STUDY OF THE KINETIC EFFECT OF ALUMINOSILICATE GEL FORMATION ON FLY ASH BASED GEOPOLYMER

by

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13679

Dissertation submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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Chemical Engineering Programme
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BACHELOR OF ENGINEERING (Hons)
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Approved by,

…………………………………..
(Dr Lukman bin Ismail)

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is of my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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NURUL HAFIZAH BINTI NIZAM

ABSTRACT

Fly ash based Geopolymer is a type of concrete based that can act as the basic building materials which is utilized in construction of roads, buildings and infrastructures and it is expected to be widely used in foreseeable future. It is formed through the reaction of fly ash with have high content of silica and alumina and alkaline solution. It is a potential alternative to Ordinary Portland Cement (OPC) in cement industry as it is not only minimizing CO_2 emission, but also contributes toward recycling waste material, fly ash which is economically feasible. Geopolymer also showed good properties such as low creep, low shrinkage, high compressive and tensile strength and good acid resistance. This research is to study the effect of kinetic formation of aluminosilicate gel formation in geopolymer. The kinetic formation is measured before setting time of the solidification of fly ash geopolymer based on 3 parameters. The parameters are type of alkaline solution, concentration of alkaline solution and process temperature. First, four different alkaline solution is tested; the mixture of sodium silicate and sodium hydroxide, the mixture of sodium silicate and potassium hydroxide, sodium hydroxide and potassium hydroxide. Second, the concentration of alkaline solution which is varied at 5, 8, 10 and 15M. Third is the process temperature where the geopolymerization is conducted at room temperature, 27^0c and at 90^0C. The fly ash based geopolymer paste would be tested using Vicat needle and the result of this study would be analyzed and explained based on the Avrami's Kinetic Theory. It was found that the addition of sodium silicate into alkaline solution will produce shortest time for solidification geopolymer at 60min followed by sodium hydroxide (NaOH) solution at 90min and potassium hydroxide (KOH) solution at 100min. The increase in concentration of alkaline solution and process temperature shortens the setting time for solidification of geopolymer at 57min for 15M at 90^0C reaction temperature and at 55min for 10M at 90^0C. From the Avrami Kinetic Theory's perspective, the growth form of crystal in the geopolymerization process exhibits mixed structure.

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To Dr. Lukman Bin Ismail, my supervisor I give a very grateful thank you for the constant help, advice, and motivation not only in finishing this project but also in the experience that he had shared all the while I am under his guidance.

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Finally, I express my thanks to all those who had helped me in completing this dissertation whether intentionally or not. To my friends, lecturers, acquaintances, thank you for all that you had given me.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1. Background of study

Fly ash based Geopolymer is a type of concrete based that can act as the basic building materials which is utilized in construction of roads, buildings and infrastructures. It is expected to be widely used in foreseeable future which replaces Ordinary Portland Cement (OPC). OPC is currently the major construction material worldwide. It becomes an important material in concrete production which binds all the aggregate together. However, OPC binder is known as source of environmental damage as it release a large amount of carbon dioxide (CO_2) and decrease of limestone. The manufacturing of OPC requires the burning of huge amount of fuel and decomposition of limestone which will result in CO_2 emission. The OPC production is responsible for 7-10% of total CO_2 emissions worldwide. This places OPC as the third biggest greenhouse gas contributor after transportation and energy generator sectors. The amount of CO_2 emissions increase as the rate grows of OPC industry increase about 5% per year. In the European Commission article, 2004 stated that CO_2 reduction measures will be required to keep the OPC emission in line with the levels set by the Kyoto Protocol. An alternative to replace OPC are being examined in order to further reduce the CO_2 emission which is geopolymer material.

Fly ash based geopolymer is a potential alternative to OPC and high-strength cement for the industry as it is not only minimizing CO_2 emission, but also contributes toward recycling waste material which is economically feasible. The two main components in geopolymer is waste material such as fly ash and alkaline solution. Fly ash is a residue from the coal combustion and rich in alumina and silica. It reacts with alkaline solution such as sodium hydroxide or potassium hydroxide in geopolymerization process to form aluminosilicate gel which binds the fine and coarse aggregates. Geopolymer is the most stable material and it is best alternating product in the earth.

In order to produce fly ash based geopolymer, a few factors need to be considered on the formation of aluminosilicate gel during geopolymerization process. The study of setting time of geopolymer is very essential to produce a good quality geopolymer. The key purpose of this research is to study the effect of different types of alkaline solution, concentration of alkaline solution, and different process temperature on the aluminosilicate gel formation of geopolymer. The main component used in the geopolymerization process is fly ash, alkaline solution such as sodium hydroxide (NaOH) and potassium hydroxide (KOH), sodium silicate (Na_2Si_3) and will be tested at room temperature and at 90^0C. The aluminosilicate gel phase will be tested using Vicat needle. The result will be explained based on the Avrami's Kinetic Theory.

1.2. Aim and Objectives

The aim of this research is to study the setting time of aluminosilicate gel formation on geopolymer concrete.

The objectives of this research that have been identified are:

i) To determine the effect of different types of alkaline solution on the aluminosilicate gel formation.

ii) To determine the effect of different concentration of alkaline solution on the aluminosilicate gel formation.

iii) To determine the effect of different curing temperature on the aluminosilicate gel formation.

1.3. Scope of Study

The main scope of this study is to investigate the aluminosilicate gel formation of geopolymer based on 3 parameters. The parameters are the type of alkaline solution, concentration of alkaline solution, and different process temperature. In this study, the waste material, fly ash is used for geopolymer formation which is rich in silica and alumina. Fly ash is reacted with alkaline solution to form aluminosilicate gel of fly ash based geopolymer. The common types of alkaline solution used in geopolymerization process are sodium hydroxide and potassium hydroxide ant the activator is sodium silicate. The concentration of alkaline solution is tested and varies from 5M to 15M which is 5M, 8M, 10M and 15M. Lastly, the effect of process temperature will be determined by set-up the temperature at room temperature 27^{o}C and 90^{o}C. All this parameter will be tested using Vicat needle and Avarami's Kinetic Theory is used to explain the formation of aluminosilicate gel of geopolymer in geopolymerization process.

1.4. Problem Statement

Geopolymer is a potential alternative to ordinary Portland cement as it is more environmental friendly. However, most of the studied related to geopolymer such as compressive strength, acid resistance, water penetrability and stability of geopolymer are based on chemical and physical properties after setting time. There are only a few researches were conducted to investigate the effect of parameters on the aluminosilicate gel before setting time and explained it from Avrami's Kinetic Theory's perspective (Pauzi, 2013). Hence, this study is focus more on the effect on aluminosilicate gel formation based different types of alkaline solution, concentration of alkaline solution and different process temperature. All the results of the transition of phase is analyzed and explained through Avrami's Kinetic Theory. Base on this theory, the transformation of aluminosilicate gel from nucleation phase until its growth is justified.

1.5. Relevancy of the Project

This project is very important as it deals with the current issue of finding an alternative source of concrete to reduce amount CO_2 emission. This study will provide as an information source in the future for the effect of kinetic formation of the aluminosilicate gel formation of geopolymer.

1.6. Feasibility of the Project

This project is feasible to be conducted in a time scope of two semesters. For the first semester, the time allocated is to gather all the source and information related to geopolymer and parameters effected the solidification of geopolymer concrete. For the second semester, it is more to technical area where all the information obtained and parameter affected is to be investigated. An experiment based and 3 parameters is conducted to study the kinetic formation, analyzed and explained based on Avrami's Kinetic Theory. This study is feasible also because all the materials and apparatus for the project are available and had already been obtained. Thus, the objective of this study will be easily achieved.

CHAPTER 2: LITERATURE REVIEW

This section explains on the concept of geopolymer, process geopolymerization as well as the concept of kinetic formation of aluminosilicate gel in geopolymer. It consists of 3 parameters including different types of alkaline solutions, different concentration of alkaline solution, and different process temperature. The Avrami's Kinetic Theory also been explained. The equipment used for this study which is Vicat needle also been covered up in this section.

2.1. Geopolymer

The term 'geopolymer' was first introduced by Davidovits in year 1978. He describe that the chemical composition of geopolymer is similar to natural zeolitic but different in the microstructure as it is amorphous. (Al-Bakari et al., 2008). Geopolymer is a type of amorphous alumino-hydroxide product that demonstrates the ideal properties of rock forming material such as hardness, chemical stability and sturdiness (Grantham et al., 2011). Geopolymer pioneered by Joseph Davidovits is an inorganic alumino-silicate polymer resulting from geochemistry (Kim, Lai, Chilingar, & Yen, 2006). It is synthesized from primarily silicon (Si) and aluminum (Al) materials of by product materials such as fly ash, Metakaolin, Granulated Blast furnace slag and other (Dave & Sahu, 2012). In order to produce Geopolymer, low-calcium fly ash required to be activated by an alkaline solution to produce polymeric Si-O-Al bonds (Hardjito, Cheak, & Ing, 2008). It is the main source used to form geopolymer binder (Bhikshma, Reddy, & Rao, 2012). Geopolymer is a better than OPC in many aspects (Sonafrak, 2010). By substituting with a coal combustion waste product which is fly ash as the constituent, CO_2 emission in cement manufacture can be reduced (Hardjito & Tsen, 2008). Geopolymer concrete also produce more durable infrastructure that can withstand for hundreds of years. It has excellent compressive strength, suffers very little drying shrinkage and low creep (Dave & Sahu, 2012). Table 2.1 shows the energy needs and CO_2 emissions for 1 tonnes of Portland cement and Rock-based Geopolymer cement according to the US Portland Cement Association 2006.

Table 2.1.1: Energy needs and CO2 emissions for 1 tonne of Portland cement and Rock-based Geopolymer cement

Energy needs (MJ/tonne)					
	Calcination	Crushing	Silicate solution	Total	Reduction
Portland Cement	4270	430	0	4700	0
GP-Cement, slag by product	1200	390	375	1965	59%
GP-Cement. Slag manufacture	1950	390	373	2715	43%
CO_2 emissions (tonne)					
Portland Cement	1.000	0.020	-	1.020	0
GP-Cement, slag by product	0.140	0.018	0.050	0.208	80%
GP-Cement. Slag manufacture	0.240	0.018	0.05	0.308	70%

There are two condition of slag that has to be taken into account. It is by product slag which is the blast furnace slag and manufactured slag that is from geological resources. It clearly shown that the total energy need for Portland cement is approximately at 4700 MJ/tonne which is higher than Geopolymer cement, slag by product and slag manufacture which is 1965 MJ/tonne and 2715 MJ/tonne respectively. In addition, there is a reduction of approximately 43% to 50% of energy needs for slag by product and manufacture respectively of Geopolymer cement while there is no reduction of energy needs during Portland cement manufacture For CO_2 emission, Portland cement produce a total of 1.020 tonnes CO_2 compared to geopolymer cement, slag by product and slag manufacture which are only 0.208 tonnes and 0.308 tonnes respectively. It shows that Portland cement emit higher amount of CO_2. There is a reduction of 70% to 80% of CO_2 emission during slag by product and manufacture of Geopolymer cement while there is no reduction of CO_2 emission during Portland cement manufacture.

2.2. Geopolymerization

Geopolymerization is a process of forming monomers in a solution and then thermally produce solid polymer. It is invented by Davidovits in 1979 as a 3 dimensional alumina silicates (Bondar, 2011) and it is an exothermic reaction process. The formula is $Mn[-(SiO_2)z-AlO_2]n$ where M is the alkaline cation which indicate the presence of a bond, n is the degree of polycondensation or polymerization and z is 1,2,3 or higher (Rangan, Hardjito, Wallah, & Sumajouw, 1987). In 1950s, a scientist, Glukhovsky working in Ukraine proposed a general mechanism for alkaline activation of material predominantly involving reactive alumina and silica (Duxson et al., 2006). The Glukhovsky model is divided into three stages. The three stages include the dissolution of Al and Si in the alkali solution which involves destruction and coagulation process, orientation or transportation of the dissolved species and condensation and crystallization process. Thus it represent polycondensation which form a three dimensional network of silica-aluminates structures, ring structure consist of Si-O-Al-O bond.

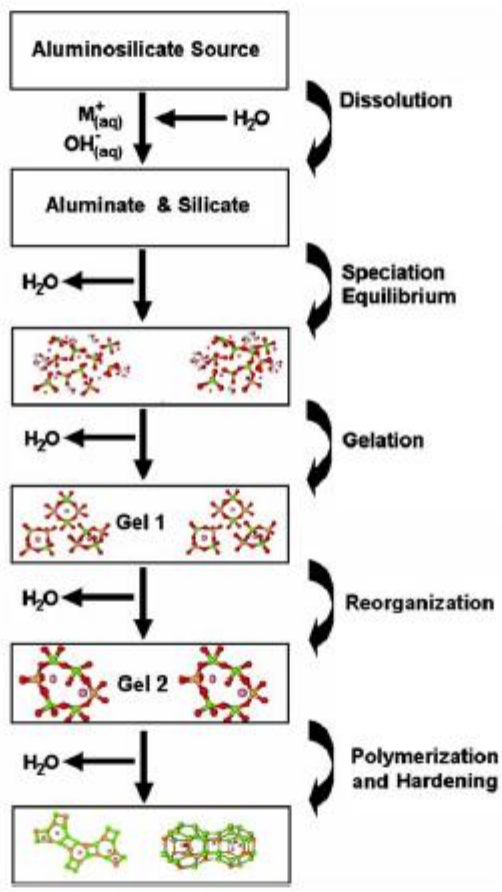


Figure 2.2.1: Conceptual model for geopolymerization (Duxson et al., 2006)

Figure 2.2.1 represents a highly simplified geopolymerization reaction mechanism which illustrate the key processes occurring in the transformation of a solid aluminoslilicate source into a synthetic alkali aluminoslilicate which is geopolymer (Duxson et al., 2006). In the process of dissolution of alumina and silica, it is dissolve by alkaline hydrolysis which consumes water. The dissolution of solid particle alumina and silica in fly ash resulting the liberation of aluminates and silicate which most likely in monomeric form. Once the species, silicate and aluminates released is merged into aqueous phase which is activating solution. A complex mixture of aluminoslilicate species formed.

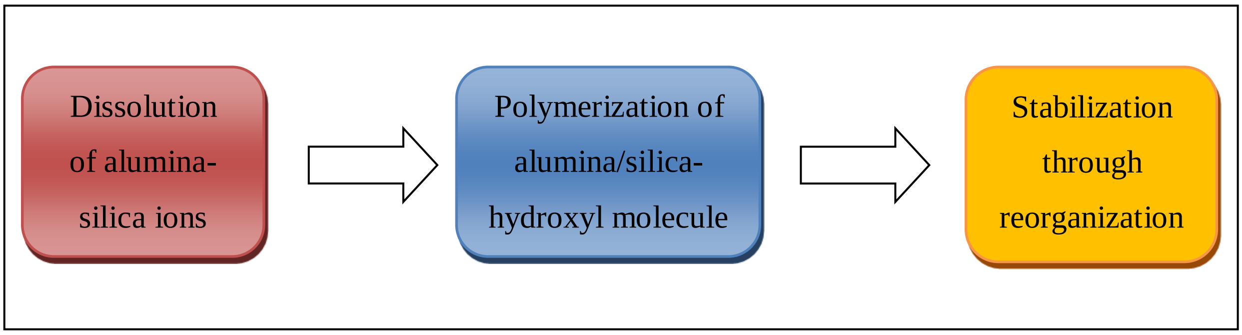
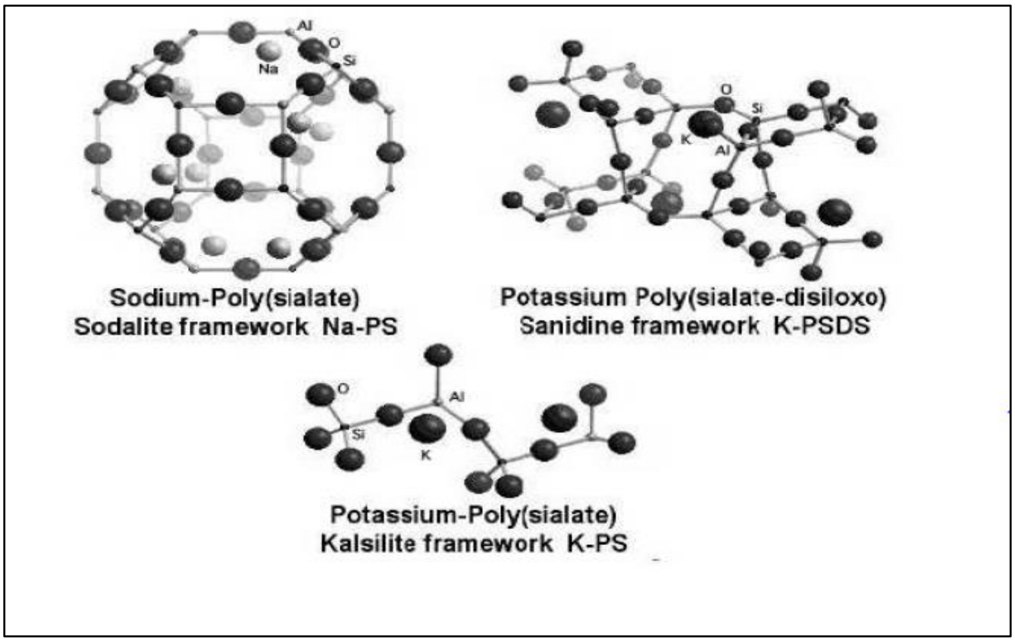


Figure 1.1.2: The summarized of geopolymerization process

There are three classification of organic polymers in geopolymer which depends on the ratio of Si/Al in their structures (Bondar, 2011). It's Si/Al molar ratios with value of 2,4 and 6 represent the below structure respectively.

a) Poly (sialite) (-Si-O-Al-O-)
b) Poly (sialate-siloxo) (-Si-O-Al-O-Si-O-)
c) Poly (sialate-disiloxo) (-Si-O-Al-O-Si-O-Si-O-)

Low Si concentration results in poly(sialate) polymer structure while high Si concentration results in poly(sialate-siloxo) and poly (sialate-disioxo) (Abdullah et al., 2011). This distribution and relative amount of each Al and Si building blocks will affect the chemical and physical properties of the absolute product. Figure below shows the polymetric structure resulting from polymerization on monomers in geopolymer (Abdullah et al., 2011).



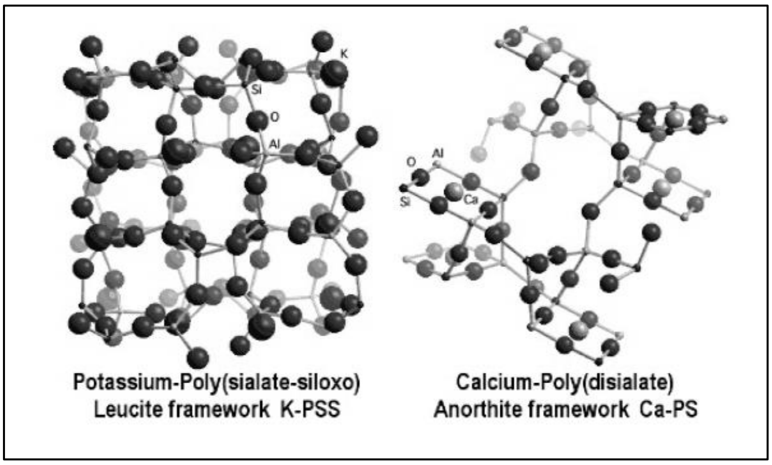


Figure 2.2.2: Polymetric Structures from Polymerization of monomers (Abdullah, Hussin, Bnhussain, & Ibrahim, 2011).

The schematic formation of geopolymer is shown in figure 2.2.3 through equation 1 and 2(Abdul Aleem & Arumairaj, 2012).

$$n(Si_2O_5,Al_2O_2) + 2nSiO_2 + 4nH_2O + NaOH/KOH \rightarrow Na^+,K^+ + n(OH)_3\text{-}Si\text{-}O\text{-}\underset{|\atop (OH)_2}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3 \quad [1]$$

(Si-Al materials) Geopolymer precursor

$$n(OH)_3\text{-}Si\text{-}O\text{-}\underset{|\atop (OH)_2}{Al^-}\text{-}O\text{-}Si\text{-}(OH)_3 + NaOH/KOH \rightarrow (Na^+,K^+)\text{-}(\text{-}\underset{|\atop O}{\overset{|}{Si}}\text{-}O\text{-}\underset{|\atop O}{\overset{|}{Al^-}}\text{-}O\text{-}\underset{|\atop O}{\overset{|}{Si}}\text{-}O\text{-}) + 4nH_2O \quad [2]$$

(Geopolymer Backbone)

Figure 2.2.3: The schematic formation of geopolymer (Abdul Aleem & Arumairaj, 2012)

2.3. Source Material

In creating geopolymer cement, it requires alumina silicate material, an alkali solution ,an alkaline activator and water (Sonafrak, 2010). For alumina silicate material, it can be made from calcined source material such as metakoalin which is calcined koalin, fly ash, slag and rice husk and the strength of geopolymer depends on the nature of source materials (Rangan et al., 1987). Using calcined source material will give higher compressive strength yield compared the synthesized from non-calcined material such as koalin clay. The source material used for geopolymerization can be either single material or a combination of several types of material (Xu & Van Deventer, 2002).

Fly ash is widely used as a source material to make geopolymer paste as the binder to produce concrete (Ramujee & Potharaju, 2013). It is a residue from the combustion of coal which is available worldwide. Thus, fly ash-based geopolymer concrete is a good substitute to overcome the abundant of fly ash (Al Bakri, Mohammed, Kamarudin, Khairul Niza, & Zarina, 2011). The use of fly ash may reduce the total energy demand for producing concrete, reduce the usage of limestone, lower the emissions of greenhouse gasses mainly carbon dioxide into the atmosphere from the concrete industry, and recycle the fly ash that otherwise only disposed in landfill (Al Bakri et al., 2011). Hence, the use of fly ash can make valuable contribution to the reduction of environmental impact from concrete industry.

Fly ash has a very high content of silica (Si) and alumina (Al) will reacts alkaline solution such as sodium hydroxide (NaOH), alkaline activator, sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3) and form aluminosilicate gel(Abdul Aleem & Arumairaj, 2012). The main reason to use fly ash in concrete is that fly ash can increase the life cycle expectancy and increase the durability associated with its use (Abdullah et al., 2011). Further, fly ash improves the concrete permeability by lower the water to cement ratio which cause the reduction in volume of capillary pores remaining in the mass. Fly ash is spherical in shape which improves the consolidation of concrete and also the reduction of permeability. The chemical and mineral compositions of fly ash class F by weight percent are presented in table 2.3.1(Palomo et al., 1998).

Table 2.3.1: The chemical and mineral composition of Fly Ash Class F(Palomo et al., 1998).

Table 1
Chemical composition of the fly ash (% wt)

SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	CaO	MnO	L.O.I.*
53.2	26.0	7.95	0.29	2.59	1.38	0.97	3.57	0.04	2.22

*Loss on ignition.

2.4. Application of Geopolymer

Geopolymer are a new material for coatings and adhesives, new binders for fiber composites, waste encapsulation and new cement for concrete (Davidovits, 2008). It has been explored in many scientific and industrial disciplines and denotes a wide range of potential applications due to its high mechanical strength. The wide variety of potential applications of geopolymer includes the following (Davidovits, 2008).

1) Fire resistant materials
2) Low energy ceramic tiles
3) Refractory items
4) Thermal shock refractory
5) Foundry application
6) Cement and concrete
7) Composite for infrastructures repair and strengthening
8) High-tech composites for aircraft interior and automobile
9) High-tech resin systems
10) Radioactive and toxic waste containment
11) Art and decoration
12) Cultural Heritage, archaeology and history of science.

2.5. Kinetic Formation of Aluminosilicate Gel in Geopolymer

The process of geopolymerization requires waste material and alkaline solution for initiation of reaction in the mineral polymer structures formation. This work will concentrate on issues pertaining the parameters that influence the formation of geopolymer. In order to measure the formation an aluminosilicate gel called geopolymer, 3 parameters need to be considered. The parameters are:

i) Effect of different types of alkaline solution on the aluminosilicate gel formation
ii) Effect of different concentration of alkaline solution on the aluminosilicate gel formation
iii) Effect of different process temperature on the aluminosilicate gel formation.

In the next section, several examples of scientific work will be presented to show the kinetic formation of aluminoslilicate gel in geopolymer based on 3 parameters**.**

2.5.1. Effect of different types of alkaline solution on the aluminosilicate gel formation

In geopolymerization process, there are two elements required in order to form a gel which is aluminoslilicate material and alkaline solution. (Palomo et al., 1998) stated that the types of alkaline solution were the factor affecting the mechanical strength of geopolymer. Sodium hydroxide and potassium hydroxide are used as basic alkaline solution while sodium silicate acts as alkaline activator. The main purpose of alkaline activator is a tool to dissolute fly ash at early stage of process. More dissolution of Si-O and Al-O bonds in presence of OH^- anions in alkaline solution where OH^- will attack the Si-O and Al-O during dissolution phase in geopolymerization process (Provis et al., 2005). It will result in faster setting time for the aluminosilicate gel to form.

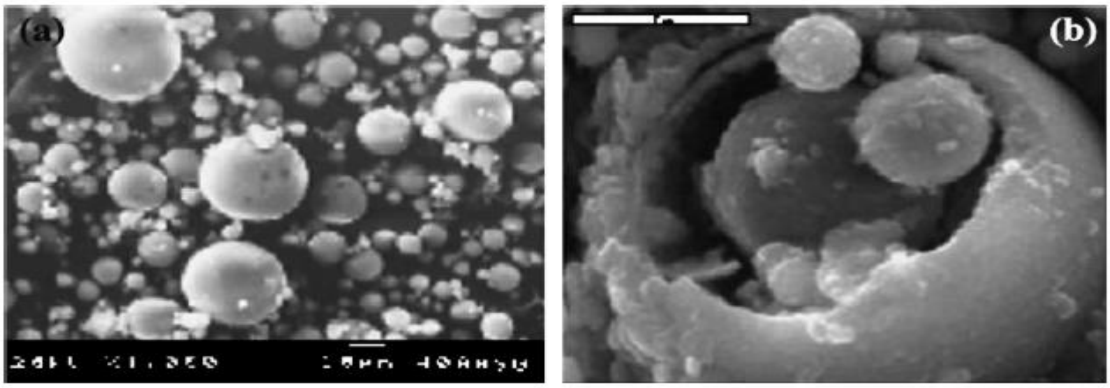


Figure 2.4.1.1: Microstructure of alkaline activation of fly ash a) Original fly ash sphere b) Broken sphere after activated with sodium hydroxide (Pacheco-Torgal, Castro-Gomes, & Jalali, 2008)

The rate of geopolymerization in sodium hydroxide solution is slightly higher than potassium hydroxide (Motorwala et al.,2013). This is due to high extent of dissolution. Thus, more Si-O-Si bond formed which shorten the solidification of geopolymer. However, the reaction between potassium hydroxide with water is slightly less exothermic. Hence, potassium hydroxide is more soluble in water as 121g of potassium hydroxide will dissolve 100ml of water while for sodium hydroxide, 100g of sodium hydroxide will dissolve 100ml of water(Rees, 2007) .This different in characteristic could affect the result of setting time in geopolymer.

(Hardjito et al., 2008) stated that the reaction rate of alkaline solution that contains soluble silicate is higher than reaction rate of basic alkaline solution without silicate. In five years, it's was proven by (Yao et al., 2009) through experiment. The study state that potassium silicate solution has better activation efficiency compared to potassium hydroxide. Figure 2.5.1.2 and 2.5.1.3 shows examples related to the effect of two different alkaline solutions in geopolymerization process.

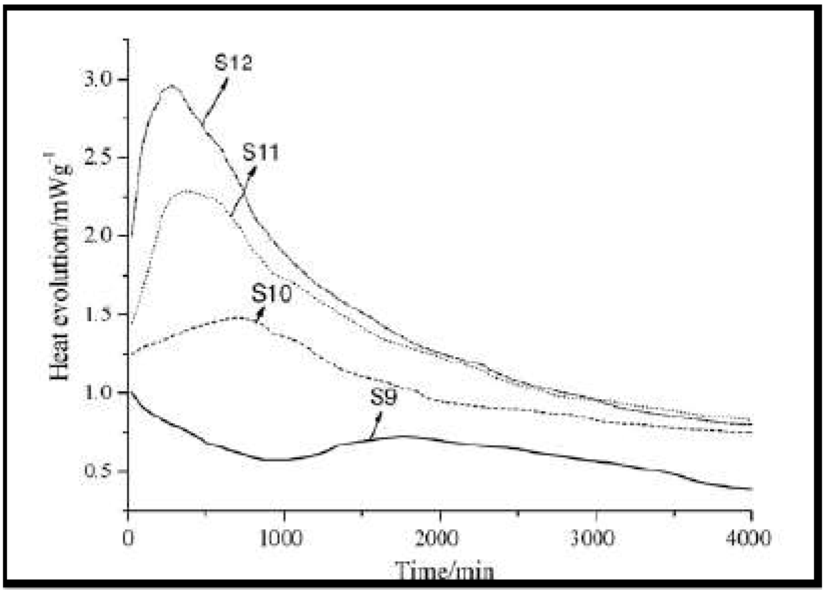


Figure 2.5.1.2: Effect of KOH solution in MK-based geopolymerization

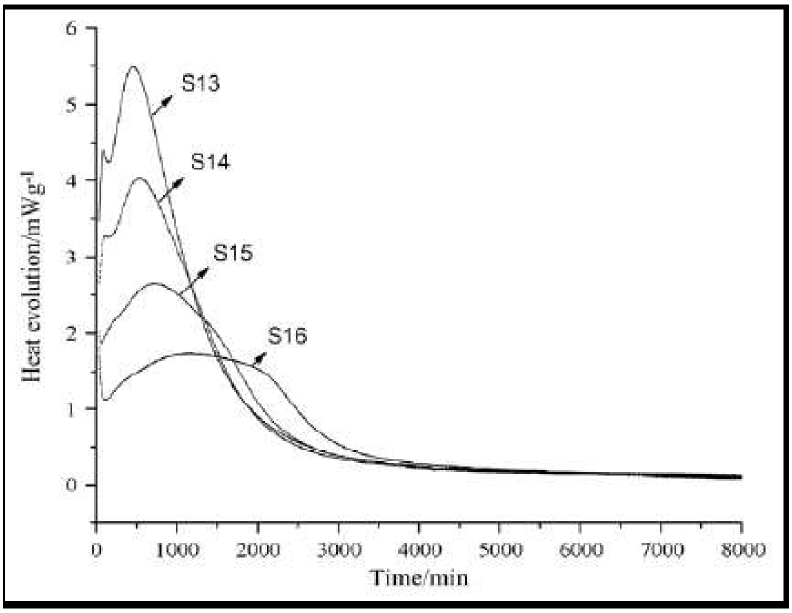


Figure 2.5.1.3:Effect of modulus K-water glass on MK-based geopolymerization(Yao et al., 2009).

Increase in waterglass content in the alkaline solution will increase the geopolymerization rate and provide better strength (Bakria et al., 2011). It helps providing extra SiO_2 in the solution which increase the ratio of SiO_2/Al_2O_3, hence more formation of Si-O-Si bonds formed. This will result to production of stronger geopolymer (Bakria et al., 2011).

2.5.2. Effect of different concentration of alkaline solution on the aluminosilicate gel formation

Different concentration of alkaline solution will produce huge different in compressive strength of geopolymer (Rangan et al., 1987). (Nugteren, Butselaar-Orthlieb, & Izquierdo, 2009) explained that the reaction between aluminosilicate with highly concentrated aqueous alkaline solution will produce a better geopolymer. The increase of soluble silicate concentration in aqueous alkaline solution will significantly increase the reactivity of a class F fly ash at room temperature. Rattanasak and Chindaprasirt, 2009 found the result of measuring the silica and alumina ions at different alkaline concentration. Figure 2.5.2.1 shows the effect of different NaOH concentration on Si^{4+} concentration.

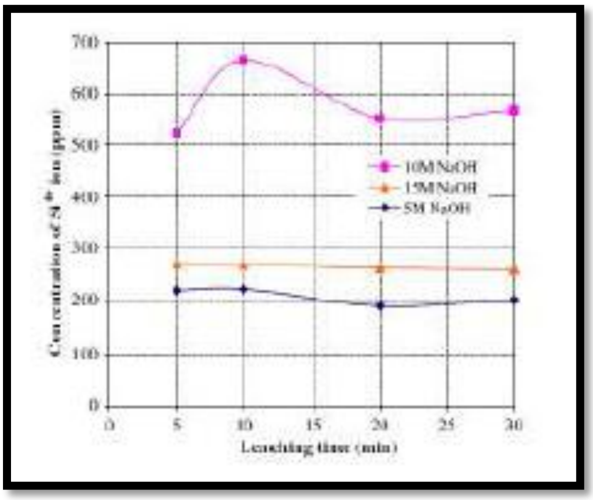


Figure 2.5.2.1: The effect of different NaOH concentration on Si4+ions concentration with fly ash/NaOH = 3: 1 in 5, 10,15M NaOH (Rattanasak & Chindaprasirt, 2009)

Based on the graph, the rate of geopolymerization is low at 5M NaOH due to low base condition, thus the dissolution is low. The highest rate of geopolymerization is at 10M NaOH as the dissolution is high. However, at 15M NaOH, the rate of geopolymerization is slightly higher than 5M NaOH but a very low compared to 10M NaOH. Due to the coagulation in silica (Bergna & Roberts, 2005).

On the other hand, figure 2.5.2.2 show the effect of different NaOH concentration on the Al^{3+} ion concentration.

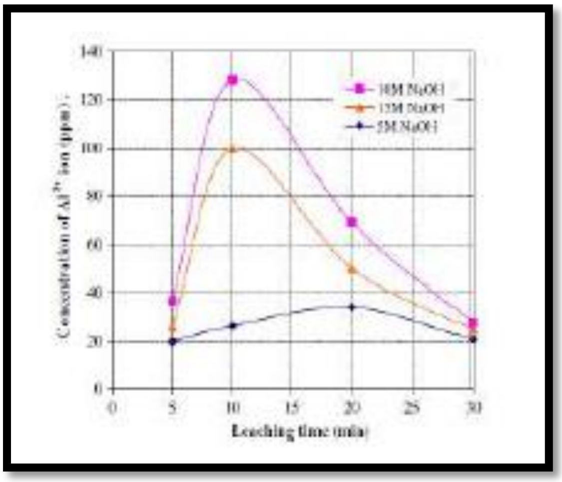


Figure 2.5.2.2: The effect of different NaOH concentration on the Al3+ ion concentration with fly ash/NaOH = 3:1 in 5,10 and 15M NaOH (Rattanasak & Chindaprasirt, 2009)

Based on the graph, a higher concentration of NaOH which is at 10M an 15M contain a higher amount in alumina ions concentration hence the reaction rate is faster compared to the 5M concentration which consequent to low dissolution and reaction rate (Rattanasak & Chindaprasirt, 2009).

Further, Rattanasak and Chindaprasirt, 2009 observed the surface of fly ash before and after leaching with different concentration of NaOH. Figure 2.5.2.3 shows the fly ash surface before and after leached with NaOH for 10 min.

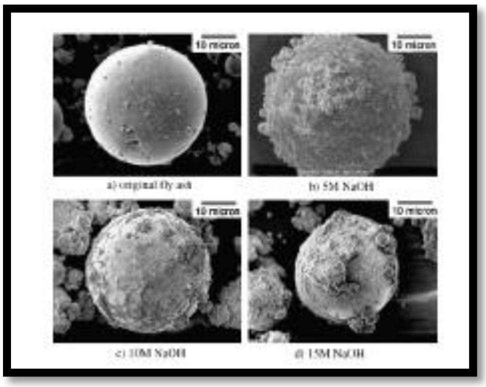


Figure 2.5.2.3: SEM of fly ash surfaces before and after leached with NaOH for 10 min (Rattanasak & Chindaprasirt, 2009)

The surface of fly ash before leaching is represented in figure 8. After leached with NaOH for 10 min, the surface become rougher will increase in concentration. Based on figure (b),(c) and (d), a low dissolution is show at 5M NaOH compared to 10M and 15M of NaOH.

2.5.3. Effect of different temperature on the aluminosilicate gel formation

Geopolymer are synthesized via reaction of aluminosilicate material such metakoalin, fly ash with alkaline silicate solutions at ambient or slightly elevated temperature (Provis, Duxson, Van Deventer, & Lukey, 2005). The effect of different temperature also is one of the major factor that affecting the setting time and the compressive strength of geopolymer(Chanh, Trung, & Tuan, 2008). The rate of geopolymerization will speed up as the temperature increase. Figure 2.5.3.1 shoes the effect of temperature in setting time. The setting time is measured at room temperature and at 60^{o}C. The initial and final setting time is recorded.

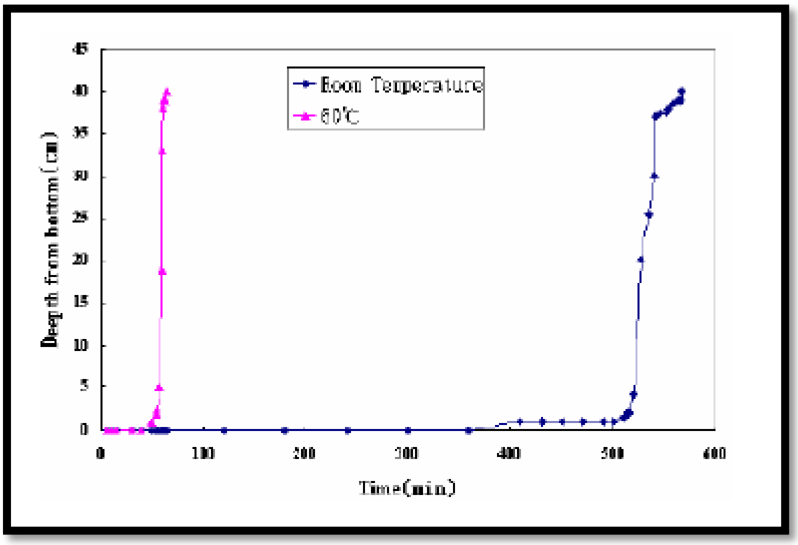


Figure 2.5.3.1: The effect of temperature on setting time at room temperature and at 60°C (Wang and Cheng, 2008)

Based on the graph, It clearly seen that geopolymer at setting time 60°C go faster that at room temperature as the time taken for geopolymer to reach final setting is about 1.5 hours at 60°C while about 9.5 hours at room temperature (Wang & Cheng, 2003). The reason behind this is at 60°C which is the temperature higher than room temperature, a lot of water is loss and hence increase the setting time. It is observed that the best geopolymerization process occurred at the optimum temperature of 60°C and the fact has been proved in the study of influence of temperature on metakaolin-based geopolymer by (Muñiz-Villarreal et al., 2011). Figure 2.5.3.2 shows the effect of temperature on the compressive strength of geopolymer at room temperature and at 60°C.

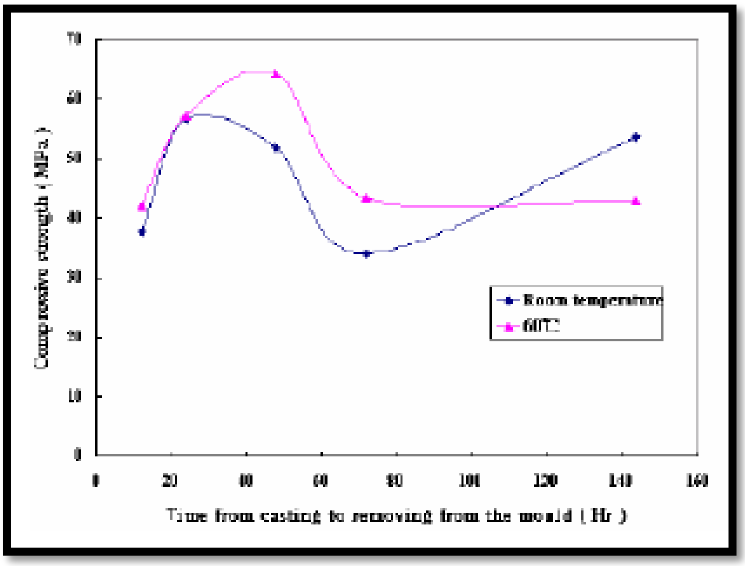


Figure 2.5.3.2: The effect of different temperature on compressive strength of geopolymer (Wang & Cheng, 2003)

Based on the graph, it shows that the compressive strength at 60°C is higher than at room temperature. The reason behind this is the factor of porosity distribution. The compressive strength of geopolymer is dependent on the porosity distribution size in geopolymerization process (Muñiz-Villarreal et al., 2011).

2.6. Avrami Kinetic Theory

The kinetic of transformation theory commonly describes by a standard mathematical equation known as Kolmogorov-Johnson-Mehl-Avrami (KJMA). This theory describes how solids transform from one phase to another at constant temperature.

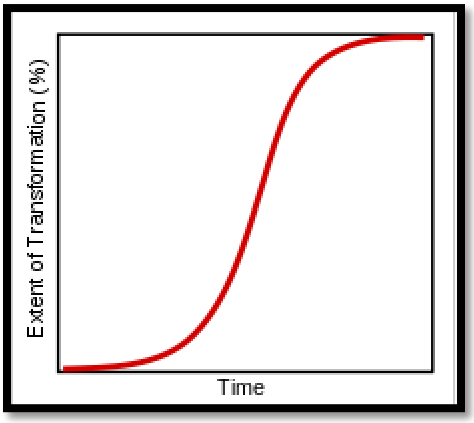


Figure 2.6.1: Isothermal Transformation Plot

Based on figure 2.6.1, the rate of transformation follows a characteristic of the kinetics which is the S-curve where the profile of the transformation rates is low at the beginning and at the end of the transformation but rapid in between. The rate is slow at the beginning because of the time required for a number of nuclei of the new phase to form and grow are long. The transformation is rapid at the transitional period due to the nuclei which grow into particles and the consumption of old phase while nuclei continue to form in the remaining parent phase. At the end of transformation where it begin to near completion, the rate of transformation is slow due to the untransformed material where the nuclei might form in less and the production of new particles begin to slow. The existing particles also contribute to the slow rate of transformation as the particle is in contact with each other and form a boundary that inhibit the crystal growth.

The equation 3 for bulk crystallization of polymers, the crystallization kinetics (Yang, McCoy, & Madras, 2005) can be describe as

$$1 - X = e^{-V_t}, \qquad [3]$$

Where X = The degree of crystallization

V_t = The volume of crystallization material

For sporadic or instantaneous nucleation, Equation can be written as

$$1\text{-}X = e^{-Ktn} \qquad [4]$$

Where K = The growth rate

n = Avrami's exponent

The Avrami exponent,n depends not only on the structure of the crystal but also on the nature of nucleation (Avrami, 1940). Referring to (Ismail et al., 2008) ,the degree of crystalline is first measured by the geopolymer deposition, ∂_r. define as the mass fraction of the crystal deposited on the wall during the cooling process. This statement can be expressed as

$$\partial r = \frac{\partial t - \partial o}{\partial \infty - \partial o} \qquad [5]$$

Where ∂t = deposition at time (min)

$\partial\infty$ = maximum or asymptotic deposition from deposition curve

$\partial 0$ = initial mass of geopolymer content in liquid (g)

Replacing the X in equation 5 with ∂_r in equation 4, and taking log twice in equation 5 can be written as

$$\log[-\ln(1-\delta_r)] = \log K + n\log(t) \qquad [6]$$

Equation 6 the equation of straight line y=mx+c the graph where the graph of log [-ln(1- ∂_r)] versus log(t). The gradient of the straight line in the graph represent the Avrami's exponent,*n* while y-intercept is log K. The graph of log [-ln(1- ∂_r)] versus log(t) can be represented in figure 2.6.2.

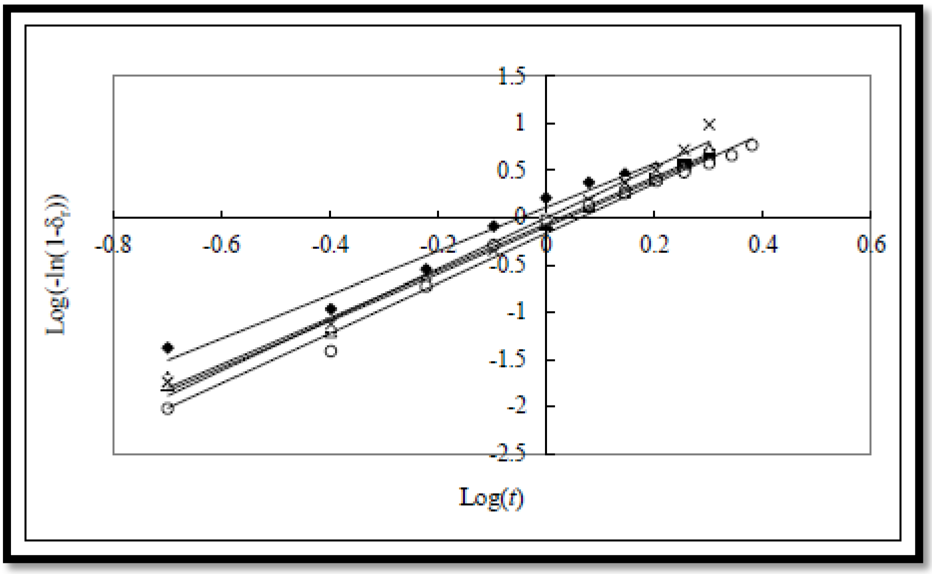


Figure 2.6.2: log [-ln(1- ∂_r)] versus log(t) (Ismail et al., 2008)

2.7. Vicat Needle

Vicat needle is the most common apparatus used to measure the setting time of cement, aluminosilicate gel in geopolymer where it measure from liquid phase to solid phase. Two test methods are given subjected on material. First, Method a known as Reference Test Method whereby using manually operated standard Vicat apparatus while Method B permit the use of an automatic Vicat machine (International Standard Worldwide). The values stated in the Vicat measurement is in millimeter (mm) that shows the depth of penetration on the sample tested in order to determine the material's hardness as shown in Figure 2.15.

Figure 2.7.1: Manual (left) and automatic (right) Vicat apparatus

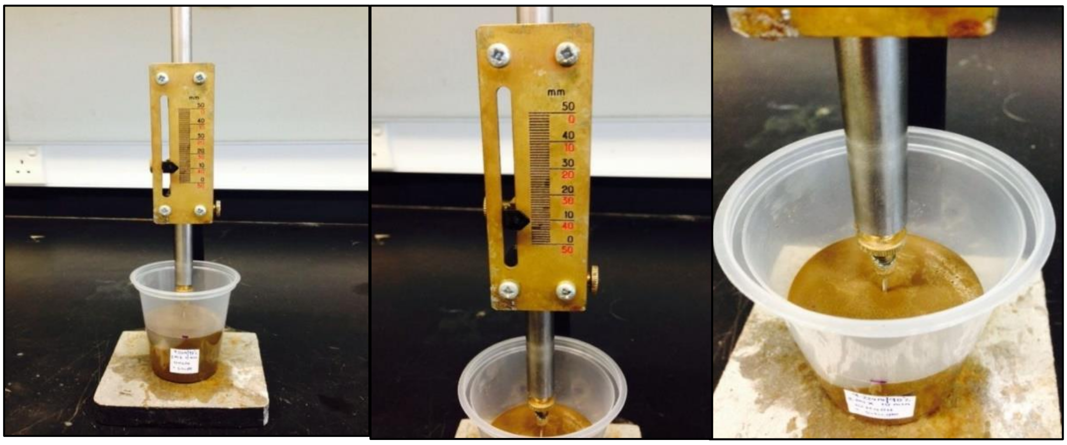


Figure 2.7.2: Vicat needle used to measure the transformation phase from liquid to solid

Vicat needle apparatus is used in geopolymer field in order to measure the setting time for aluminosilicate gel formation process from liquid to solid. Normally, the Vicat Needle ASTM C191-04 is used in testing the geopolymer's hardening with the needle's diameter of 1.00±0.05mm and 10.00±0.05mm. However, the best needle's diameter o be used in measuring the setting time of geopolymer's hardening is 1.00±0.05mm (Nath & Sarker, 2012).

The working principle of Vicat needle is beginning with material tested with the depth of 40 mm will be placed at the centre of the specimen under the 10mm end of Vicat needle and the movable rod is lowered until the needle end makes contact with the material phase. The indicator of measurement is set at zero and movable rod will be allowed to free fall for penetration of needle. The depth of penetration will be recorded and repeated every five minutes until the material solidified. The solidification of material can be identified once the Vicat needle unable to penetrate the material (Hardjito et al., 2008).

CHAPTER 3: METHODOLOGY

This chapter explains in detail all the related procedures during conducting the experiment. Overall process flow diagram of the research methodology to study the kinetic formation of aluminosilicate gel of geopolymer in present study is presented in research methodology section 3.1. Experimental methodology is presented in section 3.2.

3.1. Research Methodology

The methodology used in conducting this research project is based on the discovery and experiment. First, gather all the important information about geopolymer from the previous journal, paper work and engineering book and compiled it as literature review. The research continues with conducting the pre-experiment to determine the feasibility of equipment's used in solidification of geopolymer followed by other experiments to determine effects of parameters on the solidification of geopolymer. Parameters selected in this research are different types of alkaline activator, different concentrations of alkaline solution and different temperature curing. Lastly, all the results from the experiment will be demonstrated and analyzed based on the Avrami's Kinetic Theory.

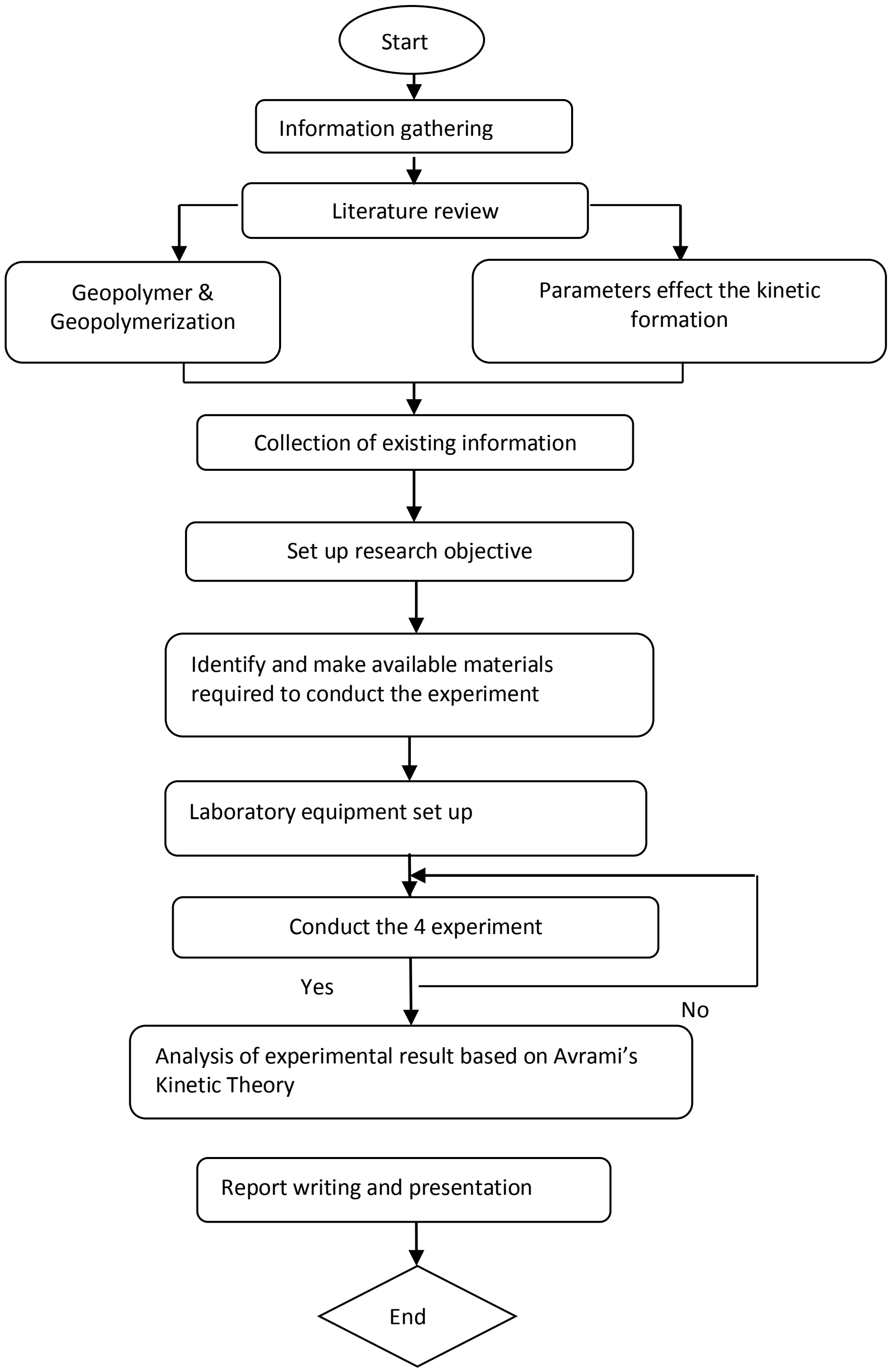


Figure 5: Figure 3.1: Flow chart of The Kinetic Formation of geopolymer Study

3.2. Experimental Methodology

There are 3 sets of different experiment need to be carried out in order to fulfill the objectives of this research. Each parameter proposed in the objectives will be tested using different experimental method to achieve an accurate result. However, all methodology for these 3 sets is similar but differs in term of type of alkaline activator, concentration alkaline activator and process temperature. The ratio of solid to liquid is set to 3:1 as it is not too dilute and not too concentrated.

Below are the key steps in conducting the experiment for geopolymerization process.

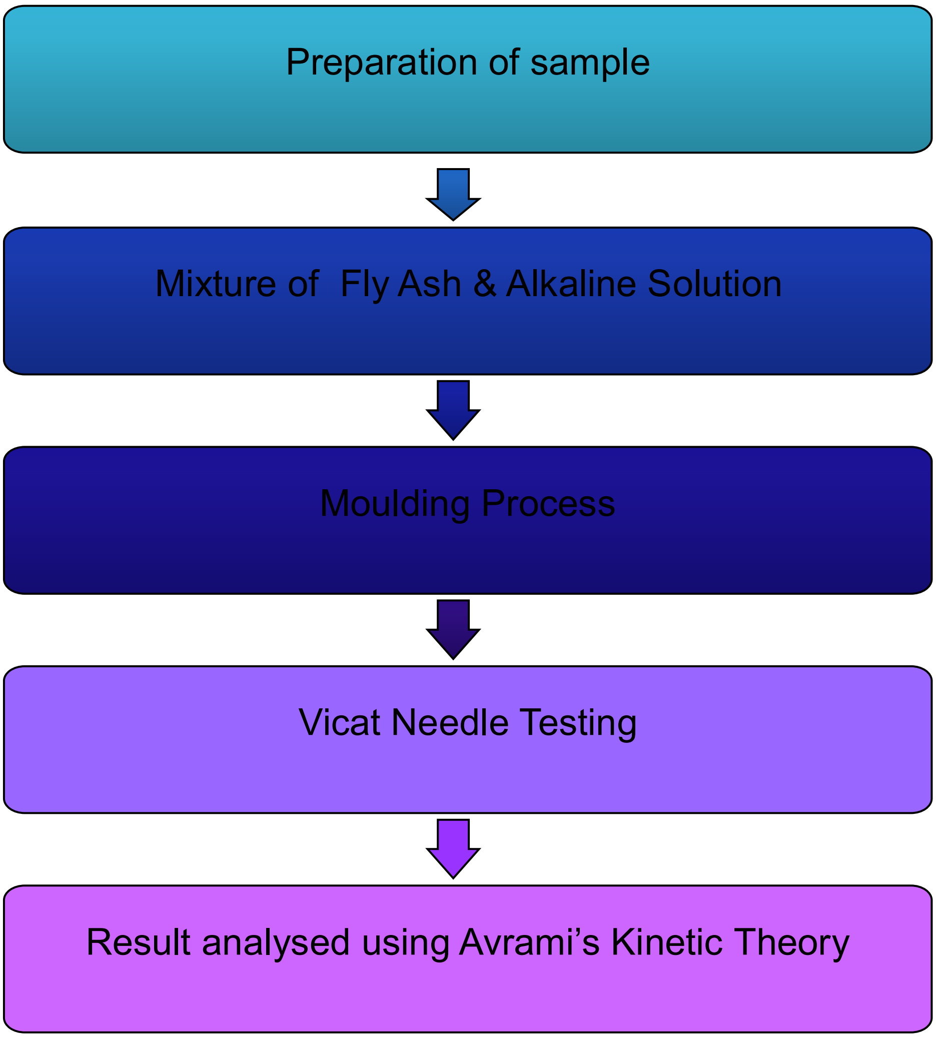


Figure3.2.1: The key steps to produce fly ash based geopolymer

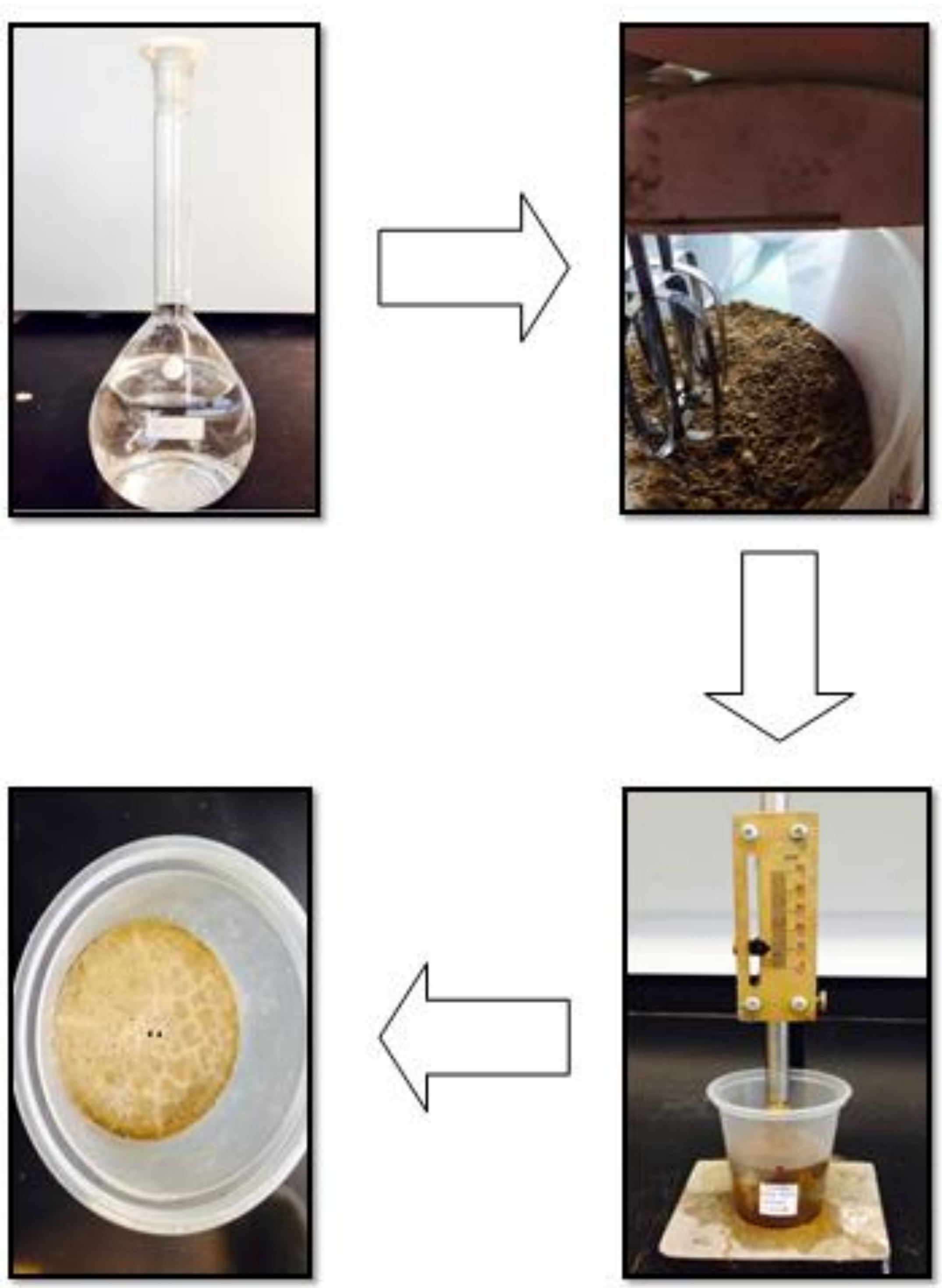
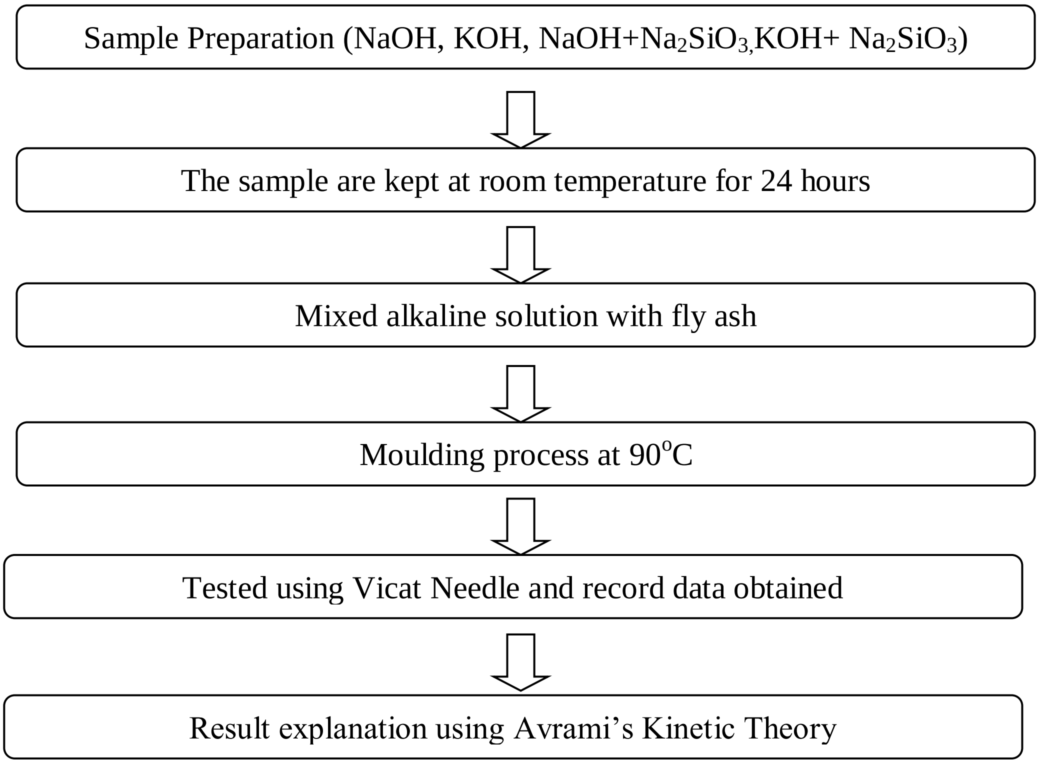


Figure 3.1.2: The diagram of fly ash based geopolymer formation process

3.2.1. Experiment 1: Effects of different types of alkaline activator

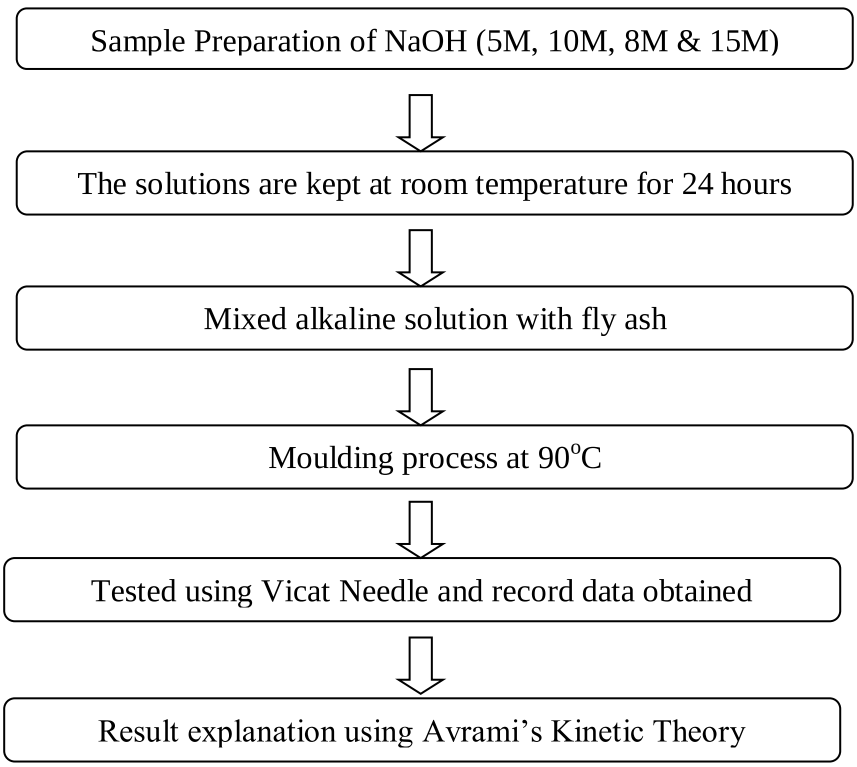
In this experiment, there are three types of alkaline solution proposed to be used which are sodium hydroxide solution (NaOH), potassium hydroxide (KOH) and sodium silicate solution (Na_2SiO_3). First, 1 sets of samples of NaOH, KOH and NaOH + Na_2SiO_3 with concentration of 10M (high dissolution of ions) are prepared. The solutions are kept in store at room temperature for 24 hours to release heat. Next, the sample are then mixed and molded with fly ash powder. The mixture is exposed it to the setting temperature (90^{o}C) .The mould is tested using Vicat needle in every 5 minutes until the material solidified. The solidification of material can be identified once the Vicat needle unable to penetrate the material and data is recorded. Finally the result is analyzed based on the Avrami's Kinetic Theory.



Summary of procedure for Experiment 1

3.2.2. Experiment 2: The Effect of different concentration of alkaline solution

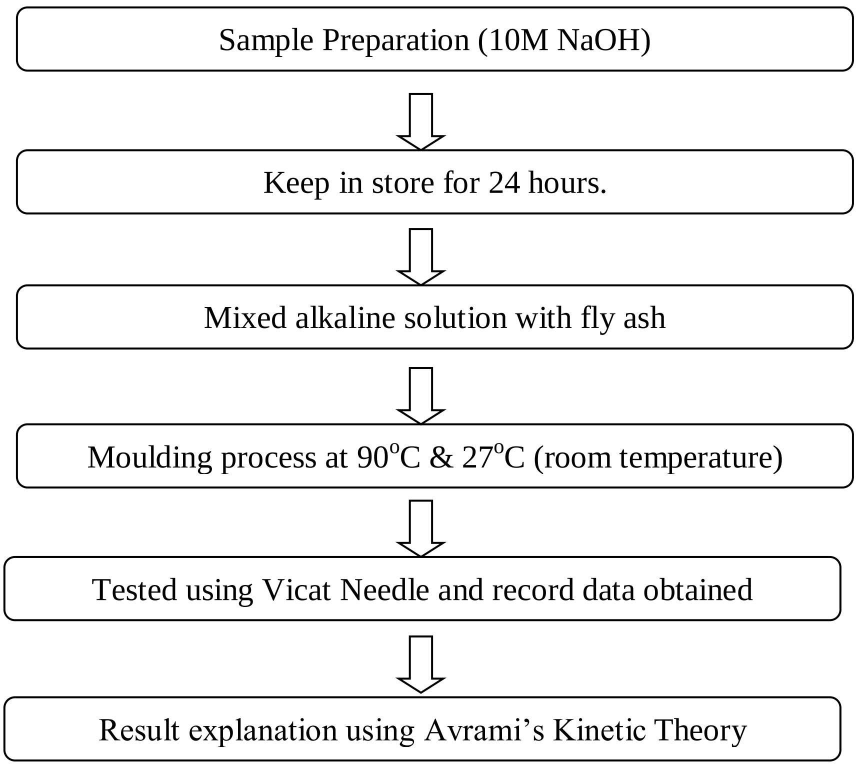
In this experiment, there are 4 values of different concentration of alkaline solution where the concentration of the solution at 5M, 8M, 10M and15M (Muduli et al., 2013). First, 1 sets samples of NaOH solution with concentration of 5M, 8M, 10M and 15M are prepared. All solutions are kept in store at room temperature for 24 hours to release heat. Next, the samples are then mixed and molded with fly ash powder. The mixture is exposed it to the setting temperature (90°C). The mould is tested using Vicat needle in every 5 minutes until the material solidified. The solidification of material can be identified once the Vicat needle unable to penetrate the material and data is recorded. Finally the result is analyzed based on the Avrami's Kinetic Theory. Repeat for error analysis/statistical analysis.



Summary of procedure for Experiment 2

3.2.3. Experiment 3: The effect of Different process Temperature

In this experiment, there are two temperature of alkaline solution proposed to be used which are 90^{o}C and room temperature, 27^{o}C. First, 1 sets of samples of NaOH solution with concentration of 10M (high dissolution of ions) are prepared. Both solutions are kept in store at room temperature for 24 hours to release heat. Next, Na_2SiO_3 solution is added into one of NaOH solution. These sets of samples are then mixed and molded with fly ash powder. The mixture is exposed it to the setting temperature (90^{o}C) and room temperature (27^{o}C). The mould is tested using Vicat needle in every 5 minutes until the material solidified. The solidification of material can be identified once the Vicat needle unable to penetrate the material and data is recorded. Finally the result is analyzed based on the Avrami's Kinetic Theory.



Summary of procedure for Experiment 3

3.3. Key Milestones

Several key milestones for this research project must be achieved in order to meet all the objectives of this project:

Problem Statement and Objective of the project

Identifying and understanding the purpose of the kinetic formation study of geopolymer

↓

Literature Review

Gathering as much information as possible for geopolymer, parameter involves from various sources such as journals, books and websites

↓

Experiment Design

Identifying the parameters that need to be investigated and the experimental procedures, as well as the chemicals needed and the collection of results to be analyzed in Avrami's Kinetic Theory

↓

Data Analysis and Interpretation

The findings obtained are analysed based on Avrami's Kinetic Theory and interpreted critically.

↓

Documentation and Reporting

The whole research project will be documented and reported in detail. Recommendations or aspects that can be further improved in the future will also be discussed.

3.4. Gantt chart and Key Milestones

Final Year Project II

N	Detail Work	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Experiment Data Gathering and progress report														
2	Submission of Progress Report							•							
3	Experiment Data Gathering continued (analysed based on avrami kinetic theory)and pre-sedex														
4	Pre-Sedex Presentation and preparation final										•				
5	Submission of Draft final report														
6	Submission of soft bound dissertation												•		
7	Submission of technical paper												•		
8	Viva													•	
9	Submission of project dissertation –hard bound														•

Key Milestones or Agendas:

- Submission of Progress Report
- Poster Preparation and Pre- sedex Presentation
- Submission of Soft bound Dissertation
- Submission of technical paper
- Project Viva
- Submission of hard bound project dissertation

CHAPTER 4: RESULT AND DISCUSSION

This chapter discusses on the results obtained from the experiments conducted and the kinetic analysis from Avrami's theory. The study of setting time of aluminosilicate gel formation on geopolymer concrete is conducted based on 3 parameters. Thus, the chapter is divided into subchapters which are

4.1. Experiment 1: The effect of different alkaline solution
4.2. Experiment 2: The effect of alkaline concentration
4.3. Experiment 3: The effect of different temperature
4.4. Kinetic Analysis

4.1. Experiment 1: The effect of different alkaline solution

The purpose of conducting this experiment is to study the effect of different type of alkaline solution on aluminosilicate gel formation of geopolymer concrete. There are four types of alkaline solution is tested in this experiment which are 10M sodium hydroxide (NaOH), 10M potassium hydroxide (KOH), 10M sodium hydroxide + sodium silicate (NaOH + Na_3Si_2) and 10M potassium hydroxide + sodium silicate (KOH + Na_3Si_2). The experiments are carried out at 90^0C. Figure 4.1.1 illustrates the result of different type of alkaline solution.

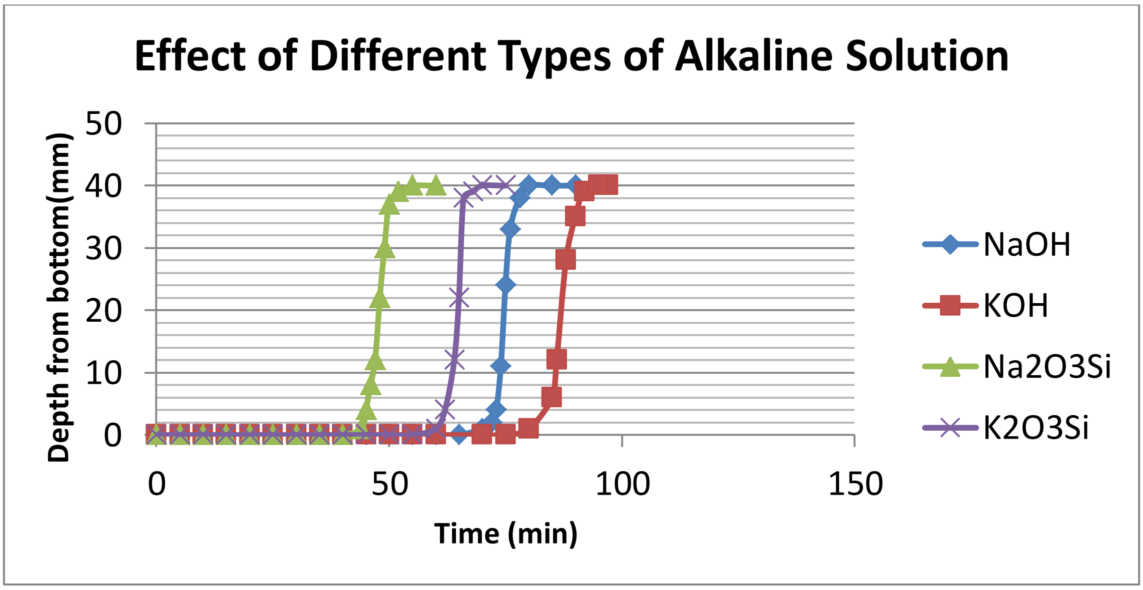


Figure 6: The Effect of Different Types of Alkaline Solution

Based on the figure 11, it is shown that the types of alkaline solution affect the setting time of aluminosilicate gel of geopolymer. From the graph, it is observed that the time taken for geopolymer to solidify for NaOH is 90min, KOH is 100min, NaOH + Na_3Si_2 is 60min and KOH + Na_3Si_2 is 75min. First, the addition of silicate to the NaOH and KOH in the geopolymerization process gives a faster reaction solidification compared to NaOH and KOH without silicate addition which is to be expected. The purpose of adding the activator is to dissolute more at the early stage which will accelerate the process of geopolymerization. The mixture of NaOH + Na_2SiO_3 with a ratio of 0.85:0.15 give the fastest setting time among the others followed by the mixture of KOH + Na_2SiO_3, the NaOH solution, and lastly KOH solution. The theory stated that KOH gives a faster reaction than NaOH as KOH is less exothermic. However, the value of NaOH and KOH is fluctuated due to parallax error during taking the measurement.

The result clearly showed the types of alkaline activator or solution are the factor affecting the setting time of aluminosilicate gel formation in geopolymer (Palomo et al., 1998). The addition of sodium silicate to the alkaline solution gives faster reaction due increase Si^{4+} content in the sodium silicate. As the number of Si^{4+} increase, more dissolution of Si^{4+} in presence of OH^- anions in alkaline solution during dissolution phase in geopolymerization process (Provis et al., 2005) which make the reaction solidify faster thus possess shorter setting time.

Figure 4.1.2: The mixture of NaOH + sodium silicate have a numerous crack on the surface of geopolymer (left) while NaOH reaction with little crack (right)

4.2. Experiment 2: The effect of alkaline concentration

The purpose of conducting this experiment is to study the effect of different alkaline concentration on aluminosilicate gel formation of geopolymer concrete. The alkaline solution used is sodium hydroxide at 90^{0}C and the concentrations are varied from 5M, 8M, 10M and 15M. Figure 4.2.1 illustrates the result of different alkaline concentration.

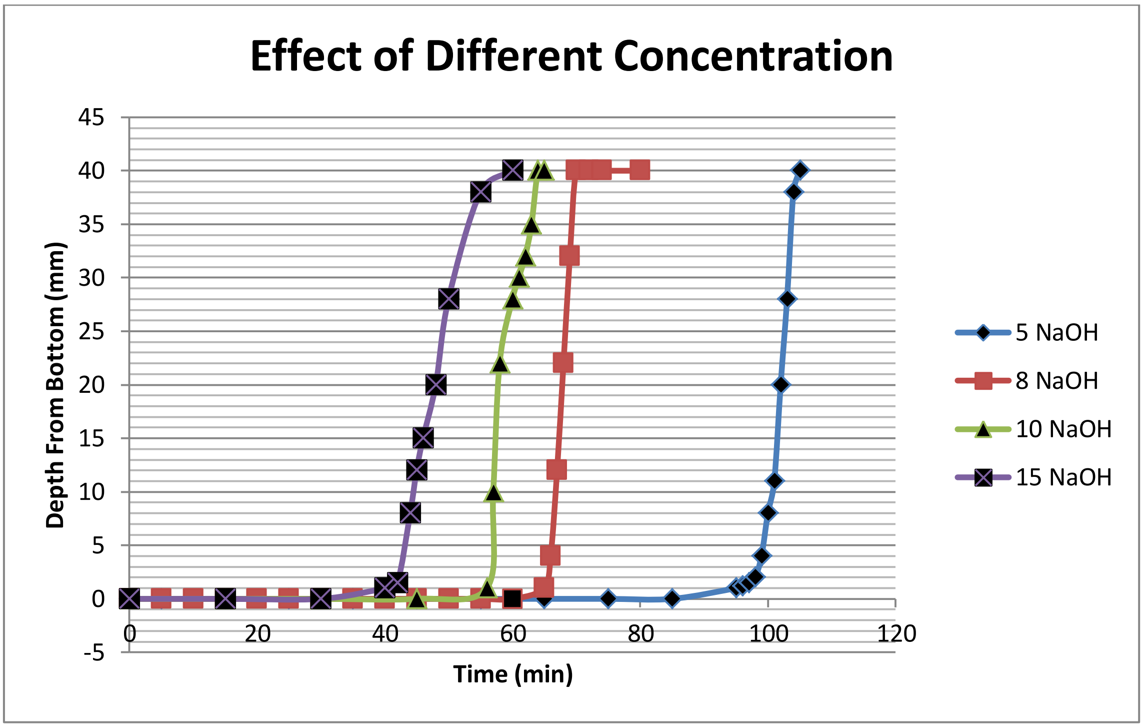


Figure 4.2.1: The Effect of Different Concentration of NaOH

Based on the figure 4.2.1, the different concentration of alkaline solution affects the setting time of geopolymer formation. The concentration is tested at 5M, 8M, 10M and 15 M. The result shows that 15M concentration reacts faster followed with 10M then 8M and lastly 5M. The rate of solidification at 15M is the fastest among the others which is approximately 57 min at 90^{0}C in comparison to 105 min for 5 NaOH.

During the reaction of fly ash and NaOH solution, Si and Al started to leach which lead to dissolution. The higher the concentration, more number of OH^- ions dissolute which will accelerate the process of geopolymerization due to presence of more number of Si^{4+} and Al^{3+} in the solution. Thus, the higher concentration lead to shorter setting time of aluminosilicate gel formation in geopolymer.

4.3. Experiment 3: The effect of different temperature

The purpose of conducting this experiment is to study the effect of different process temperature on aluminosilicate gel formation of geopolymer concrete. The alkaline solution used is 10M sodium hydroxide + sodium silicate and the ratio of solid to liquid is 3:1. The liquid consist of sodium hydroxide and sodium silicate with ratio the ratio of 0.85:0.15. It is varied at room temperature and 90^{o}C. Figure 4.3.1 illustrates the result of different process temperature.

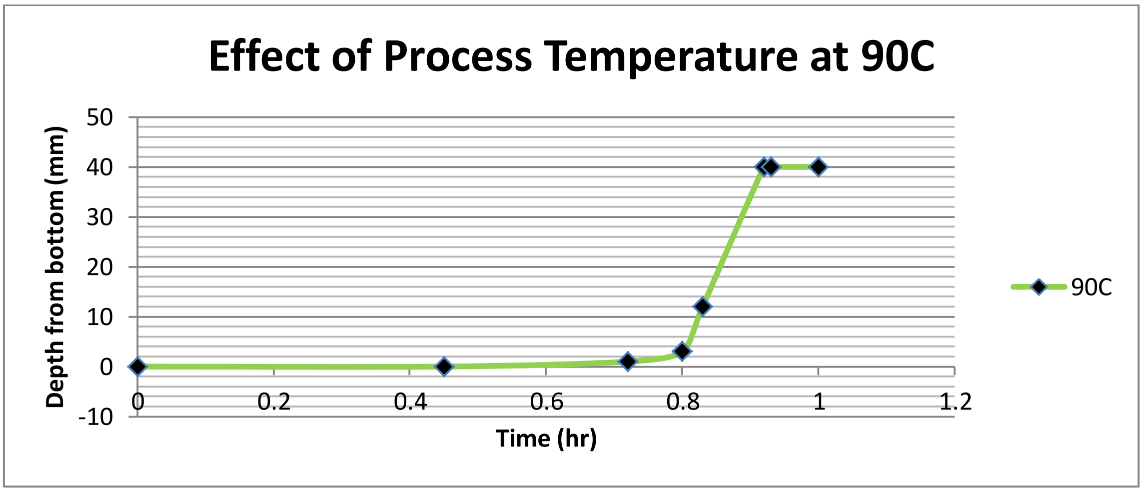


Figure 4.3.1: The Time taken for geopolymer formation at 90C

Based on the graph 4.3.1, the time taken for geopolymer to form at 90^{0}C is approximately at 55min.

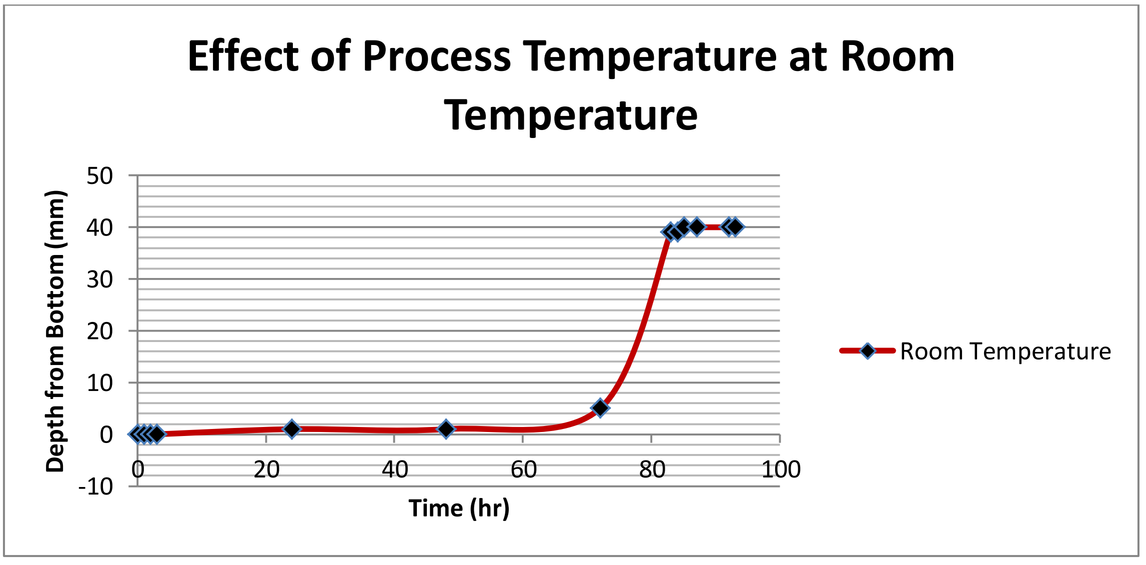


Figure 4.3.2: The Time taken for geopolymer formation at Room Temperature

Based on the graph 4.3.2, the time taken for geopolymer to form at room temperature condition is approximately 93 hours which is about 1 week for it to solidify.

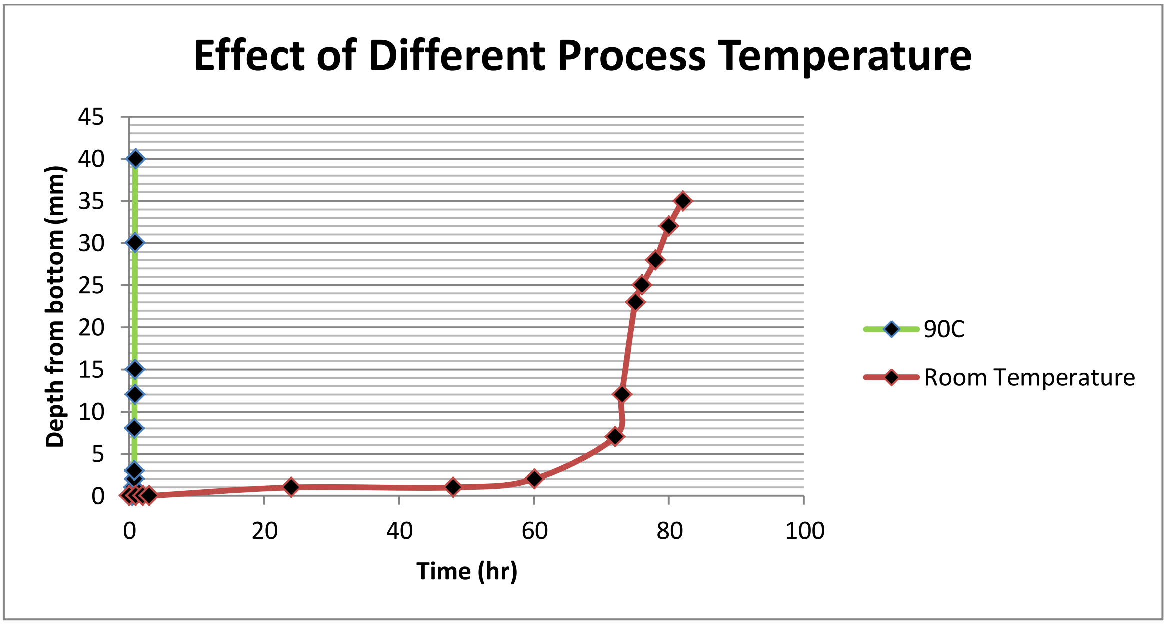


Figure 4.3.3: The Effect of Different Process Temperature

Based on the graph 4.3.3, the result shows that a reaction carried out at 90^0C give a faster reaction compared to when the reaction is carried out in room temperature condition.

The reaction reacts faster at 90^0C compared to room temperature due to the rate of water loss that decreased the setting rate (Pauzi, 2013). As the temperature increases, the kinetic reaction getting higher and faster. Thus, more water is evaporated at 90^0C compare to room temperature condition. This results in a shorter setting time for the solidification of geopolymer at 90^0C.

4.4. Kinetic Analysis

Figure 4.4.1, 4.4.2 and 4.4.3 shows the graph of Avrami's plot for the effect of different type of 10M alkaline solution, different concentration of NaOH and different process temperature of 10M NaOH on the kinetic formation of aluminosilicate gel formation on geopolymer respectively. From the Avrami's plot, the value of Avrami's exponent (n) and growth rate (K) is tabulated in Table 4.4.1, 4.4.2 and 4.4.3.

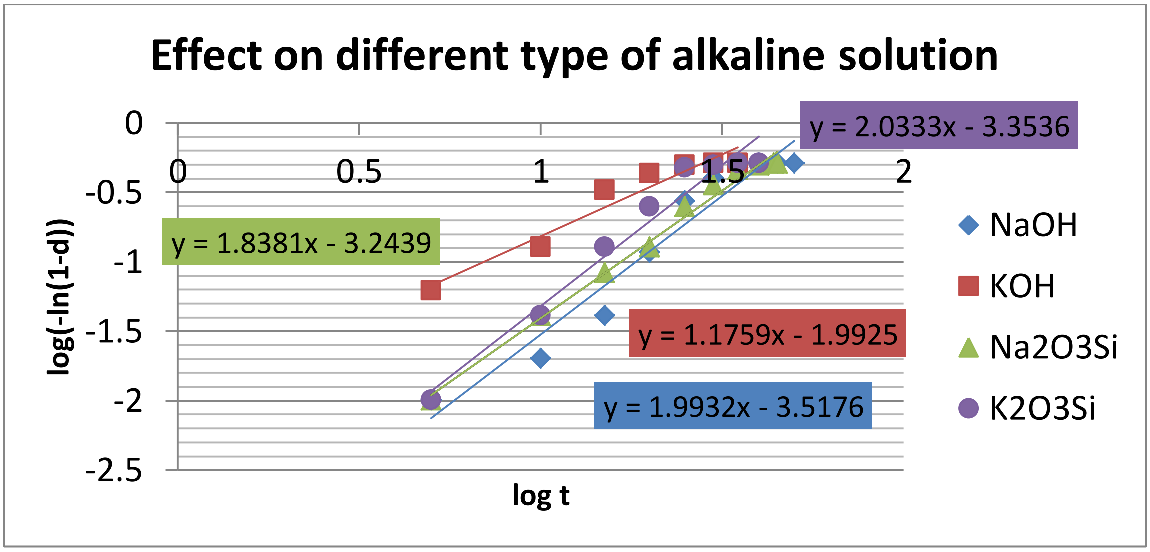


Figure 4.4.17: The Avrami Plot for Different Type of Alkaline Solution at 10M

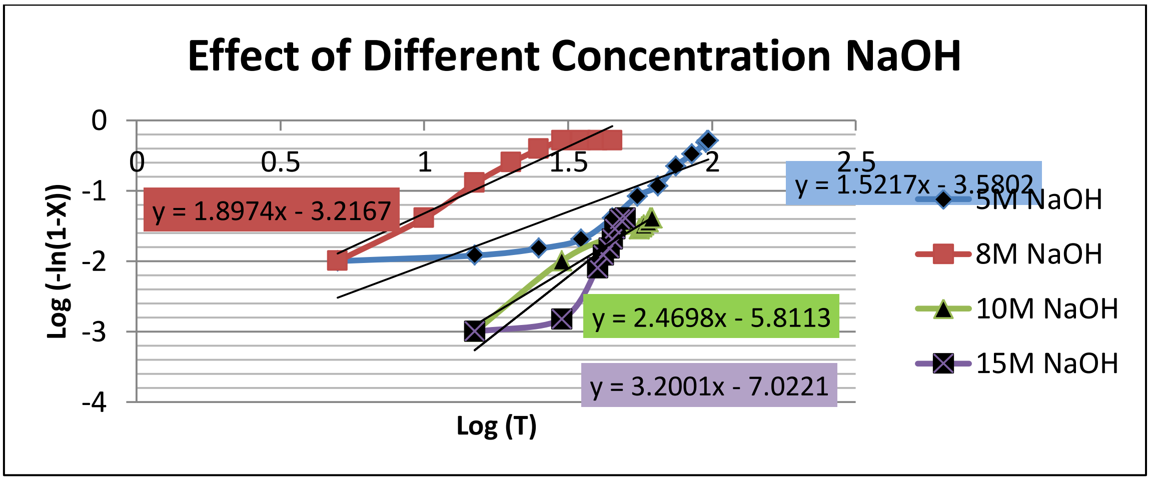


Figure 8: The Avrami Plot for Different Concentration of NaOH

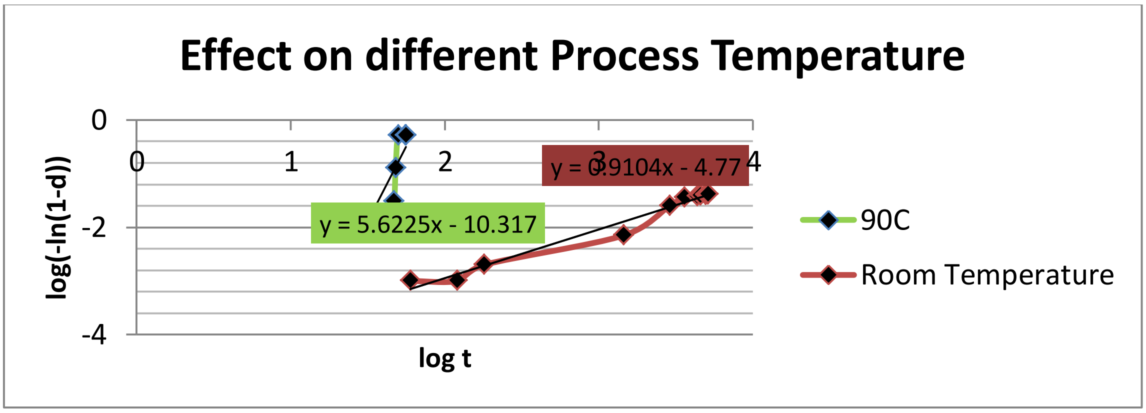


Figure 9: The Avrami's Plot for Different Process Temperature

Table 4.4.1: The Avrami's Exponent (n) and Growth Rate of different types of alkaline solution at 10M

Types of 10M Alkaline Solution	Avrami's Exponent (n)	Growth Rate (K), min^{-1}
NaOH	1.9932	3.0367 x 10 ^-4
KOH	1.1759	1.017 x 10 ^2
Na2O3Si	1.8381	5.703 x 10 ^-4
K2O3Si	2.0333	4.43 x 10 ^ -4

Table 4.4.2: The Avrami's Exponent (n) and Growth Rate of different concentration of NaOH

Concentration of NaOH	Avrami's Exponent (n)	Growth Rate (K), min^{-1}
5M	1.5217	2.629 x 10 -4
8M	1.8974	6.072 x 10 -4
10M	2.4698	1.544 x 10 -6
15M	3.2001	9.504 x 10 -8

Table 4.4.3: The Avrami Exponent (n) and Growth Rate(K), of different process temperature of 10M NaOH

Process Temperature	Avrami's Exponent (n)	Growth Rate (K), min^{-1}
Room Temperature	5.6225	4.819 x 10 -11
90	0.9104	1.698 x 10 -5

From the geopolymer paste profile above, some general trends can be observed. First, as the concentration of NaOH increase, the Avrami's exponent decrease. Second, as the temperature of 10M NaOH increase, the Avrami's exponent decrease. The Avrami's exponent is ranging from 0.9 to 5.6. The smallest value of exponent is 0.9104 which is 10M at 90^0C while the highest value of exponent is 5.6225 which is 10M at room temperature.

The Avrami's exponent is very important for determining the geopolymer's growth form. Table 4.4.4 show a derived model for spheres, discs and rods representing 3, 2, and 1 dimensional forms of growth (Hay, 1971).

Table 4.4.4: The Avrami's parameters for crystallization of polymer

Crystallization mechanism	n	Growth form
Spheres		
Sporadic	4	Three dimension
Instantaneous	3	Three dimension
Discs[a]		
Sporadic	3	Two dimension
Instantaneous	2	Two dimension
Rods[b]		
Sporadic	2	One dimension
Instantaneous	1	One dimension

[a] Constant thickness
[b] Constant radius

In table 4.4.1, it shows that exponent of 10M KOH is approximately at 1 which tend to be rod-like shape, in comparison to discs-like shape in 10M NaOH, 10M Na_2O_3Si and 10M K_2O_3Si. This is due to the transition mechanism of geopolymerization. In table 4.4.2, it is observed that 15M NaOH tend to be spherical shape in comparison to discs-like shape at 5M, 8M and 10M NaOH. This result may approach four suggesting sporadic nucleation and the net result of the motion is to change the discs-like crystal into spherical-like crystals (Ismail et al., 2008). In table 4.4.3, it is clearly seen that at 90^0C, 10M NaOH tend to be rod-like shape.

The growth rate (K) is very important for determining the speed of geopolymerization process. The value of Avarami's exponent (n) is inversely proportional to the growth rate (K) value. The value of K will decreases as the value of n increases (Nurhanie., 2012). Based on the profile, it shows that the growth rate of KOH is higher than NaOH which is to be expected. The result is consistent to the theory as KOH will accelerate the geopolymerization process due to less exothermic than NaOH. It is expected the addition of silicate will accelerate the geopolymerization process and higher concentration will accelerate the growth rate. However, the value of K for Na_2O_3Si and K_2O_3Si in experiment 4.1 and concentration of NaOH in experiment 4.2 fluctuated might due to the parallax error during taking the measurement as it diverge from the theory respectively. For the process temperature, it is expected that the growth rate at 90^0C is higher than at room temperature at the water loss faster at higher temperature.

CHAPTER 5: CONCLUSION

5.1. Relevancy to Objective

As a conclusion, this research is important as it deals with alternative ways of concrete. It is believed that geopolymer is the best alternating concrete in reducing CO_2 emission.

The setting time of solidification of geopolymer can be measured based on 3 parameters which are, the type of alkaline solution, concentration of alkaline solution and process temperature. This 3 parameters play s significant role in the kinetic formation of aluminosilicate gel in geopolymer. It can be concluded that:

- The best alkaline solution for geopolymerization is alkaline solution with an addition of sodium silicate as an alkaline activator.
- When no addition of activator, KOH is a better alkaline solution in comparison with NaOH.
- Increase in concentration up to 15M will increase the rate of geopolymerization which give a faster growth rate according to Avrami's kinetic theory.
- Increase in temperature up to 90^0C will increase the rate of geopolymerization which give a faster growth rate according to Avrami's kinetic theory.
- The Avrami's exponent plays an important role for determining the growth form of geopolymer while growth rate to determine the speed of solidification of geopolymer.
- 15M NaOH tends to form spherical-like shape which growth form of 3 dimensional.

The study is showing good progress .The project is within capability of a final year student to be executed with the help and guidance from the supervisor and the coordinator. The time frame is also feasible and the project can be completed within the time allocated. It is hoped that the acquiring of equipment and materials needed for the experiment runs smoothly for the accomplishment of this project at the end.

5.2. Research Continuation

Further research work can be done with the experiment. Another parameter can be investigated in this study is:

- The effect of speed of the reaction during the mixing time of fly ash and alkaline solution on the kinetic formation of geopolymer.
  It is to measure the kinetic formation of geopolymer based on the speed of reaction during mixing. The value can be varied from 5min, 10min 15min and 20min.
- The effect of liquid to solid ratio on the kinetic formation of geopolymer.
  It is to measure the kinetic formation of geopolymer based on ratio of liquid to solid. The value can be varied from a very dilute solution to a very concentrated solution such as liquid to solid ratio is set at 1:3, 2:2 and 3:1.
- The effect of fly ash, metakoalin and slag on the kinetic formation of geopolymer.
  It is to measure the kinetic formation of geopolymer based on raw material which is fly ash, metakoalin and slag.

5.3. Recommendation

In future work plan, there are a few recommendations are suggested to improve this project study:

- The data taken from vicat needle should be taken when the transformation of liquid to solid started and the data should be close enough to obtain an accurate result of Avrami's plot.
- The position of eyes during taking the needle measurement must be perpendicular to the scale to avoid parallax error and obtain accurate result which will affect the Avrami's exponent.

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