, the benefits shown by the Rest Period may be exploited in practice.

#### 4.2.9 Water Content of Mixture

In ordinary Portland cement (OPC) concrete, water in the mixture chemically reacts with the cement to produce a paste that binds the aggregates. In the fly ash-based geopolymer concrete, water in the mixture does not cause a chemical reaction because the chemical process that occurs to produce the binder is due to polymerisation. However, laboratory experience showed that water content in the geopolymer concrete mixture affected the properties of concrete in the fresh state as well as in the hardened state. In order to establish the effect of water content in the mixture, tests were performed.

In order to plan this series of tests, the past research on geopolymer pastes was first considered. Davidovits (1982) proposed that the ranges of the oxide molar ratios suitable to produce geopolymeric materials may be as follows:  $0.2 < \text{Na}_2\text{O}/\text{SiO}_2 < 0.28$ ,  $3.5 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 4.5$ , and  $15 < \text{H}_2\text{O}/\text{Na}_2\text{O} < 17.5$ , where  $\text{Na}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  are respectively the sodium, silicon and aluminium oxides, and  $\text{H}_2\text{O}$  is the water. Based on tests performed on geopolymer pastes using calcined kaolin as the source material, Barbosa et al (2000) found that the optimum composition occurred when the ratio of  $\text{Na}_2\text{O}/\text{SiO}_2$  was 0.25 and the ratio of  $\text{H}_2\text{O}/\text{Na}_2\text{O}$  was 10.0.

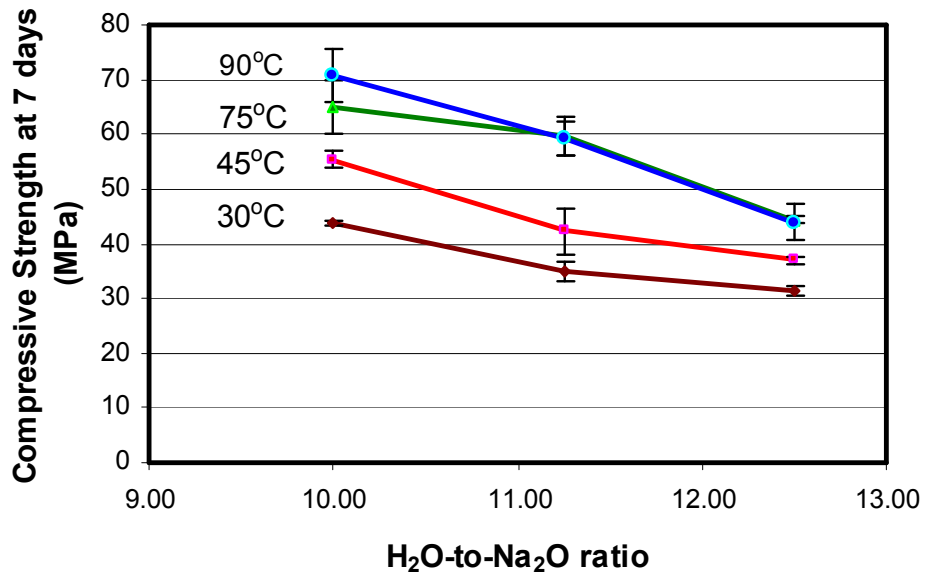
The mixture proportions for these series of tests were derived from many trial mixes. The test variables were  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio and the  $\text{Na}_2\text{O}$ -to- $\text{SiO}_2$  molar ratio. With regard to  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio, only the range from 10.0 to 14.0 was found to be feasible. For  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio less than 10.0, the concrete mixtures were not easily workable; on the other hand, for values of this ratio greater than about 14.0, considerable segregation of mixture ingredients occurred due to the presence of excess water.

No suitable concrete mixture could be prepared within the range of  $\text{Na}_2\text{O}$ -to- $\text{SiO}_2$  molar ratio as proposed by Davidovits (1982). This might be due to the difference in the type of source material and the aggregates used in the manufacture of concrete. Davidovits used pure calcined kaolinite, named **KANDOXI** (**KA**olinite, **Na**crite, **Dickite OXI**de), by calcining kaolin clay at 750°C for 6 hours as the source material

(Davidovits 1999). In contrast, low calcium (ASTM Class F) fly ash was used as the source material in the current research. Also, the mixtures used by Davidovits were geopolymer pastes with no aggregates. In order to suit the solid materials and the activator liquids used, the range of Na<sub>2</sub>O-to-SiO<sub>2</sub> ratio between 0.095 and 0.120 was selected for this series of tests.

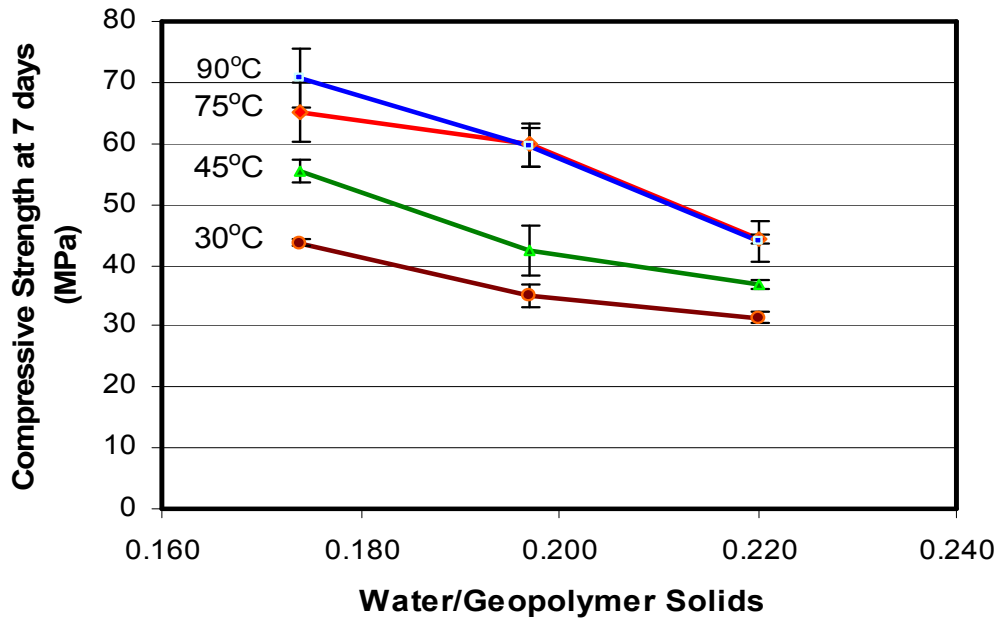
In order to investigate the effect of water content in the mixture, two sets of mixtures were made. In the first set, Mixtures 13, 14, and 15 were made. The details of these Mixtures are given in Table 4.1 and 4.2. The purpose of this set was to investigate the effect of H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio on the compressive strengths of concrete, while the molar ratios of other oxides in the mixtures, viz, Na<sub>2</sub>O-to-SiO<sub>2</sub> and SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> were kept constant at 0.115 and 3.89 respectively. The calculations of molar ratios of various oxides in the Mixtures are given in Appendix B.

The H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio of Mixture 13 was 10.01. By adding extra water of 10.6 kg/m<sup>3</sup> to this mixture, the H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio became 11.25, and by adding extra water of 21.2 kg/m<sup>3</sup>, this ratio was 12.49.



**Figure 4.10: Effect of H<sub>2</sub>O-to-Na<sub>2</sub>O Molar Ratio on Compressive Strength**

The test cylinders were cured for 24 hours at various temperatures. Figure 4.10 shows the effect of H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio on the compressive strength of geopolymer concrete for various curing temperatures. An increase in this ratio decreased the compressive strength of concrete. Obviously, as the H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio increased, the mixtures contained more water and became more workable.

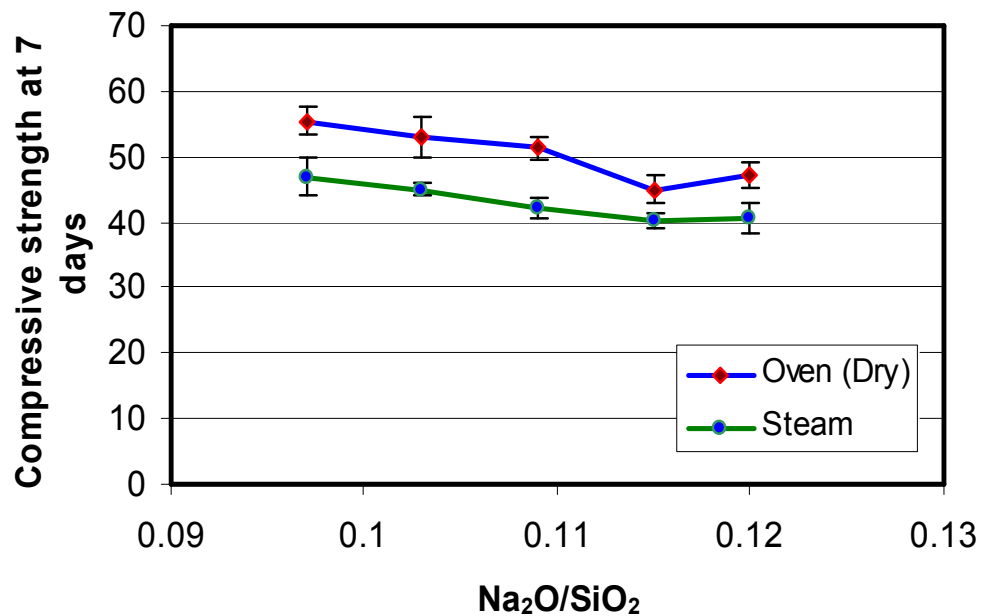


**Figure 4.11: Effect of Water-to-Geopolymer Solids Ratio by Mass on Compressive Strength**

The test results shown in Figure 4.10 are recast in engineering terms in Figure 4.11 in order to illustrate the effect of water-to-geopolymer solids ratio by mass on the compressive strength. The total mass of water is the sum of the mass of water contained in the sodium silicate solution, the mass of water in the sodium hydroxide solution, and the mass of extra water, if any, added to the mixture. The mass of geopolymer solids is the sum of the mass of fly ash, the mass of sodium hydroxide solids, and the mass of solids in the sodium silicate solution (i.e. the mass of Na<sub>2</sub>O and SiO<sub>2</sub>). The calculations of water-to-geopolymer solids ratio by mass of Mixtures



13, 14, and 15 are given in Appendix B. The test data presented in Figure 4.11 show that the compressive strength of geopolymer concrete decreased as the ratio of water-to-geopolymer solids by mass increased. This test trend is analogous to the well-known effect of water-to-cement ratio on the compressive strength of Portland cement concrete.

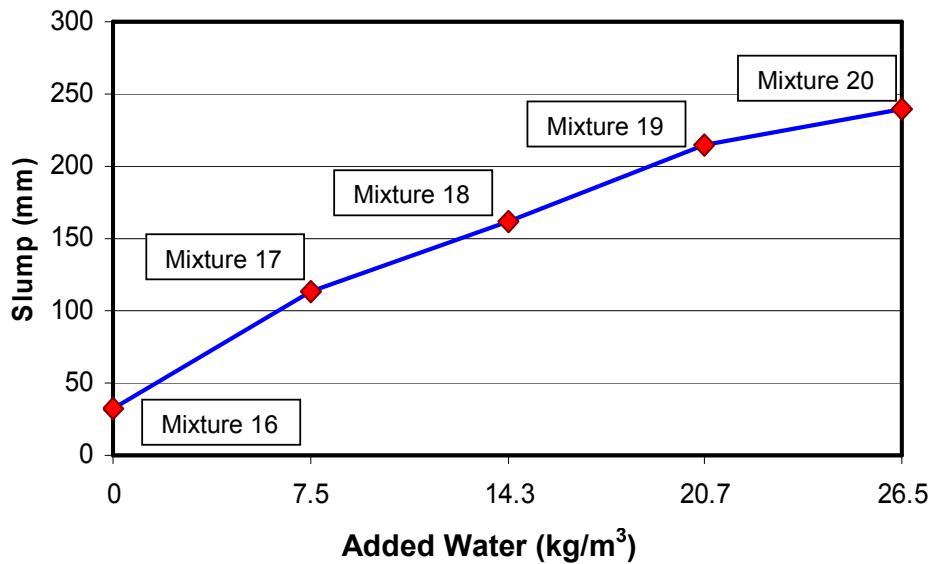


**Figure 4.12: Effect of the Molar Na<sub>2</sub>O-to-SiO<sub>2</sub> Ratio on Compressive Strength**

In the second set, Mixtures 16 to 20 were made to study the effect of the molar Na<sub>2</sub>O-to-SiO<sub>2</sub> ratio on the compressive strength. The details of these Mixtures are given in Table 4.2. The test cylinders were cured at 60°C for 24 hours. Ten cylinders were made for each Mixture; five of the cylinders were cured in an oven, and the other five were cured in the steam curing chamber.

In Mixtures 16 to 20, the molar ratio of SiO<sub>2</sub>-to-Al<sub>2</sub>O<sub>3</sub> was 3.89, and the molar ratio of H<sub>2</sub>O-to-Na<sub>2</sub>O was approximately constant around 12.42. The calculations of molar ratios of various oxides in these Mixtures are given in Appendix B.

Figure 4.12 shows the influence of  $\text{Na}_2\text{O}$ -to- $\text{SiO}_2$  molar ratio on the compressive strength of fly ash-based geopolymer concrete. It can be seen that the compressive strength decreased only marginally when the  $\text{Na}_2\text{O}$ -to- $\text{SiO}_2$  molar ratio increased from 0.098 to 0.120. In these Mixtures, as can be observed from the data given in Table 4.2, the required  $\text{Na}_2\text{O}$ -to- $\text{SiO}_2$  molar ratio was achieved by increasing the sodium hydroxide concentration and by adding extra water to keep the  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio approximately constant. Therefore, Mixture 17 contained more water than Mixture 16, and so on. These test data show that any change in the water content alone does not affect the compressive strength of geopolymer concrete, provided that the  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio is kept constant. This test trend is true for specimens cured in the oven (dry) as well as for the specimens cured in the steam curing chamber (Figure 4.12). However, the presence of extra water in the mixture improved the workability fresh concrete, as illustrated by the slump test data of these Mixtures plotted in Figure 4.13.



**Figure 4.13: Slump Values for Mixtures 16 to 20**

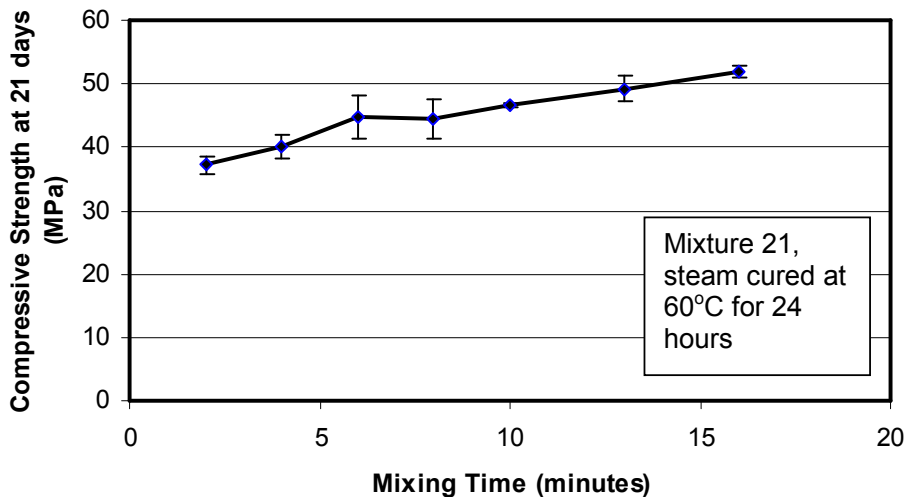
#### 4.2.10 Mixing Time

In order to study the effect of mixing time of fresh concrete on the compressive strength of hardened concrete, two sets of tests were performed.

##### Discontinuous Mixing

Mixture 21 was used for the first set of tests. The details of the Mixture 21 are given in Table 4.2. In this case, the dry materials and the liquids were mixed together for two minutes. The mixing then stopped for about twenty minutes to take some of the fresh concrete in order to make five test cylinders. The mixing of the remaining concrete continued for another two minutes and stopped again for about twenty minutes to extract fresh concrete to make five more test cylinders. This process continued for several steps until the total mixing time reached sixteen minutes.

The test cylinders were steam cured at 60°C for 24 hours, and tested in compression at an age of 21 days. The results are shown in Figure 4.14. The test data plotted in Figure 4.14 shows that the compressive strengths significantly increased as the mixing time increased.



**Figure 4.14: Effect of Mixing Time on Compressive Strength: Discontinuous Mixing**

The slumps of fresh concrete at each step of mixing were also measured. These results showed that the slump values decreased from 240 mm for two minute mixing time to 210 mm when the mixing time increased to sixteen minutes.

### **Continuous Mixing**

The second set of tests used Mixture 22. The details of Mixture 22 are given in Table 4.2. It can be seen in Table 4.2, Mixture 22 considered less quantity of added water and the maximum size of coarse aggregate was smaller than used in the case of Mixture 21. Therefore, the slump of fresh concrete made using Mixture 22 was expected to be smaller than that of Mixture 21.

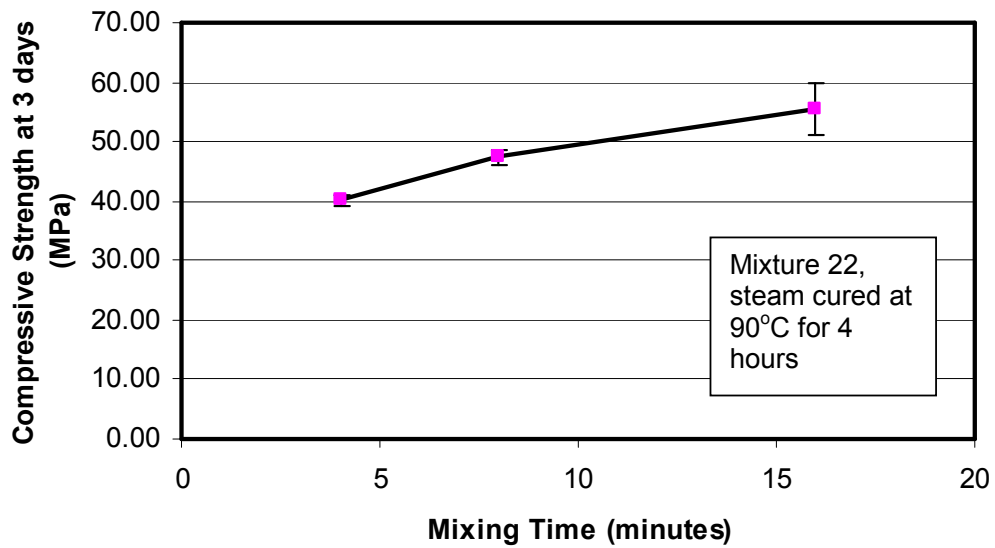
In this case, three different batches of concrete were made. The dry materials and the liquids of each batch of concrete were continuously mixed for a certain period of time. At the end of the mixing, each batch of concrete was used to make five test cylinders.

The mixing time for the first batch of concrete was four minutes, for the second batch eight minutes, and for the third batch sixteen minutes.

The test cylinders were steam cured at 90°C for 4 hours, and tested in compression at an age of 3 days. The results are shown in Figure 4.15.

The test trend observed in Figure 4.15 is similar to that shown in Figure 4.14. The compressive strength significantly increased as the mixing time increased. Also, similar to the case of Mixture 21, the measured slump of the fresh concrete using Mixture 22 decreased from 90 mm for a mixing time of four minutes to 50 mm when the mixing time increased to sixteen minutes.

The above test data show that the compressive strength of fly ash-based geopolymer concrete can be increased by an increase in the mixing time for a slight loss in the slump of fresh concrete. This is true whether the mixing process is discontinuous or continuous, as demonstrated above.



**Figure 4.15: Effect of Mixing Time on Compressive Strength: Continuous Mixing**

#### 4.2.11 Age of Concrete

Figure 4.16 shows the effect of age of concrete on the compressive strength. The test cylinders were prepared using Mixture 2 (see Table 4.1 and 4.7), and cured in the oven at 60°C for 24 hours.

Because the chemical reaction of the heat-cured geopolymer concrete is due to substantially fast polymerisation process, the compressive strength does not vary with the age of concrete. This observation is in contrast to the well-known behaviour of OPC concrete, which undergoes hydration process and hence gains strength over time.

Another series of tests was performed to investigate the effect of age on the compressive strength of fly ash-based geopolymer concrete. The test cylinders were prepared using Mixture 22 (See Table 4.2), with mixing times of 4, 8 and 16 minutes, and steam cured at 90°C for 4 hours. Figure 4.17 shows the effect of age on the compressive strength for these specimens. This Figure confirms that the compressive

strength of heat-cured fly ash-based geopolymer concrete does not vary with age of concrete.

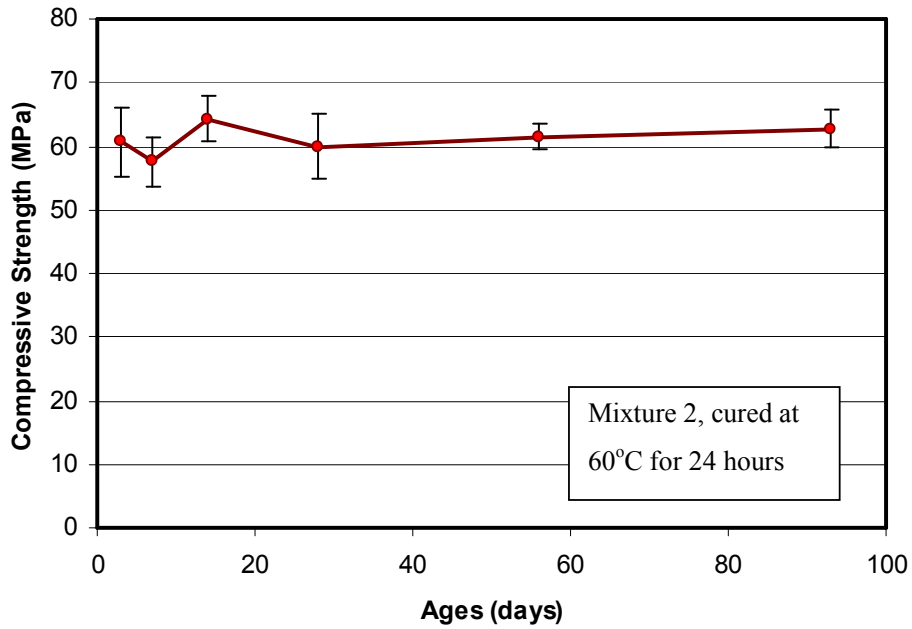


Figure 4.16: Compressive Strength at Different Ages for Mixture 2

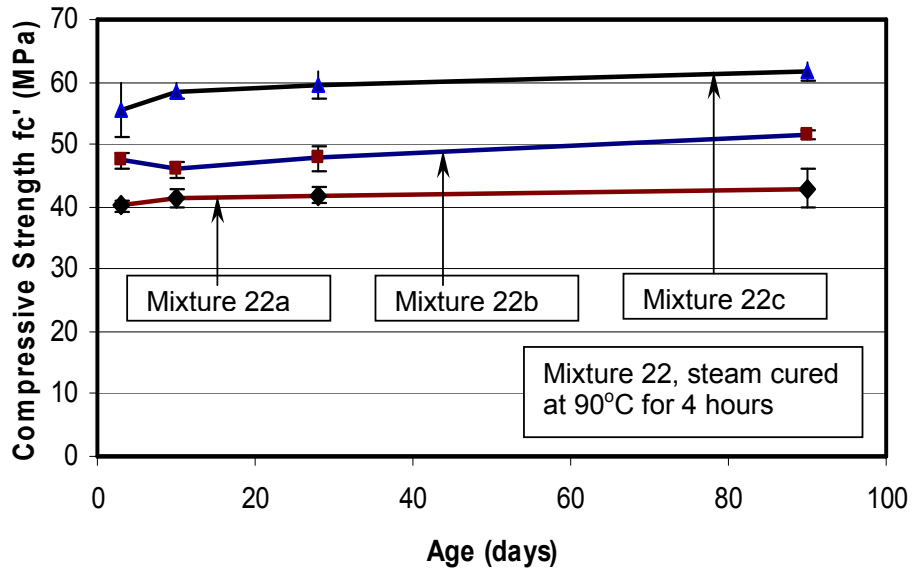


Figure 4.17: Compressive Strength at Different Ages for Mixture 22

### 4.3 MODULUS OF ELASTICITY AND POISSON'S RATIO

Mixtures 23 to 26 were made in order to measure the modulus of elasticity and Poisson's ratio. The details of these four Mixtures are given in Table 4.2. These Mixture proportions covered compressive strengths ranging from 40 to 90 MPa.



**Figure 4.18: Test Set-Up for Measuring the Elastic Constants**

The Young's modulus or elastic modulus,  $E_c$ , of fly ash-based geopolymer concrete was determined as the secant modulus measured at the stress level equal to 40 percent of the average compressive strength of concrete cylinders. Tests were carried out in accordance with the Australian Standard AS 1012.17 (1997).

For each Mixture, five 100x200 mm concrete cylinders were made. Three of these cylinders were used to determine the elastic modulus and Poisson's ratio. Two other cylinders were tested to determine the average compressive strength. All the specimens were capped in accordance with the Australian Standard AS 1012.9 (1999). The tests were performed in a 2500 kN capacity Avery-Denison universal test machine.

Two LVDTs (Linear Voltage Differential Transducers) were used to measure the axial deformation of the concrete cylinders, while one LVDT was used to measure the lateral deformation of the test cylinder at mid-height. The test set-up for measuring the elastic constants is shown in Figure 4.18.

**Table 4.10: Young's Modulus and Poisson's Ratio**

<b>Mixture No.</b>	<b>Mean compressive strength</b>	<b>Age of concrete (days)</b>	<b>Modulus of Elasticity (GPa)</b>	<b>Poisson's Ratio</b>
<b>23</b>	89	90	30.8	0.16
<b>24</b>	68	90	27.3	0.12
<b>25</b>	55	90	26.1	0.14
<b>26</b>	44	90	23.0	0.13

Table 4.10 shows the values of modulus of elasticity and Poisson's ratio of specimens from Mixtures 23 to 26. As expected, the modulus of elasticity increased as the compressive strength of concrete increased.

For OPC concrete, the Australian Standard (2005) recommends the following expression to calculate the value of the modulus of elasticity within an error of plus or minus 20 %:

$$E_c = \rho^{1.5} \times (0.024 \sqrt{f_{cm}} + 0.12) \quad (\text{MPa}) \quad (4.1)$$

where  $\rho$  is the density of concrete in  $\text{kg/m}^3$ , and  $f_{cm}$  is the mean compressive strength in MPa.



American Concrete Institute (ACI) Committee 363 (1992) has recommended the following expression to calculate the modulus of elasticity.:

$$E_c = 3320 \sqrt{f_{cm}} + 6900 \quad (\text{MPa}) \quad (4.2)$$

The average density of fly ash-based geopolymer concrete was 2350 kg/m<sup>3</sup>. Table 4.11 shows the comparison between the measured value of modulus of elasticity of fly ash-based geopolymer concrete with the values determined by Equation 4.1 and Equation 4.2.

**Table 4.11: Comparison between Calculated Values using Equation 4.1 and 4.2 and Measured Values of Modulus Elasticity**

$f_{cm}$	$E_c$ measured (GPa)	$E_c$ (Equation 4.1) (GPa)	$E_c$ (Equation 4.2) (GPa)
89	30.8	$39.5 \pm 7.9$	38.2
68	27.3	$36.2 \pm 7.2$	34.3
55	26.1	$33.9 \pm 6.8$	31.5
44	23.0	$31.8 \pm 6.4$	28.9

It can be seen from Table 4.11, the measured values were consistently lower than the values calculated using Equation 4.1 and Equation 4.2. This is due to the type of coarse aggregates used in the manufacture of geopolymer concrete.

The type of the coarse aggregate used in the test programme was of granite type. Even in the case of specimens made of Mixture No. 26 ( $f_{cm}=44$  MPa), the failure surface of test cylinders cut across the coarse aggregates, thus resulting in a smooth failure surface. This indicates that the coarse aggregates were weaker than the geopolymer matrix and the matrix-aggregate interface (Zia et al. 1997).

For OPC concrete using granite type coarse aggregate, Aitcin and Mehta (1990) reported Young's modulus values of 31.7 GPa and 33.8 GPa when  $f_{cm}=84.8$  MPa and 88.6 MPa, respectively. These values are similar to those measured for geopolymer concrete reported in Table 4.10.

The Poisson's ratio of geopolymer concrete falls between 0.12 and 0.16 (Table 4.10). For Portland cement concrete, the Poisson's ratio is usually between 0.11 and 0.21, with the most common value taken as 0.15 (Warner et al. 1998) or 0.15 for high strength concrete and 0.22 for low strength concrete (Neville 2000). These ranges are similar to those measured for the geopolymer concrete.

#### **4.4 STRESS-STRAIN RELATION IN COMPRESSION**

Tests to obtain the stress-strain curves in compression were performed using an Instron Testing Machine at the Laboratory of School of Civil and Environmental Engineering, The University of New South Wales, Sydney, Australia.

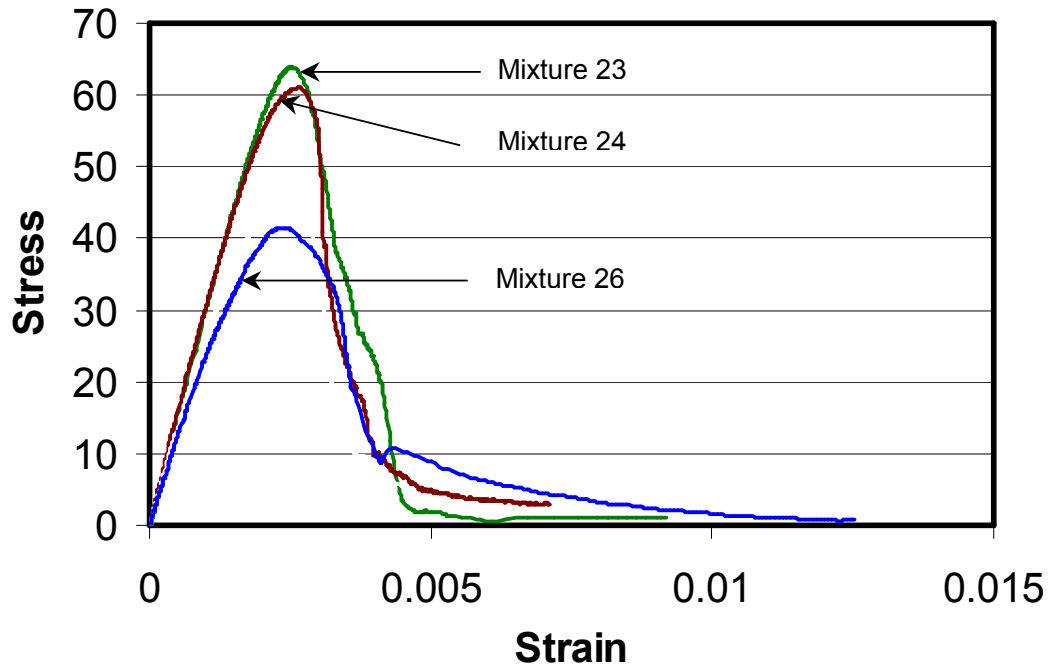
Mixtures 23 to 26 were chosen to study the stress-strain relation of the fly ash-based geopolymer concrete. The details of these four Mixtures are given in Table 4.2.

The tests on 100x200 mm concrete cylinders were performed by using the displacement-control mode available in the test machine. It took approximately 50 to 90 minutes to complete each test in order to obtain both the ascending and the descending branches of the stress-strain curves.

According to Neville (2000), loading in compression over a period between 30 and 240 minutes has been found to cause about 15% reduction in the measured value of the compressive strength of test cylinders. The loading rate also influences the measured compressive strength of concrete (Zia et al. 1997). Therefore, the measured compressive strength of test cylinders made using Mixtures 23 to 26 in this series of tests were lower than those reported in Table 4.10.

Figure 4.19 shows the stress-strain relation of fly ash-based geopolymer concrete made using Mixtures 23, 24 and 26. Due to unknown technical problems in the

process of gathering the data, the stress-strain relation for the test cylinder made using Mixture 25 was lost.



**Figure 4.19: Stress-Strain Relations of Geopolymer Concrete**

The values of compressive strength, the strain at peak stress, and the modulus of elasticity obtained from the stress-strain curve are given in Table 4.12.

**Table 4.12: Test Data from Stress-Strain Curves**

Mixture No	Compressive Strength (MPa)	Strain at Peak Stress	Modulus of Elasticity (GPa)
23	64	0.0025	30.6
24	61	0.0026	30.8
26	41	0.0024	24.7

The strains at the peak stress are in the range of 0.0024 to 0.0026. These values are similar to those reported for OPC concrete (Warner et al. 1998). The values of modulus of elasticity are similar to those given in Table 4.10.

Collins et al (1993) have proposed that the stress-strain relation of OPC concrete in compression can be predicted using the following expression:

$$\sigma_c = f_{cm} \frac{\varepsilon_c}{\varepsilon_{cm}} \frac{n}{n-1 + (\varepsilon_c/\varepsilon_{cm})^{nk}} \quad (4.3)$$

where

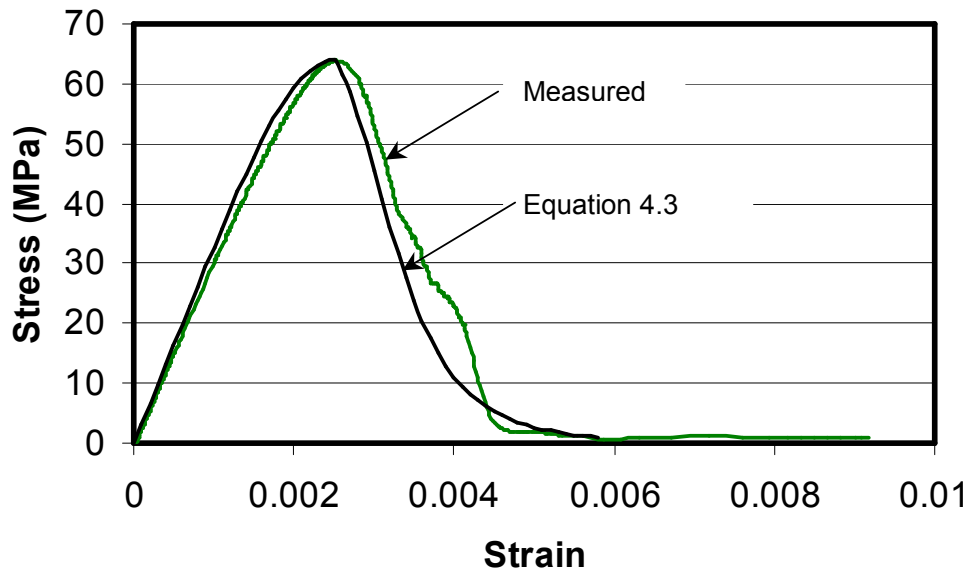
$f_{cm}$  = peak stress

$\varepsilon_{cm}$  = strain at peak stress

$n = 0.8 + (f_{cm}/17)$

$k = 0.67 + (f_{cm}/62)$  when  $\varepsilon_c/\varepsilon_{cm} > 1$

$= 1.0$  when  $\varepsilon_c/\varepsilon_{cm} \leq 1$



**Figure 4.20: Predicted and Test Stress-Strain Relations for Concrete made from Mixture 23**

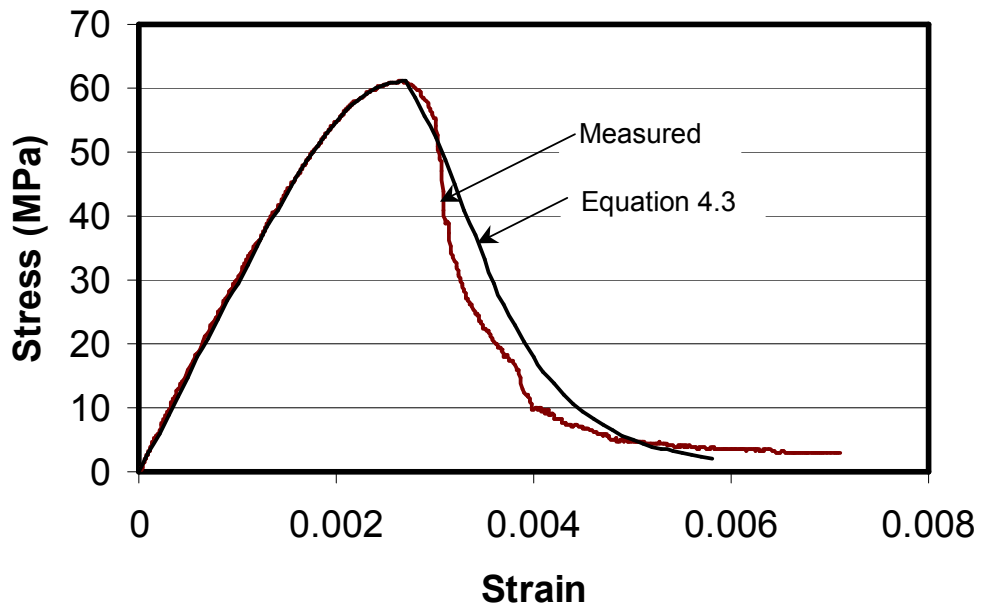


Figure 4.21: Predicted and Test Stress-Strain Relations for Concrete made from Mixture 24

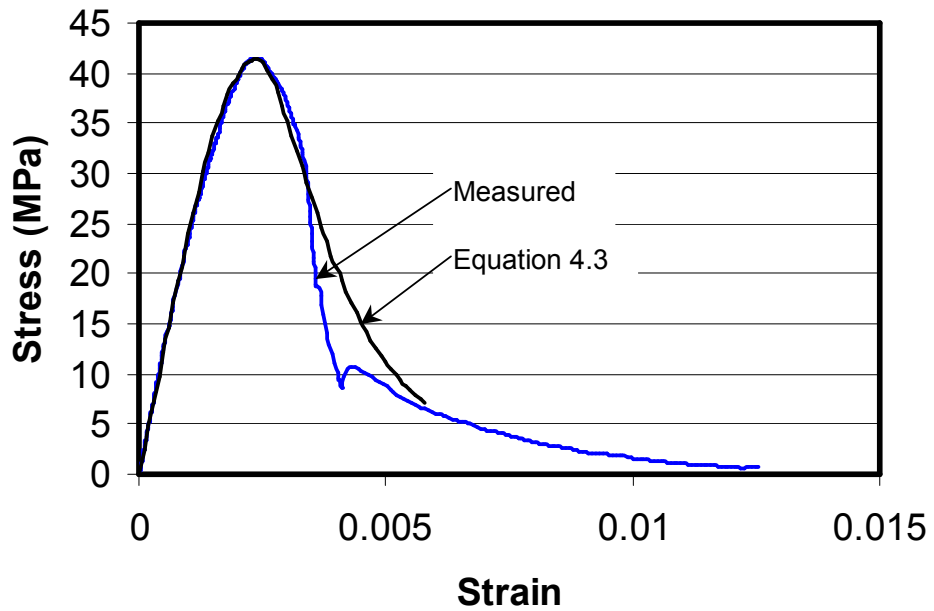


Figure 4.22: Predicted and Test Stress-Strain Relations for Concrete made from Mixture 26

In Figures 4.20 to 4.22, the stress-strain relations predicted by Equation 4.3 are compared with the test curves given in Figure 4.19. The analytical curves were obtained by using the measured values of  $f_{cm}$  and  $\epsilon_{cm}$  in Equation 4.3. This comparison reveals that the stress-strain relations of fly ash-based geopolymer concrete can be predicted by using Equation 4.3 developed for Portland cement concrete.

#### 4.5 INDIRECT TENSILE STRENGTH

The tensile strength of fly ash-based geopolymer concrete was measured by performing the cylinder splitting test on 150x300 mm concrete cylinders in accordance with the Australian Standard 1012.10-2000 (2000). The test results are given in Table 4.13.

These test results show that the tensile splitting strength of geopolymer concrete is only a fraction of the compressive strength, as in the case of Portland cement concrete.

Standards Australia (2001) recommends the following design expression to determine the characteristic principal tensile strength of OPC concrete:

$$f'_{ct} = 0.4 \sqrt{f_{cm}} \quad (\text{MPa}) \quad (4.4)$$

Neville (2000) recommended that the relation between the tensile splitting strength and the compressive strength of OPC concrete may be expressed as:

$$f'_{ct} = 0.3 (f_{cm})^{2/3} \quad (\text{MPa}) \quad (4.5)$$

The calculated values of  $f'_{ct}$  using Equations 4.4 and 4.5 are also tabulated in Table 4.13.

**Table 4.13: Indirect Tensile Splitting Strength**

<b>Mixture No</b>	<b>Mean Compressive Strength (MPa)</b>	<b>Mean Indirect Tensile Strength (MPa)</b>	<b>Characteristic principal tensile strength, Equation (4.4) (MPa)</b>	<b>Splitting Strength, Equation (4.5) (MPa)</b>
<b>23</b>	89	7.43	3.77	5.98
<b>24</b>	68	5.52	3.30	5.00
<b>25</b>	55	5.45	3.00	4.34
<b>26</b>	44	4.43	2.65	3.74

Table 4.13 shows that the indirect tensile strength of fly ash-based geopolymer concrete is larger than the values recommends by the Standards Australia (2001) and Neville (2000) for OPC concrete.

#### **4.6 DENSITY**

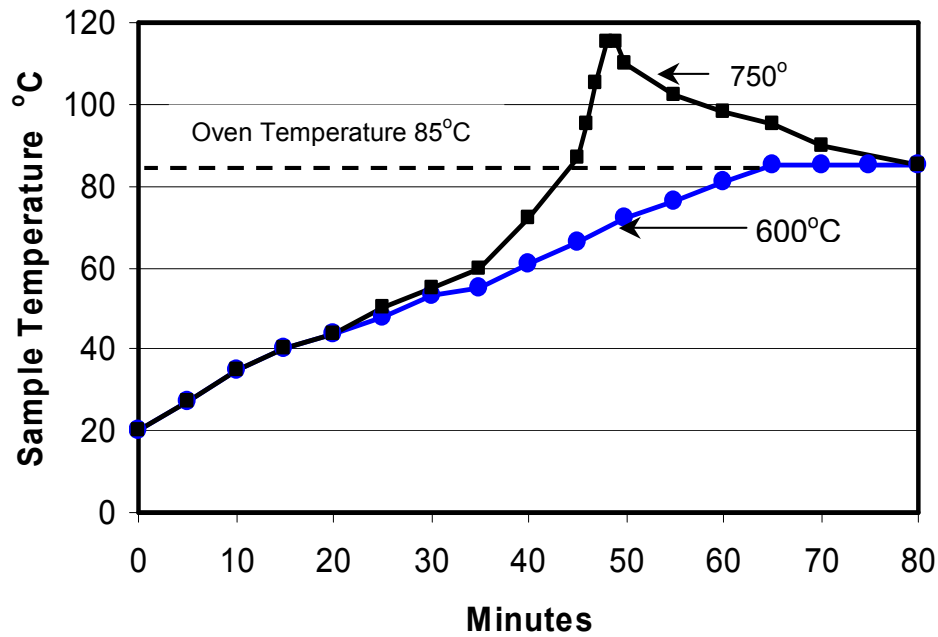
The density of concrete primarily depends on the unit mass of aggregates used in the mixture. Because the type of aggregates in all mixes did not vary, the density of the fly ash-based geopolymer concrete varied only marginally between 2330 to 2430 kg/m<sup>3</sup>.

#### **4.7 TEMPERATURE HISTORY DURING CURING**

Davidovits (1999) found that geopolymer material manufactured using calcined kaolin, called KANDOXI, is strongly exothermic. The test specimen was cured in an oven at 85°C and at atmospheric pressure (see Figure 4.23).

To obtain the geopolymerisation thermograph for fly ash-based geopolymer material during curing at elevated temperature, fly ash-based geopolymer mortar specimens of 75x75x75 mm were prepared. The mixture composition of the mortar is given in

Table 4.14. The mean compressive strength of these cubes was 47 MPa with density of 2035 kg/m<sup>3</sup> at 7 days.



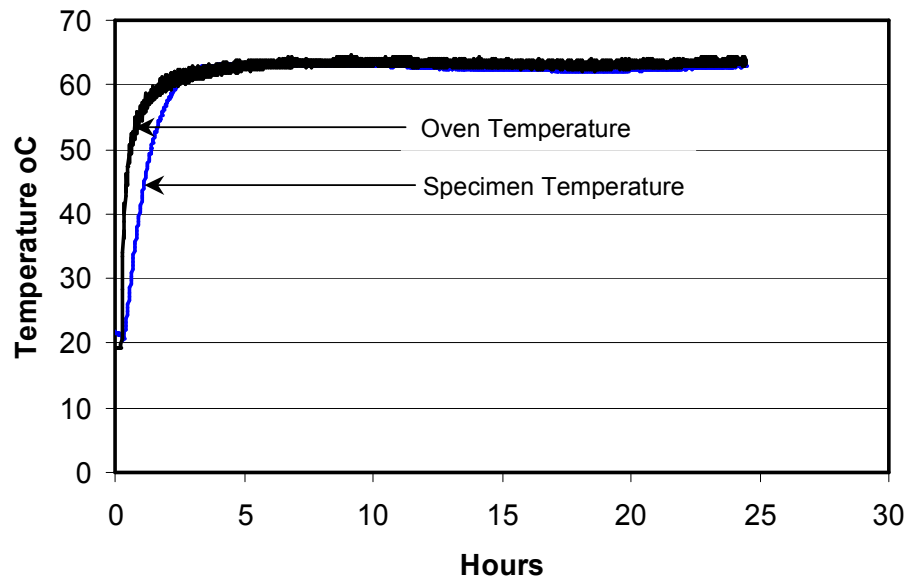
**Figure 4.23: Geopolymerization Thermograph for Standard KANDOXI, after Firing of Standard Kaolinitic Clay for 6 Hours at 600°C and 750°C (Davidovits 1999)**

**Table 4.14: Mixture Composition for Geopolymer Mortar**

Materials	Mass, in percentage
Fine Sand, in SSD	50.1
Fly Ash (ASTM Class F)	36.9
Sodium hydroxide solution (8M)	3.7
Sodium silicate solution	9.3
Super plasticiser	1.5% of the mass of fly ash



The geopolymer mortar specimen was cured in an oven at 65°C. The temperature of the specimen during curing was measured using a thermocouple. Data were measured every minute using a data taker for the duration of 24 hours. The geopolymerization thermograph of fly ash-based mortar specimen is shown in Figure 4.24.



**Figure 4.24: Geopolymerization Thermograph of Fly Ash-Based Geopolymer Mortar**

Figure 4.24 reveals that fly ash-based geopolymer mortar does not show any exothermicity, as shown by metakaolin-based geopolymer paste or mortar (Davidovits 1999).

In the case of metakaolin-based geopolymer material, Davidovits (1999) observed that whenever the specimens did not show any exothermicity, the compressive strength was very low. For instance, in Figure 4.23, when the kaolinite clay was fired at 600°C for 6 hours, instead of at 750°C for 6 hours, there was no exothermicity and the geopolymer specimens made using this material reached only low strength. Fly

ash-based geopolymers did not show any such correlation between exothermicity and compressive strength. It appears that the geopolymerisation that occurs in fly ash-based geopolymers may be different to that of metakaolin-based geopolymers.

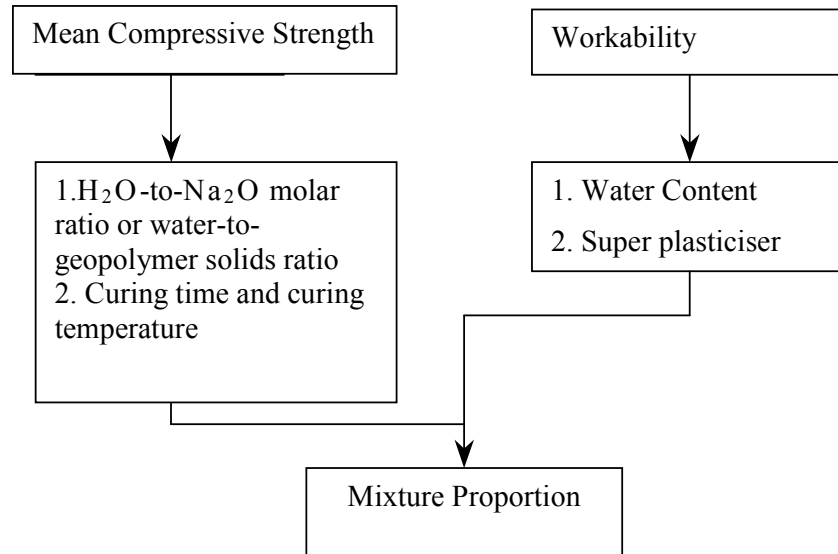
#### **4.8 MIXTURE DESIGN PROCESS**

Concrete mixture design process is vast and generally based on performance criteria. Based on the test data gathered in this research, a preliminary mixture design process for fly ash-based geopolymer concrete is proposed.

The role and influence of aggregates are considered to be the same as in the case of OPC concrete. The performance criteria depend on the application. In this illustration, the compressive strength of hardened concrete and the workability of fresh concrete are selected as the performance criteria.

The process of selecting the required mixture proportion is shown in Figure 4.25, which has been adopted from a similar approach used in the case of OPC concrete (Neville 2000).

Figure 4.25 identifies the salient parameters to meet the specified compressive strength and the workability of a low-calcium fly ash-based geopolymer concrete. The test data reported in the earlier parts of this Chapter can be used to arrive at a suitable mixture by using a trial-and-error process.



**Figure 4.25: Preliminary Mixture Design Process**

## **5. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS**

### **5.1 INTRODUCTION**

This Chapter presents a summary of the present study, the major conclusions, and some recommendations for future research.

When this study started in 2001, the published literature contained only limited knowledge and know-how on the process of making fly ash-based geopolymer concrete. Most of the literature dealt with the use of metakaolin or calcined kaolin as the source material for making geopolymer paste and mortar. Moreover, the exact details regarding the mixture compositions and the process of making geopolymers were kept undisclosed in the patent and commercially oriented research documents.

With the generic information available on geopolymers, a rigorous trial-and-error method was adopted to develop a process of manufacturing fly ash-based geopolymer concrete using the technology currently used to manufacture OPC concrete. In order to reduce the number of variables in this trial-and-error approach, the study was restricted to low-calcium (ASTM Class F) dry fly ash obtained from Collie Power Station in Western Australia, and to the type of aggregates used locally to make OPC concrete.

After some failures in the beginning, the trial-and-error method yielded successful results with regard to manufacture of low-calcium (ASTM Class F) fly ash-based geopolymer concrete. Once this was achieved, tests were performed to quantify the effect of the salient parameters that influence the short-term properties of fresh and hardened geopolymer concrete.

In the following Sections, the outcomes of the study are summarised.

## **5.2 MANUFACTURING PROCESS**

### **5.2.1 Material Preparation**

Aggregates used in the manufacture the fly ash-based geopolymer concrete were in a saturated surface dry (SSD) condition. The aggregate selection and proportion were in accordance with the current practice used in making OPC concrete.

The alkaline liquid consisted of a combination of sodium silicate solution and sodium hydroxide solution. The sodium silicate solution was purchased from a local supplier. The sodium hydroxide solution was prepared by dissolving the solids, purchased from a local supplier in flakes or pellets form, in water. Both the solutions were premixed the day before use. The alkaline liquid was mixed with the super plasticiser, if any, and the extra-added water, if any, to prepare the liquid component of the geopolymer concrete mixture.

### **5.2.2 Mixing, Placing and Compaction**

The aggregate and the fly ash were mixed dry in a pan mixer for about three minutes. The liquid component of the mixture was then added to the solids particles, and mixing continued for another four minutes in most cases.

The fresh fly ash-based geopolymer concrete remained workable up to at least two hours without any sign of setting and degradation in compressive strength. The fresh geopolymer concrete could easily be placed, compacted, and finished in moulds in that time. In all these operations, the equipment and the facilities currently used for OPC concrete were used.

For cylinder specimens of 100x200 mm, the mixture was cast in three layers. Each layer received 60 manual strokes, and vibrated for 10 seconds on a vibrating table. In some cases, the common internal needle vibrator was also utilised to successfully compact the fly ash-based geopolymer concrete.

### 5.2.3 Curing

After finishing, the test specimens were covered by a vacuum bagging film. Curing at an elevated temperature was achieved either in the dry curing environment in an oven, or in the steam curing chamber, for a specified period of time.

After curing, the concrete specimens were allowed to cool down in the moulds to avoid drastic change in the environment for at least six hours. After releasing from the moulds, the test specimens were left to air dry in the ambient conditions in the laboratory until the day for testing.

## 5.3 TEST SPECIMENS AND TEST VARIABLES

The test specimens in this study were mainly of 100x200 mm cylinders; larger size 150x300 mm cylinders were used to measure the indirect splitting tensile strength.

The concentration of sodium hydroxide solution was in the range between 8 M and 16 M. The sodium silicate solution-to-sodium hydroxide solution ratio by mass was in the range of 0.4 to 2.5; for most Mixtures, this ratio was 2.5. The solution-to-fly ash ratio by mass was approximately 0.35 in most cases, except for the Mixtures with extra-added water.

In order to study the effect of mixture composition on the compressive strength of fly ash-based geopolymer concrete, the test variables were the H<sub>2</sub>O-to-Na<sub>2</sub>O molar ratio in the range between 10.00 and 14.00, and the Na<sub>2</sub>O-to-SiO<sub>2</sub> molar ratio between 0.095 and 0.120. These ranges of variable were selected after several trials. Outside these ranges, geopolymer concrete mixtures were either too dry for handling or too wet causing segregation of aggregates. For these ranges of variables, the water-to-geopolymer solids ratio by mass in the geopolymer paste varied from 0.17 to 0.22.

The mass of naphthalene sulphonate-based super plasticiser varied from 0% to 4% of the mass of fly ash. Workability was measured by the conventional slump test. The influence of water content on the slump value was also studied by varying the mass of extra water added to a reference mixture in the range of 0 to 26.5 kg/m<sup>3</sup>.

The range mixing time studied was between two and sixteen minutes.

For curing, temperature ranges from 30°C to 90°C were studied. The curing time ranged from four hours to four days, either in the dry curing environment in the oven or in the steam curing chamber. The influence of age at test was studied up to the age of 90 days.

## 5.4 CONCLUSIONS

Based on the experimental work reported in this study, the following conclusions are drawn:

1. Higher concentration (in terms of molar) of sodium hydroxide solution results in higher compressive strength of fly ash-based geopolymer concrete (Table 4.9).
2. Higher the ratio of sodium silicate-to-sodium hydroxide ratio by mass, higher is the compressive strength of fly ash-based geopolymer concrete (Table 4.9).
3. As the curing temperature in the range of 30°C to 90°C increases, the compressive strength of fly ash-based geopolymer concrete also increases (Figures 4.1 and 4.2).
4. Longer curing time, in the range of 4 to 96 hours (4 days), produces higher compressive strength of fly ash-based geopolymer concrete (Figure 4.3). However, the increase in strength beyond 24 hours is not significant.
5. The addition of naphthalene sulphonate-based super plasticiser up to approximately 4% of fly ash by mass, improves the workability of the fresh fly ash-based geopolymer concrete with very little effect on the compressive strength of hardened concrete (Figure 4.5, 4.6 and 4.7).
6. The slump value of the fresh fly-ash-based geopolymer concrete increases with the increase of extra water added to the mixture (Figure 4.13).
7. The Rest Period, defined as the time taken between casting of specimens and the commencement of curing, of up to 5 days increases the compressive strength of hardened fly ash-based geopolymer concrete. The increase in strength is substantial in the first 3 days of Rest Period (Figure 4.8 and 4.9).

8. The fresh fly ash-based geopolymer concrete is easily handled up to 120 minutes without any sign of setting and without any degradation in the compressive strength (Figure 4.4).
9. As the  $\text{H}_2\text{O}$ -to- $\text{Na}_2\text{O}$  molar ratio increases, the compressive strength of fly ash-based geopolymer concrete decreases (Figure 4.10).
10. As the ratio of water-to-geopolymer solids by mass increases, the compressive strength of fly ash-based geopolymer concrete decreases (Figure 4.11).
11. The effect of the  $\text{Na}_2\text{O}$ -to- $\text{Si}_2\text{O}$  molar ratio on the compressive strength of fly ash-based geopolymer concrete is not significant (Figure 4.12).
12. The compressive strength of heat-cured fly ash-based geopolymer concrete does not depend on age (Figures 4.16 and 4.17).
13. Prolonged mixing time of up to sixteen minutes increases the compressive strength of fly ash-based geopolymer concrete (Figures 4.14 and 4.15).
14. The average density of fly ash-based geopolymer concrete is similar to OPC concrete.
15. The measured values of the modulus elasticity of fly ash-based geopolymer concrete with compressive strength in the range of 40 to 90 MPa, were similar to those of OPC concrete. The measured values are at the lower end of the values calculated using the current design Standards due to the type of coarse aggregate used in the manufacture of the geopolymer concrete (Table 4.11).
16. The Poisson's ratio of fly ash-based geopolymer concrete with compressive strength in the range of 40 to 90 MPa falls between 0.12 and 0.16 (Table 4.10). These values are similar to those of OPC concrete.
17. The stress-strain relations of fly ash-based geopolymer concrete in compression fits well with the expression developed for OPC concrete (Figures 4.19, 4.20, 4.21 and 4.22), with the strain at peak stress in the range of 0.0024 to 0.0026 (Table 4.12).
18. The indirect tensile strength of fly ash-based geopolymer concrete is only a fraction of the compressive strength, as in the case of Portland cement concrete. The measured values are higher than those recommended by the relevant Australian Standard (Table 4.13).



19. Fly ash-based geopolymer mortar does not show any exothermic action, as shown by metakaolin-based geopolymer paste or mortar (Figure 4.24). In spite of this, the fly ash-based geopolymer shows high compressive strength.

## **5.5 RECOMMENDATIONS FOR FUTURE RESEARCH**

To date, the reaction mechanism of geopolymerisation is still not clear. Fundamental research in this area would increase the potential of the material. For example, a study is needed to identify the scientific reason for increase in strength after a longer resting period, and to investigate the role of water in geopolymerisation.

Although the present work identified many salient parameters that influence the properties of fresh and hardened fly ash-based geopolymer concrete, a large database should be built on the engineering properties of various mixtures using fly ash from different sources. Such a database may identify additional parameters, and lead to familiarise the utilisation of this material in many applications.

Further research should identify possible applications of geopolymer technology. This would lead to research areas that are specifically oriented towards applications. The geopolymer technology has the potential to go beyond making concrete; there could be possibilities in other areas of infrastructure needed by the community.

## **APPENDIX A**

**Details of Preliminary Study:  
Mixture Proportions, Curing Details, and Properties.**

## Appendix A:

### Details of Preliminary Mixtures: Mixture Proportions (kg/m<sup>3</sup>), Curing Details, and Properties.

t No	Aggregate			Fly Ash (kg)	NaOH Solution		Sodium Silicate (kg)	Added Water (kg)	Super- plasticiser (kg)	Curing			Age at Test (days)	Slump (mm)	Density (kg/m <sup>3</sup> )	Compressive Strength (MPa)	Standard Deviation	Special Features
	10 mm (kg)	7 mm (kg)	Fine Sand (kg)		Mass (kg)	Molarity				Time (hours)	Temp. (°C)	Method						
P1	554	647	647	408 <sup>a)</sup>	41	14M <sup>*)</sup>	103	10.3	6.1	24	60	Steam	13	75	2356	85	4.03	Rest Period 3 days
P2	554	647	647	408 <sup>a)</sup>	41	14M <sup>*)</sup>	103	15.5	6.1	24	60	Steam	13	170	2338	77	1.35	Rest Period 3 days
P3	554	647	647	408 <sup>a)</sup>	41	16M <sup>*)</sup>	103	18.5	6.1	24	60	Steam	14	170	2335	73	3.66	Rest Period 3 days
P4	554	647	647	408 <sup>a)</sup>	41	16M <sup>*)</sup>	103	18.5	6.1	24	90	Steam	14	170	2332	84	1.07	Rest Period 4 days
P5	554	647	647	408 <sup>a)</sup>	41	14M <sup>**)</sup>	103	17.6	6.1	24	60	Steam	11	215	2306	57	2.50	Rest Period 3 days
P6	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	16.5 <sup>x)</sup>	8.2	4	90	Steam	1	39	2378	29	2.10	
P7	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	16.5 <sup>x)</sup>	8.2	4	90	Steam	7	39	2367	30	0.66	
P8	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	16.5 <sup>x)</sup>	8.2	4	90	Steam	28	39	2340	33	0.68	
P9	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	16.5 <sup>x)</sup>	8.2	4 + 20 <sup>+) )</sup>	90	Steam	28	39	2349	39	0.50	
P10	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	20.7 <sup>x)</sup>	8.2	4	90	Steam	1	60	2360	24	0.52	
P11	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	20.7 <sup>x)</sup>	8.2	4	90	Steam	7	60	2346	26	0.88	
P12	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	20.7 <sup>x)</sup>	8.2	4	90	Steam	28	60	2317	28	0.16	
P13	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	20.7 <sup>x)</sup>	8.2	4 + 20 <sup>+) )</sup>	90	Steam	28	60	2322	33	1.11	
P14	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	24.8 <sup>x)</sup>	8.2	4	90	Steam	1	168	2366	17	0.44	
P15	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	24.8 <sup>x)</sup>	8.2	4	90	Steam	7	168	2347	18	0.39	
P16	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	24.8 <sup>x)</sup>	8.2	4	90	Steam	28	168	2313	19	1.07	
P17	-	1309	561	408 <sup>c)</sup>	35	14M <sup>**)</sup>	88	24.8 <sup>x)</sup>	8.2	4 + 20 <sup>+) )</sup>	90	Steam	28	168	2307	25	0.38	
P18	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	20.7 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	4	182	2319	36	0.22	Compaction: needle vibrator
P19	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	20.7 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	7	182	2327	37	0.49	Compaction: needle vibrator
P20	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	20.7 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	14	182	2298	38	1.34	Compaction: needle vibrator
P21	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	20.7 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	28	182	2288	36	3.96	Compaction: needle vibrator
P22	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	1	204	2282	15	2.21	Compaction: needle vibrator
P23	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	3 + 21 <sup>++)</sup>	60	Steam	2	204	2280	34	1.59	Compaction: needle vibrator
P24	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	4	90	Steam	4 hrs	128	2338	21	1.97	Compaction: needle vibrator
P25	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	4 + 20 <sup>+) )</sup>	90	Steam	12	128	2308	44	1.21	Compaction: needle vibrator
P26	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	24	60	Steam	4	202	2295	36	2.24	Compaction: needle vibrator
P27	-	1294	554	408 <sup>c)</sup>	51	14M <sup>**)</sup>	103	18.6 <sup>x)</sup>	6.1	24	60	Steam	5	202	2295	37	2.24	Compaction: needle vibrator

<sup>+) )</sup> 4 hrs curing, allow to cool, de-moulded, continued curing for another 21 hrs    <sup>++)</sup> 3 hrs curing, allow to cool, de-moulded, continued curing for another 20 hrs.    <sup>a)</sup> Batch I    <sup>b)</sup> Batch II    <sup>c)</sup> Batch III    <sup>\*)</sup> Tech. Grade    <sup>\*\*)</sup> Com. Grade

## **APPENDIX B**

**Calculation of Molar Ratio of Mixtures 13 to 17 and 20 to 22, and  
Water-to-Geopolymer Solids Ratio of Mixtures 20 to 22**

## Calculation of the Molar Ratio of Mixtures No 13 to 17 and No 20 to 22

### I. Mixture Proportion (kg/m<sup>3</sup>)

	Mix #13	Mix #14	Mix#15	Mix #16	Mix#17	Mix #20	Mix #21	Mix #22
Fly Ash	408	408	408	408	408	408	408	408
Sodium Silicate Solution	103	103	103	103	103	103	103	103
NaOH solution	41	41	41	41	41	41	41	41
Added water	0	7.476	14.338	20.648	26.478	0	10.64	21.28
Molarity of NaOH solution	8 M	10 M	12 M	14 M	16 M	14 M	14 M	14 M

### II. Some Chemical Compounds of Fly Ash Batch I (% by mass)

	%
SiO <sub>2</sub>	53.36
Al <sub>2</sub> O <sub>3</sub>	26.49
Na <sub>2</sub> O	0.37

### III. Chemical Composition of Sodium Silicate (% by mass)

Oxides	%
SiO <sub>2</sub>	29.4
Na <sub>2</sub> O	14.7
Water	55.9

### IV. % of NaOH Flakes in Various Molarity

NaOH solution	%
NaOH 8 M	26.23
NaOH 10 M	31.37
NaOH 12 M	36.09
NaOH 14 M	40.43
NaOH 16 M	44.44

### V. Molecular Weight of Some Oxides

Oxides	gr
SiO <sub>2</sub>	60.09
Al <sub>2</sub> O <sub>3</sub>	101.96
Na <sub>2</sub> O	61.98
H <sub>2</sub> O	18.00
NaOH	39.99

### VI. Calculation of the moles of the geopolymer constituents and the molar ratio

Mix #	NaOH Solution	Fly Ash			Sodium Silicate			NaOH solution		Added Water	Total Moles (per m <sup>3</sup> )				Molar Ratio			
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	SiO <sub>2</sub>	Na <sub>2</sub> O	H <sub>2</sub> O	Flakes	Water		Na <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	Na <sub>2</sub> O/SiO <sub>2</sub>	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O/Na <sub>2</sub> O	
Mix #13	8 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	134.46	134.46	1680.32	0.00	403.11	4126.99	1060.02	5013.50	0.098	3.89	12.44
Mix #14	10 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	160.81	160.81	1563.24	415.33	429.46	4126.99	1060.02	5338.11	0.104	3.89	12.43
Mix #15	12 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	185.01	185.01	1455.73	796.56	453.65	4126.99	1060.02	5636.01	0.110	3.89	12.42
Mix #16	14 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	207.26	207.26	1356.87	1147.11	475.90	4126.99	1060.02	5909.96	0.115	3.89	12.42
Mix #17	16 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	227.81	227.81	1265.53	1471.00	496.46	4126.99	1060.02	6163.07	0.120	3.89	12.41
Mix #20	14 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	207.26	207.26	1356.87	0.00	475.90	4126.99	1060.02	4762.85	0.115	3.89	10.01
Mix #21	14 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	207.26	207.26	1356.87	591.11	475.90	4126.99	1060.02	5353.96	0.115	3.89	11.25
Mix #22	14 M	3623.05	1060.02	24.36	503.94	244.29	3198.72	207.26	207.26	1356.87	1182.22	475.90	4126.99	1060.02	5945.07	0.115	3.89	12.49

Calculation of Water-to-Geopolymer Solids Ratio for Mixtures No 20 to 22										
I. Mixture Proportion (kg/m <sup>3</sup> )										
			<b>Mix #20</b>	<b>Mix #21</b>	<b>Mix #22</b>					
Fly Ash			408	408	408					
Sodium Silicate Solution			103	103	103					
NaOH solution			41	41	41					
Added water			0	10.64	21.28					
Molarity of NaOH solution			14 M	14 M	14 M					
II. Chemical Composition of Sodium Silicate (% by mass)					III. % of NaOH Flakes in Various Molarity					
<b>Oxides</b>		<b>%</b>				<b>NaOH solution</b>		<b>%</b>		
SiO <sub>2</sub>		29.4				NaOH 8 M		26.23		
Na <sub>2</sub> O		14.7				NaOH 10 M		31.37		
Water		55.9				NaOH 12 M		36.09		
						NaOH 14 M		40.43		
						NaOH 16 M		44.44		
IV. Calculations of Water-to-Geopolymer Solids by mass										
	<b>NaOH</b>	<b>NaOH solution</b>		<b>Sodium Silicate Sol.</b>		<b>Fly Ash</b>	<b>Added</b>	<b>Total</b>		
		<b>Solids</b>	<b>Water</b>	<b>Solids</b>	<b>Water</b>		<b>Water</b>	<b>Water</b>	<b>Solids</b>	<b>Water /</b>
		<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>kg</b>	<b>Solids</b>
Mix #20	14 M	16.58	24.42	45.42	57.58	408.00	0.00	82.00	470.0	0.174
Mix #21	14 M	16.58	24.42	45.42	57.58	408.00	10.64	92.64	470.0	0.197
Mix #22	14 M	16.58	24.42	45.42	57.58	408.00	21.28	103.28	470.0	0.220