GEOPOLYMER FORMATION ANALYSIS

By

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

Approved by,

____

(Dr. Lukman Bin Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is 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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(NORHANISAH BINTI MANSUR)

ABSTRACT

Inorganic polymer concretes, or ‘geopolymers,’ have become engineering materials with the potential to become an important element in environmentally sustainable construction and building products industry. These materials are commonly formed by alkali activation of industrial aluminosilicate waste materials such as fly ash and blast furnace slag. Geopolymer concrete production emits almost zero greenhouse gases which is CO_2 when compared to traditional concretes or ordinary Portland Cement (OPC). With correct mixture and formulation development, geopolymeric materials derived from fly ash or other materials can exhibit superior chemical and mechanical properties to ordinary Portland cement (OPC), and be highly cost effective. The present production of geopolymer concrete include low or high strength concretes with good resistance to chloride penetration, fire and/or acid resistant coatings, and waste immobilization solutions for the chemical industries. The study of geopolymer formation will contribute to the greater understanding on geopolymer strength attributes and will helps the engineers to adapt the parameters for suitability of geopolymer production. Later in this project, the subject of geopolymer will be discuss further and several experiment will be conduct to study the geopolymerization process with certain parameter setting. The research will focusing on three main parameter which are study on addition of additives on geopolymer formation, different alkali-activator, and solid loading varition. The result will later tested using Vicat Needle, and will be describe more using Avrami Kinetic Theory.

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Praise to Allah the Almighty, who had blessed me with His guidance and giving me strength to complete this Final Year Project. I feel very grateful that I was given the strength and courage to complete this project even there are lots of obstacle and challenge to be faced in order to complete my task. I believe all of this has been planned carefully by him as He is the best planner.

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Last but not least, all of these would not materialize without my family and friends who have been supporting me throughout my final year. I would like to thank my family and friends who always giving me an encouragement and supports along my journey of studies. All of their motivation and support always keep me going throughout the semester.

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CHAPTER 1: INTRODUCTION

1.1 Project Background

A major issue of the environment nowadays is the climate change due to global warming. Global warming is caused by the emission of greenhouse gases, such as Carbon Dioxide (CO_2) which contribute to about 65 % of global warming (McCaffrey, 2002). From cement manufacturing alone, the forecasted green house gas emission is expected to rise about 6% annually from 1988 to 2015(Davidovits, 1994). Ordinary Portland Cement (OPC) is the main ingredient used in the production of concrete, the most widely used construction material in the world (Kong and Sanjayan, 2008). According to Kong and Sanjayan (2008), the manufacturing of OPC requires the burning large quantities of fuel and decomposition of lime stone results in the significant emission of Carbon dioxide. For every tons of OPC manufacturing, approximately one ton of CO_2 being produced and reported to emits up to 1.5 Billion tons of CO_2 into the atmosphere every year. Portland Cement Association (2006) reported, significant increases in cement production have been observed and were anticipated to increase due to the massive increase in infrastructure and industrialization in India, China and South America. Thus, an environmental alternative has become the driving force to search for new sustainable and environmentally friendly composites to replace the current concrete produced from OPC.

In the year of 1978, Davidovits has introduced the inorganic polymer or geopolymer as an alternative cement material which have similar properties with ceramic. According to Davidovits (1984, 2008, 2010), geopolymer cement represent a broad range of material characterized by chain of inorganic molecule. Geopolymer concrete does not utilize any Portland cement in its production. These geopolymer rely on thermally activated natural materials (example: kaolin clay) or industrial by product (example: fly ash or slag), which is dissolved in an alkaline activating solution and subsequently polymerizes into molecular chains and networks to creare the hardened binder, where such systems are often referred as alkali-activated cements or inorganic polymer cement (CCTP technology program, 2010). According to Aleem and Umairaj (2012), the main constituent of geopolymer is fly ash, rich with the Silica and Alumina that react with alkaline solution like sodium silicate to form gel that binds the fine and coarse aggregates. As opposed to OPC, the manufacture of fly-ash based geopolymer does not consume high levels of energy, as fly ash is already an industrial by product (Kong and Sanjayan, 2008). Gartner (2004), mention that the geopolymer technology has the potential to reduce the emission of CO_2 by 80% to the atmosphere caused by the cement and aggregate industries. Geopolymers offer many advantages such as early strength, high temperature resistance, and acid/alkaline resistance and considered fine engineering material with broad application range (Lyu et al., 2013). It is supported by Yen et al. (2006), where study shows that the geopolymer is the most stable material and best alternative for cement the earth can offer.

To produce geopolymer concrete, there are several factors need to be considered especially during the solidification phase in geopolymerization phase. Duxson et al.(2007), mention that the geopolymer are a highly complex and as yet relatively poorly understood material, there are clearly many areas in which further works is required. While Rovnanik (2010) reported that the mechanical properties of a geopolymer can be examined by analyzing the process parameter .The study of the formation phase is important to produce good geopolymer quality with regards to its chemical and mechanical strength. There are numbers of factors that might affect the final properties of geopolymer likes curing temperature, ageing time, water content as well as types and concentration of alkaline solution (De Silva and Sagoe-Crenstil, 2009). The main purpose of this research is to study the effect of addition of additive (fly ash and 10% kaolin), the effect of different alkaline activator during geopolymerization and the effect of solid and liquid ratio in geopolymer formation. The material used in this research will be fly ash and metakaolin, and will undergo different temperature variation and solid liquid ratio. The solidification phase will be tested using Vicat Needle. The result will be explained and presentated based on Avrami’s Kinetic Theory.

1.2 Problem Statement

Several studies and researches have been carried out on the geopolymer since it been introduced by Davidovits (Nugteren et al., 2008). Most of the works done were covering on the chemical and physical properties of geopolymer after setting time for example, the compressive strength, acid resistance, water penetrability and stability upon firing of geopolymer. According to Duxson et al. (2006), the study about the ability to achive an excellent compressive strength of geopolymetric materials by proper mix design are well-documented. However, there are only few researches on the effect of parameters before the setting time and well explained in term of Avrami's Kinetic Theory. Thus, study on the effect of parameters before setting time of geopolymer will be useful engineers especially in construction industry. This study will be focusing on different parameters that will affect the geopolymer formation and then will be tested using vicat needle for solidification test.

1.3 Aim and Objectives

The aim for this project is to conduct a study and analysis on the geopolymer formation (solidification phase). This research will be conducted based on addition of additives in material mixture with different alkaline solution, at different solid loading value (solid base to alkaline solution ratio). The aim and objectives of the research are;

a) To study effects of addition of additives (flyash with 10% kaolin) with alkaline solution on the geopolymer formation;

b) To study effects of different type of alkaline-activator used (KOH and NaOH) on the geopolymerization

c) To study effects solid loading on the of geopolymer formation.

1.4 Scope of Study

The parameters that will be tested in this project are of addition of additives (flyash with 10% kaolin), different type of alkaline activator and solid loading. The common types of alkaline solution used to produce geopolymer are Sodium Hydroxide and Potassium Hydroxide. The fly ash will react with Sodium Hydroxide or Potassium Hydroxide to forms gel. The alkaline activator that will be used in this research is Sodium Hydroxide and Potassium Hydroxide, and the concentration of Sodium Hydroxide will be set to specific concentration which is 8M. The effect of temperature will be tested by observing the crystallization process of geopolymer at set up temperature at $70^{o}C$ using the Vicat needle. The effect of temperature shall be observed referring to the setting time measurement (Wang and Cheng, 2008). The research will continue solid loading variation where the ratios that will be using in this project are from 2.0 to 3.0 between solid and liquid. All the parameters then will be related with the Avrami Kinetic Theory. The variables tested are limited to ensure that the project shall be completed on time.

1.5 Feasibility, viability and relevancy of the project

The final product of geopolymerization is significant to its parameter setting. This research will further study and investigate on the geopolymer formation that later will be beneficial for the designers and engineers especially in the construction industry for the improvement of geopolymer in the future. This study will help for further understanding on the mechanism of geopolymer formation which now are not most research are focusing on the strength test of the geopolymer product. The project is considered as feasible as all the equipment and material are available at the laboratory in Chemical Engineering Department. The time provided for the research is sufficient for the experiments and research to be conducted and shall be completed within the time specified in the project Gantt chart.

CHAPTER 2: LITERATURE REVIEW

2.1 Geopolymer

In the 1970s, Davidovits used the term geopolymer to describe a type of amorphous-structural material synthesized by the alkaline, alkali-silicate, or phosphoric acid activation of solid alumina and silica containing precursor materials at or above ambient temperatures (Cui et al.,2010; Davidovits, 1991; Duxson et al., 2006; Liu et al.,2010). Geopolymers are amorphous three dimensional aluminosilicate materials with ceramic-like properties that are produced and hardened at ambient temperature. Under highly alkaline conditions, in the presence of alkali hydroxide and silicate solution, polymerization takes place when reactive aluminosilicates are rapidly dissolved and free [SiO4] and [AlO4] tetrahedral units are released in solution. The tetrahedralunits are alternatively linked to polymeric precursors by sharing oxygen atoms forming thus amorphousgeopolymers.

The amorphous to semi-crystalline three dimensional silico-aluminate structures are illustrated in Fig. 1.

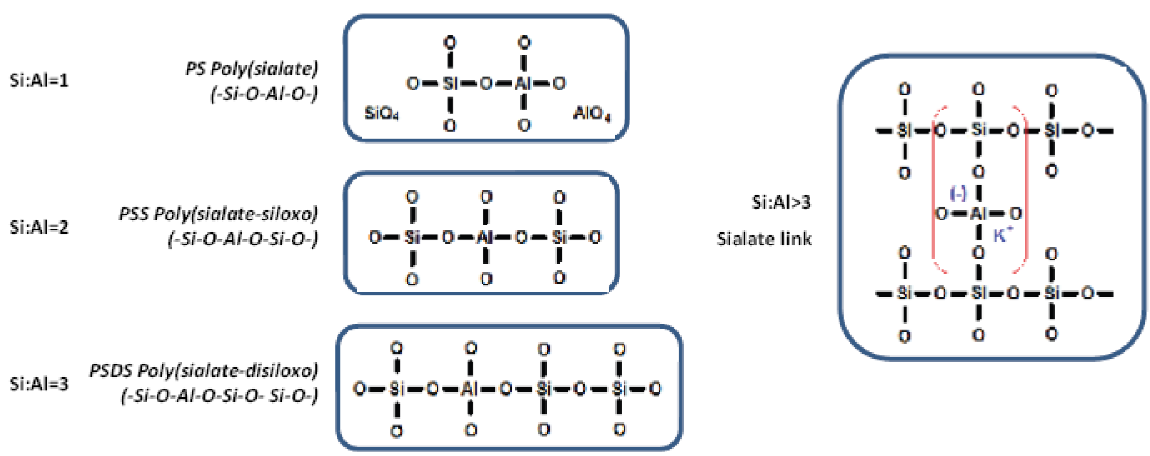

Figure 1: Geopolymer Terminology (Komnitsas, 2011)

In a broader sense geopolymers indicate transformation of geomolecules through geochemical processes during diagenesis and can be classified into two major groups: pure inorganic and organic containing synthetic analogues of naturally-occurring macromolecules. The term geopolymer as initially proposed refers mainly to pure inorganic materials but could be extended to include geomaterials with organic content. It is known than ancient Egyptians used straw and riverine mud containing organics (e.g. humic materials) to manufacture construction components of remarkable strength and durability. Roman concretes also contained mud as a binding agent. It is therefore important during geopolymerisation to consider crosslinks between inorganic and organic species (Kim D et al., 2006)

Table 1 Chronological summary of Geopolymer literature review

Year	**Reference**	**Title**	**Findings**
2003	Wang and Cheng	Production geopolymer materials by coal fly ash	• Geopolymer with high fire resistance • High temperature for setting time contribute to higher compressive strength • At 60°C, time taken to harden is 1hour compared to room temperature(9.5hours)
2007	Provis and Deventer	Geopolymerization kinetic 1 (in-situ energy dispersive X-ray diffractrometry)	• The rate of reaction decreases with increasing silica content when others held constant • Na, K with moderate SiO_2/Al_2O_3 behave similarly to pure Na- or K compositions
		Geopolymerization Kinetic 2 (reaction	• Development of mathematical and computational technique

		kinetic modeling)	can be applied on geopolymetric aluminosilicate material
2008	Djwantoro Hardjito	Strength and thermal stability of fly-ash based geopolymer mortar	• High concentration alkaline and use ratio silicate to hydroxide will produce high compressive strength
2009	Bo Zhang et al	Crystalline phase formation in metakaolinite geopolymers activated with NaOH and sodium silicate	• When sodium silicate is used as and activator the reaction product is amophous
2009	Ubolluk and Prinya	Influence of NaOH solution on the synthesis of fly-ash geopolymer	• Leaching depend on NaOH concentration and leaching time
2011	Olivia and Nikraz	Strength and water penetrability of fly ash geopolymer concrete	• Strength of geopolymer increased by reducing the water binder and aggregate binder ratio
2012	Aleem and Umairaj	Optimum mix for the geopolymer concrete	• Compressive strength increase with the optimum increase of aggregate
2012	Anuradha et al	Modified guidelines for geopolymer	• Geopolymer as alternative solution • Have excellent compressive

		concrete mix design using Indian standard	strength
2012	Aleem and Umairaj	Geopolymer concrete- A review	• High concentration of NaOH, high compressive strength • High curing temperature and longer time, increased compressive strength
2013	M. Rashad	A comprehensive overview about the influence of different admixtures and additives on the properties of alkali-activated fly ash	• Higher compressive strength with curing time • Different solidification time with different material addition

2.2 Geopolymerization

Geopolymerization is occurring at complex multistep mechanism. The geopolymerization process is as follow. “Firstly, the alumino-silicate oxide in MOH solution (M= Na or K) will dissolute. After that, the dissolved Al and Si complexes will diffuse from particle surface to interparticle surface. Then, a gel phase will formed resulting from the polymerization between an added silicate solution and Al and Si complexes. Lastly, the geopolymeric product will produce after the gel phase is hardened by exclusion of spare water” (Xu et al., 2001).

Material with three dimensional polymeric chain and ring structure consisting Si-OAl-O bonds will appear after the reaction between fly ash and aqueous solution like mixture of Sodium Hydroxide and Sodium Silicate. The equations A and B will be used to describe the schematic formation of geopolymer material (Aleem and Arumairaj, 2012).

In the 1950s Glukhovsky (1959) proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina. Figure 2 presents a highly simplified reaction mechanism for geopolymerization. The reaction mechanism shown in Figure 2 outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate. It should be noted that the potential requirement for processing of raw materials by fine grinding, heat treatment etc. to vary the reactivity of aluminum in the system is not shown for the sake of simplicity. Though presented linearly, these processes are largely coupled and occur concurrently.

Dissolution of the solid aluminosilicate source by alkaline hydrolysis (consuming water) produces aluminate and silicate species. The volume of data available in the field of aluminosilicate dissolution and weathering represents a whole field of scientific endeavor in itself (Mater, 2007), and will not be reviewed in detail here.

It is important to note that the dissolution of solid particles at the surface resulting in the liberation of aluminate and silicate (most likely in monomeric form) into solution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerization. This assumption does have almost overwhelming scientific merit based on the literature describing alkaline dissolution, and so is shown in Figure 2. Despite this, the actual process of particle-to-gel conversion has never been confirmed in the highly alkaline and poorly solvated conditions prevailing during geopolymer synthesis.

Without the benefit of conclusive mechanistic understanding of solid particle conversion, surface dissolution will be assumed in the simplistic mechanistic model described here. Once in solution the species released by dissolution are incorporated into the aqueous phase, which may already contain silicate present in the activating solution. A complex mixture of silicate, aluminate and aluminosilicate species is thereby formed, and the speciation equilibria within these solutions have been studied extensively [Salerno et al, 1994, 1998).

Dissolution of amorphous aluminosilicates is rapid at high pH, and this quickly creates a supersaturated aluminosilicate solution. Inconcentrated solutions this results in the formation of agel, as the oligomers in the aqueous phase form large networks by condensation. This process releases the water that was nominally consumed during dissolution. As such, water plays the role of a reaction medium, but resides within pores in the gel. This type of gel structure is commonly referred to as bi-phasic, with the aluminosilicate binder and water forming the two phases. The time for the supersaturated aluminosilicate solution to form a continuous gel varies considerably with raw material processing conditions and solution composition and synthesis conditions (Ivanova et al., 1994). Despite this, some systems never gel. These are typically dilute, and the concentration of dissolved silicon and aluminum is observed to oscillate due to the slow response of the system far from equilibrium (Faimon, 1996).

After gelation the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in the three-dimensional aluminosilicate network commonly attributed to geopolymers. Figure 2 describes the activation reaction as an outcome of two successive and controlling stages. Nucleation, or the dissolution of the aluminosilicate material and formation of polymeric species, is highly dependent on thermodynamic and kinetic parameters and encompasses the two first steps proposed by Glukhovsky. Growth is the stage during which the nuclei reach a critical size and crystals begin to develop. These processes of structural reorganization determine the microstructure and pore distribution of the material, which are critical in determining many physical properties [(Duxson, 2006)

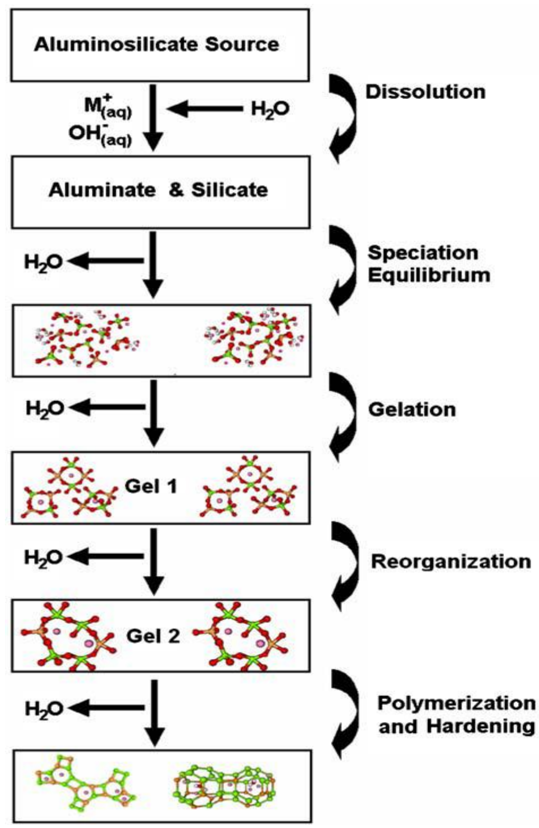

Figure 2: Conceptual Model for geopolymerization (Duxson et al., 2006)

2.3 Geopolymer versus Ordinary Portland cement

Geopolymer versus Portland cement (PC) Portland cement is the conventional binding agent for concrete and widely used due to the availability of raw materials over the world. The limestone is the raw material for the PC and it is assumed that the shortage of limestone will occur after 25 to 50 years (Anuar et al., 2011; Aleem and Arumairaj, 2012). However, during the manufacturing process for the cement production, approximately one ton of Carbon Dioxide (CO2) will be released to atmosphere for every one ton PC produced. About half of CO2 is produce due to calcinations of limestone and another half is from combustion of fossil fuel (Sreevidyaet al., 2012). The CO2 is the major threat for the environment and PC is contributes about 7% of the world's CO2 (Olivia and Nikraz,2007; Aleem and Arumairaj, 2012). The global warming will occur due to the greenhouse gasses like CO2 (Anuar et al., 2011). In addition, a huge energy and extremely resources also required for the PC production (Anuar et al., 2011; Aleem and Arumairaj, 2012).

Figure 3: Ordinary Portlant Cement

Hydration reaction will occur if the PC is mixed with water which produces primary hydration product calcium silicate hydrate and calcium hydroxide. This will give impact on the mechanical and chemical properties of the concrete like low resistance to heat and chemical attack (Aleem and Arumairaj, 2012). Water is very harmful to the concrete as it is able to leach calcium hydroxide from the cement paste. It is also carry harmful dissolve species like acid or chloride into the concrete. Water also will form the ice in large pores in the paste and it may cause leaching of compound from concrete.

Hence, the alternative binder is essential to reduce the use of PC in concrete. Several studies and researched has been done to find the alternative binder. The abundant availability of thermal industry waste and supplementary cement material such as fly ash, silica fume, granulated blast furnace slag, rice husk ash and metakaolin creates opportunity to utilize them as a substitute for PC to manufacture concrete (Vijai et al., 2010; Anuar et al., 2011; Aleem and Arumairaj, 2012). Basically the thermal industry waste and supplementary cement material will be simply dumped on earth and it will occupy large area. The above mentioned issue shall be solved by producing the geopolymer concrete.

Furthermore, the production of cement shall be reduced as geopolymer concrete doesn't use any cement. Moreover, the emission of CO_2 to atmosphere will be minimized (Aleem and Arumairaj, 2012). In contrast, the geopolymer do not required water for bonding as the alkaline solution will react with silicon and Aluminum that contain in the fly ash and instead water is expelled during curing and subsequent drying. This geopolymer will provide better chemical and physical properties such as more resistant to heat and absorption of water (Aleem and Arumairaj, 2012).

The structure between the PC and geopolymer is dissimilar from each other. The structure for the PC is coarse stacking of grains matter and this may causes crack and weakness for the PC. However, for the geopolymer structure is smooth and homogenous. Thus, it will give it additional ability in strength as compare to the PC.

Figure 4: Geopolymer Concrete

2.4 Kaolin as geopolymer base

First discovered in China, kaolin has been used in the making of porcelain and fine china for centuries. Today, however, kaolin is an important and cost-effective pigment in many paper and paperboard, paints and coatings, plastics, wire and cable and in concrete among many others. Kaolin is derived from the mineral Kaolinite which comes from the Earth's crust. It is an aluminum silicate represented as Al_2O_3•$2SiO_2$•$2H_2O$. Kaolin was first found in China. The name comes from two Chinese characters that mean "high hill" (Kao-Ling)

Kaolin was formed in the Earth's crust by hydrothermal weathering of feldspar 80 to 100 million years ago. In its natural state kaolin is a white, soft powder consisting principally of the mineral kaolinite, which, under the electron microscope, is seen to consist of roughly hexagonal, platy crystals ranging in size from about 0.1 micrometre to

10 micrometres or even larger. These crystals may take vermicular and booklike forms, and occasionally macroscopic forms approaching millimetre size are found. Kaolin as found in nature usually contains varying amounts of other minerals such as muscovite, quartz, feldspar, and anatase.

The chemical makeup of kaolin can be seen in the image below.

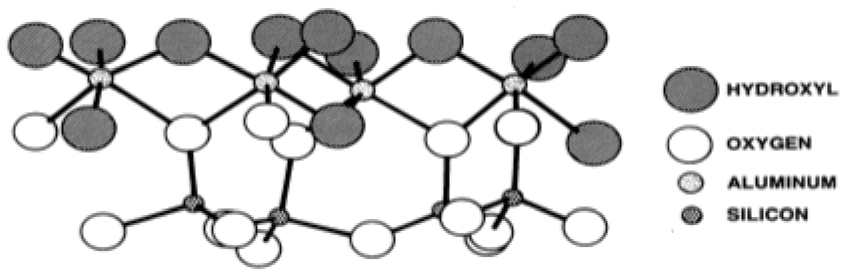

Figure 5: Chemical structure of kaolin

Figure 6: Powder form of kaolin

2.5 Avrami's Kinetic Theory

Kinetic of transformation typically describes as a standard equation known as Kolmogorov-Johnson-Mehl-Avrami (KJMA) phenomenological model (Fanfoni et al., 1996). This theory described the isothermal solids transform from one phase to another phase at constant temperature (isothermal). The kinetic transformation of solid is related to the nucleation of new particles and growth rate of particles into spherical shape.

According to Lukman et al (2008), the degree of crystallinity at first being measured by the geopolymer deposition, δr, defined as the mass fraction of the deposition that obtains after cooling process using the Equation 1;

$$\partial r = \frac{\partial t - \partial \text{o}}{\partial \infty - \partial o}$$

δ_t - deposition at time (min)
δ_∞ - maximum or asymptotic deposition from deposition curve
δ_0 - initial mass of geopolymer content in liquid (g)

After that, the KJMA is applied in order to describe the crystallization kinetic in geopolymer by Equation 2;

$$1 - X = e^{-Kt^n}$$

X - volume fraction of crystalline material
K – growth rate
n – Avrami exponent

Replacing the X in Equation 2 with δr from Equation 1 and taking log twice for Equation 2 it can be written as:

$$\log\ [-\ln(1-\partial r) = \log\ K + n\log\ (t)]$$

Referring to the Equation 2, the graph can be plotted using the left side as y-axis versus log (t). Then, the straight line slope n and intersection K will be obtain from the graph.

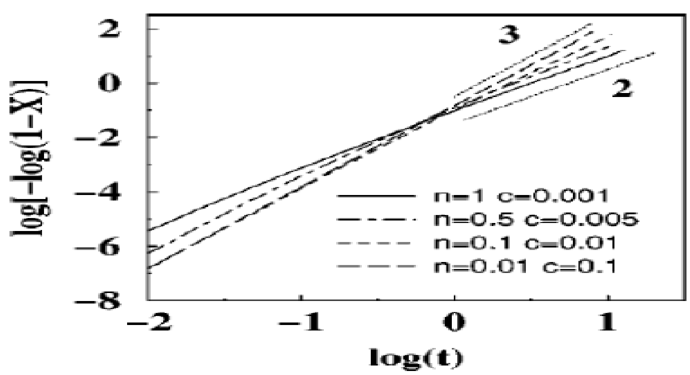

Figure 7: KJMA plots for different sets of parameters.
Log [-ln(1- δr)] vs log (t) (Maris Castro, 1999)

CHAPTER 3: METHODOLOGY

3. 1 Research Methodology

The main purpose of this research is to study about the geopolymer formation analysis study where it involves several parameters. The main methodology used in this research is based on experiment and discovery as well as study on previous paper work and journals. All the important information will be gathering from the related sources (journals, articles, paper work and books) as the literature review of the research. The research will continue with the experiments using parameters that have been set. The parameters that will be use is addition of additives (10% kaolin), different alkaline activator for geolymerization (Potassium Hydroxide and Sodium Hydroxide) and the effect of solid loading in geopolymer formation. All the results will be analyzed based on Avrami's Kinetic Theory. Figure below shows the summary of process route in conducting this research.

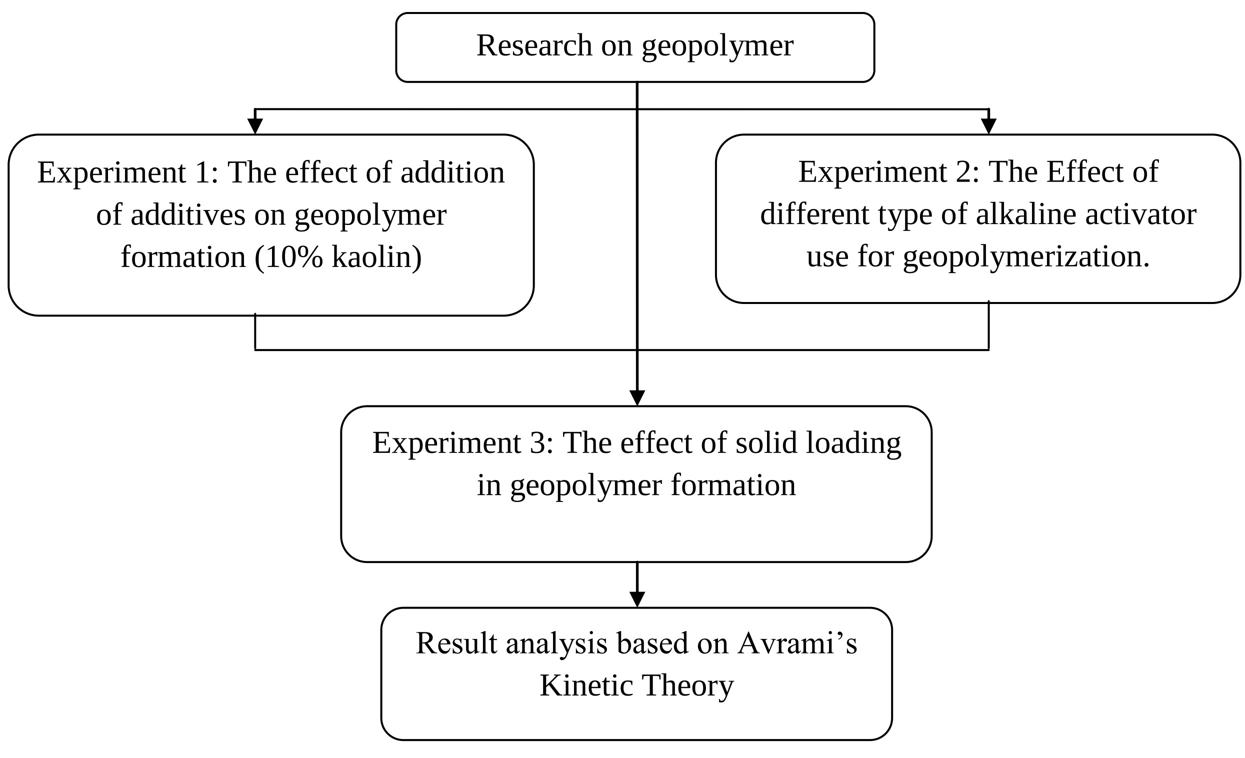

Figure 8: Steps in conducting project research

3.2 Equipment, Apparatus and Materials Required

All equipments, apparatus and materials needed for the research are available in the Chemical Engineering Department laboratory. The main equipment used for solidification test is vicat needle. The vicat needle test the degree of penetration on the geopolymer sample until zero penetration reached.

The apparatus used for conducting the experiments are basically beakers at many range volume, volumetric flask for preparation of alkaline, weighing scale for weight measurement and fume hood to store the alkaline solution in safe condition as it is in high concentration. Besides that, special container for moulding, mixer for mixing the geopolymer mixture and lastly oven for constant temperature for solidification process of geopolymer.

The materials used in this research mainly divided into two which is alkaline solution and solid base for geopolymer. The alkaline solution are prepared by using two types of chemicals which are Sodium Hydroxide and Potassium Hydroxide. The solid base for geopolymer are fly ash collected from chemical engineering department laboratory and kaolin.

3.2.1 Vicat Needle

Vicat needle can be used to test the softening point of materials that do not have definite melting point such as plastics and others. The mechanism of the testing by penetrating the specimen to a depth of 1 mm by a flat-ended needle with a 1 mm^2 circular or square cross-section and the temperature is taken. The standards that usually being use to determine the vicat softening point include ASTM D 1525 and IS0 306, which both are largely equivalent. Using this equipment to get the temperature of the sample, the heat-softening characteristics of different material can be compared.

Figure 9: Vicat Needle (from http://www.shambhaviimpex.com/vicat-needle-apparatus.html)

3.3 Project Activity

For every experiment, details procedure is one of most important thing before conducting the experiment. All the chemical, material and apparatus must be prepared accordingly especially when dealing with harmful substances or chemicals. The material and apparatus must be verified and in good condition before undergo any experiment. The in-lab safety rules and regulations involving the chemicals and equipments handling must be strictly being followed to avoid any accidents.

In the project research there will be different experiment to be conducted based on the objectives of the experiment. However, all the experiments can be summarized in the general procedure.

Sodium Hydroxide (NaOH) pellet is mixed with distilled water in a volumetric flask based on selected concentration. The hydroxide/alkaline solution are kept in store for about 24 hours. (To remove heat as the reaction is exothermic). The alkaline solution is mixed with the fly ash depends on the ratio required until well mix (later was test with addition of 10% kaolin). The mixture is molded in the mould and exposed to setting temperature (70^{o}C). The time is set and the mould is observed. The mould will be tested using vicat needle for every 5 minutes until it solidified..The recorded data from vicat needle will be related to the Avrami's Kinetic Theory.

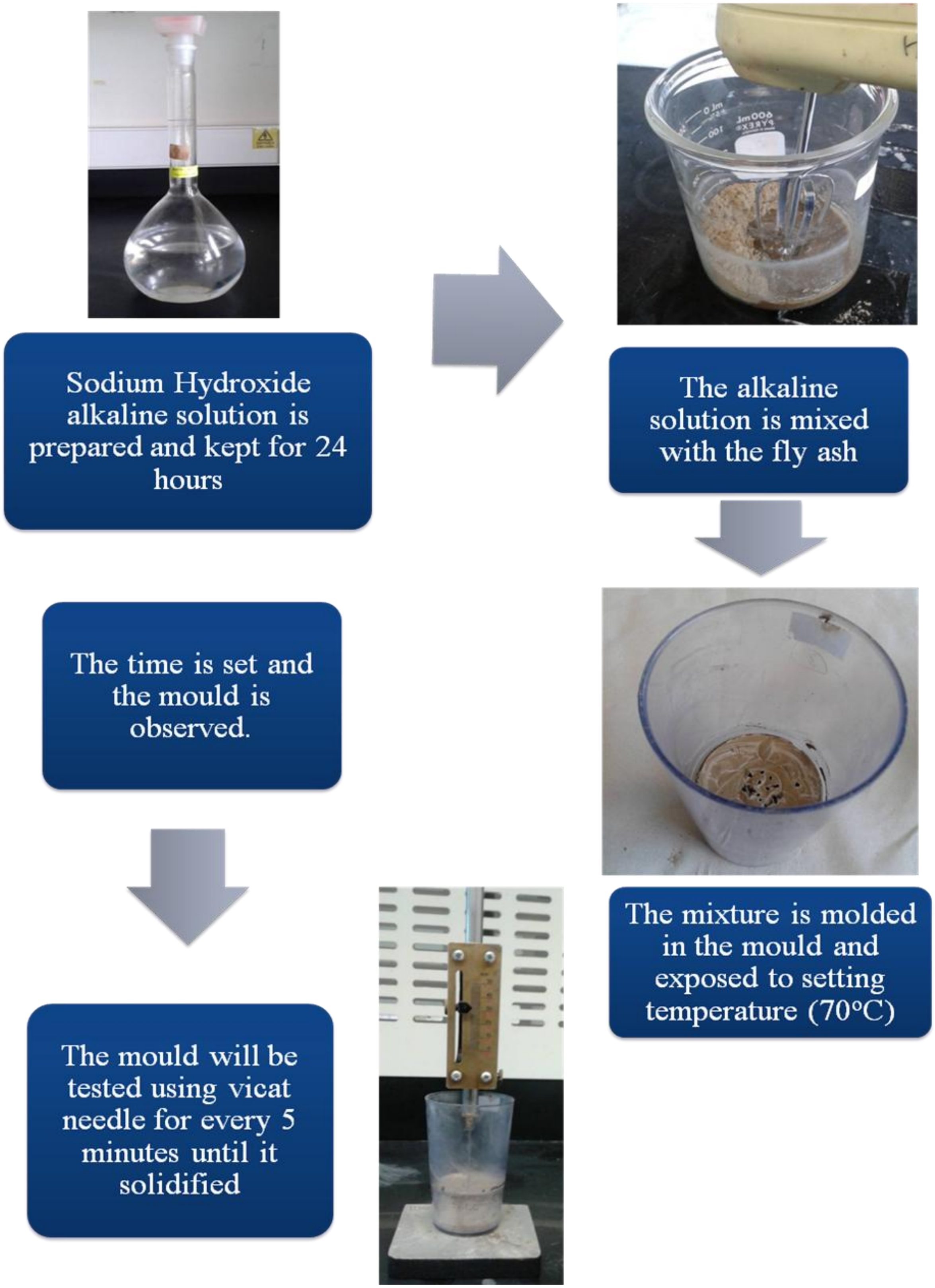

Figure 10 : General experimental procedure

3.3.1 Experiment 1: The effect of addition of additives (10% kaolin) on geopolymer formation.

For this experiment, geopolymer with different mixture (fly ash compared with fly ash with addition 10% of kaolin) will be used to test together with the alkaline-activator and different solid loading. The objective of this experiment was mainly to compare different mixture of solid performance under different parameter setting. The general procedure to test on temperature variation is, the fly ash is mixed with alkaline activator using 2.0 to 1 (100gram of fly ash, 50gram of alkali) ratio until well mixed. The test was conducted first only using fly ash, and later on addition of 10% kaolin. Then, the mixture is molded in the mould and exposed to setting temperature which is (70^{o}C). After that, the time is set and the mould is observed. The mould will be tested for every 5 minutes using Vicat Needle. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect addition of additives is shown in the step below;

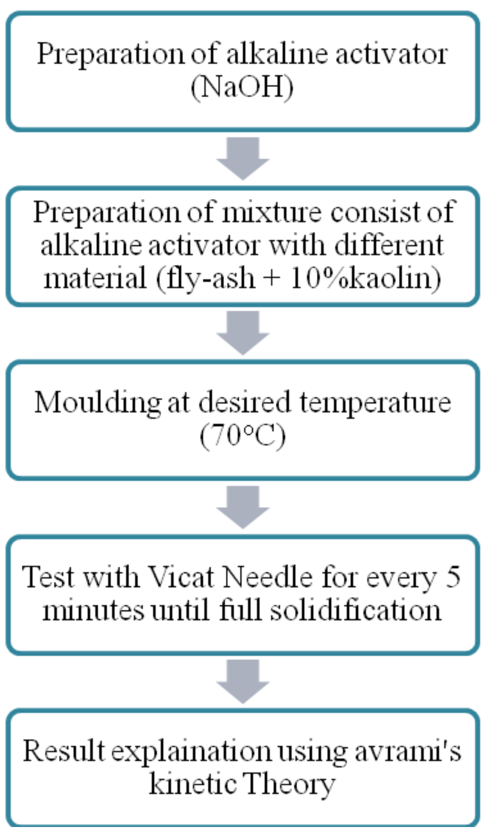

Figure 11: Procedure for effect of addition of additives on geopolymer formation

3.3.2 Experiment 2: The effect of different alkaline-activator use for geopolymerization (Potassium Hydroxide and Sodium Hydroxide)

The parameter used in this experiment will be fly ash with 10% kaolin tested with different different alkaline solution. The objective of the experiment is to test the solidification of geopolymer with different alkaline activator use. The general procedure to test on different alkaline-activator used is, the fly ash (10%kaolin) is mixed with alkaline activator using alkaline loading ratio 2 to 1 ratio. Then, the mixture is molded in the mould and exposed to setting temperature which is 70^{o}C. After that, the time is set and the mould is observed. The mould will be tested for every 5 minutes minutes using Vicat Needle. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect of different alkaline-activator is shown in the step below;

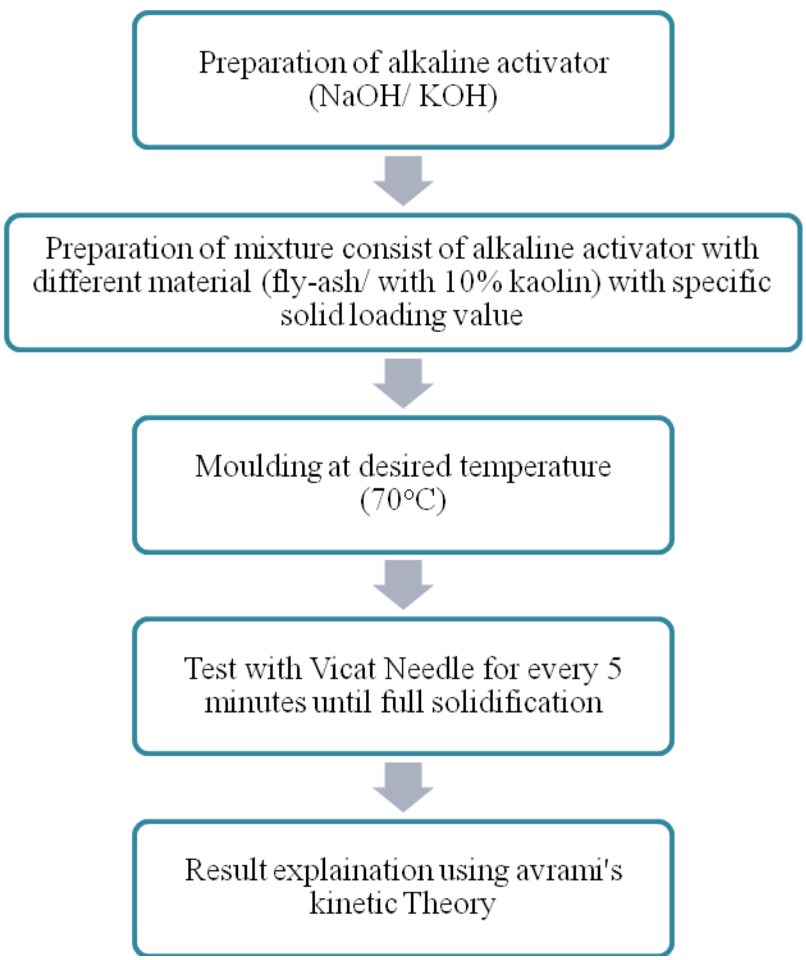

Figure 12: Procedure effect of different alkaline activator on geopolymerization

3.3.3 Experiment 3: The effect of variation of solid loading value in geopolymer formation

The parameter used in this experiment will be different material (fly-ash and fly ash with addition 10% kaolin) tested with different different alkaline solution and the raw material will mix with different ratio. The objective of the experiment is to test the solidification of geopolymer with different alkaline loading ratio value. The general procedure to test on alkaline loading used is, the fly ash/kaolin is mixed with alkaline activator using alkaline loading ratio from 2.0, 2.5 and 3 ratio. Then, the mixture is molded in the mould and exposed to setting temperature which is 70^{o}C. After that, the time is set and the mould is observed. The mould will be tested for every 5 minutes minutes using Vicat Needle. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect variation of solid loading on different material is shown in the step below;

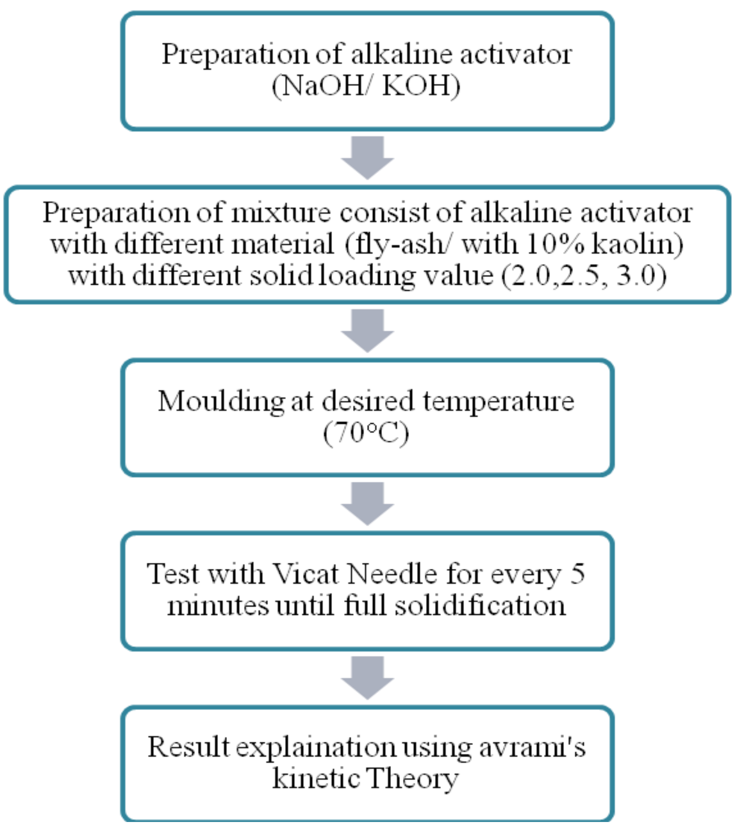

Figure 13: Procedure effect of solid loading on geopolymer formation

3.4 Gantt Chart and Key milestone

No	Details/Works	2	4	6	8	10	12	14	SEMESTER BREAK	16	18	20	22	24	26	28
1	Project title confirmation															
2	Literature Review															
3	Submission of extended proposal															
4	Proposal defense															
5	Project works continues															
6	Submission of interim report															
7	Parameter Identification and lab work															
8	Analysis of results															
9	Compilation of results															
10	Documentation of report															
11	Documentation of technical report															
12	Submission of draft report															
13	Oral presentation															
14	Submission of Final and technical report															

Suggested Keymile Stone

CHAPTER 4: RESULT AND DISCUSSION

This chapter discusses the result obtained from experiment conducted so far. The parameters that have been tested include effect of addition of additives, effect of different alkaline activator and effect of solid loading value. The vicat needle used to test the solidification stage of geopolymer. Every 5 minutes the geopolymer was tested with vicat needle for and the data was recorded versus time as below;

4.1 The effect of addition of additives (kaolin) on geopolymer formation.

In this experiment, two different geopolymer base was prepared which are fly-ash and fly ash with addition of 10 % of kaolin. The materials are then mixed with different alkali for performance comparison for different alkaline activator.

Graph below shows that, fly ash solidified faster in 8M of KOH, but fly ash with addition of kaolin reach faster in 8M of NaOH. The mixture that contains additives reach full solidification faster compared to fly ash alone in 8M of NaOH.

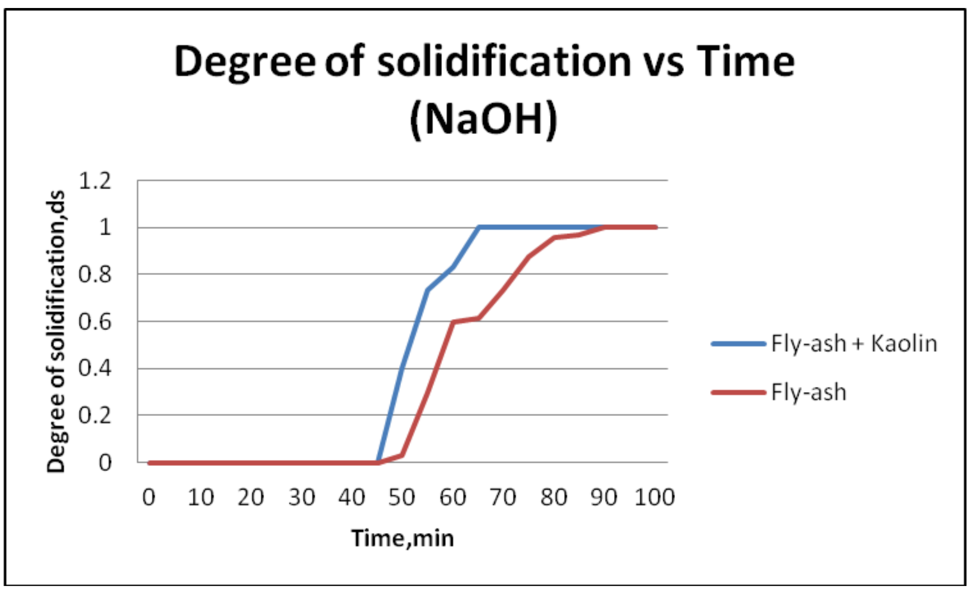

Figure 14: Graph of degree of solidification using NaOH

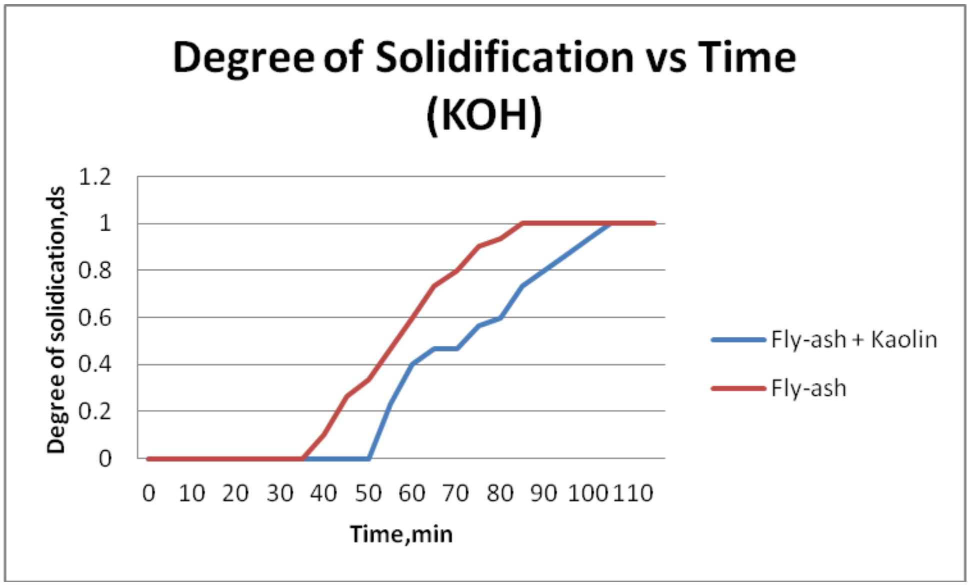

Figure 15: Graph of degree of solidification using KOH

4.2: The effect of different alkaline-activator use for geopolymerization (Potassium Hydroxide and Sodium Hydroxide)

The experiments conducted were also at different solid loading value. From the graph shows that NaOH give better solidification time compared to KOH except for 3:1 ratio in fly ash. Previous research shows that using KOH for geopolymer is only optimum at 8M and the performance will decrease with the increase of concentration (Nurhanie, 2012). While using NaOH, geopolymerization process increases in performance with the increase of concentration. This experiments show that with addition of additives, the process of solidification also faster in NaOH compared to KOH.

4.2.1 Fly-ash

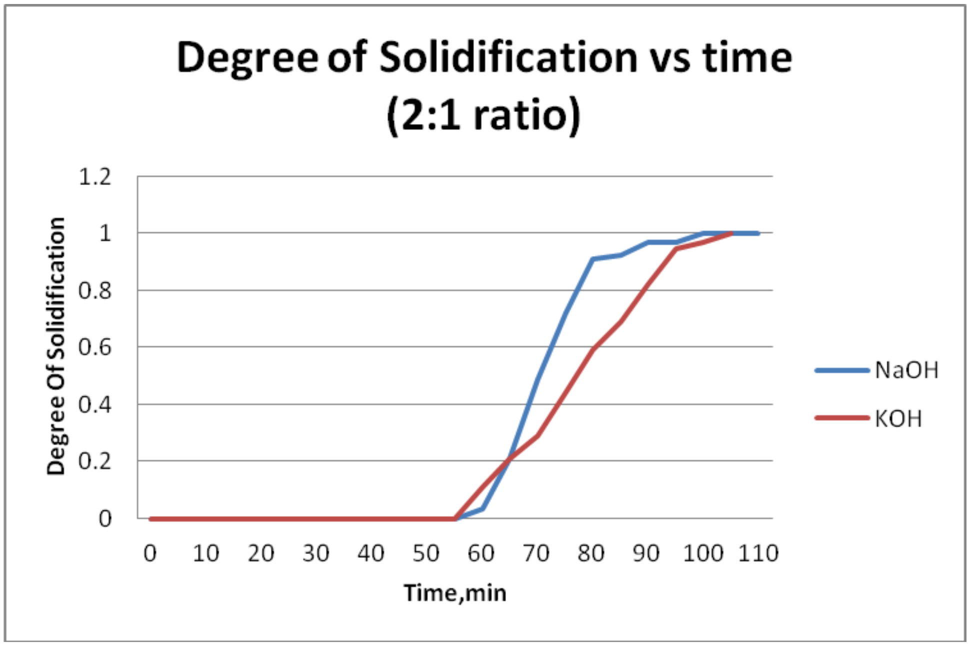

Figure 16: Graph of degree of solidification (2:1 ratio)

The degree of solidification is better with NaOH compared to KOH in 2:1 solid to liquid ratio.

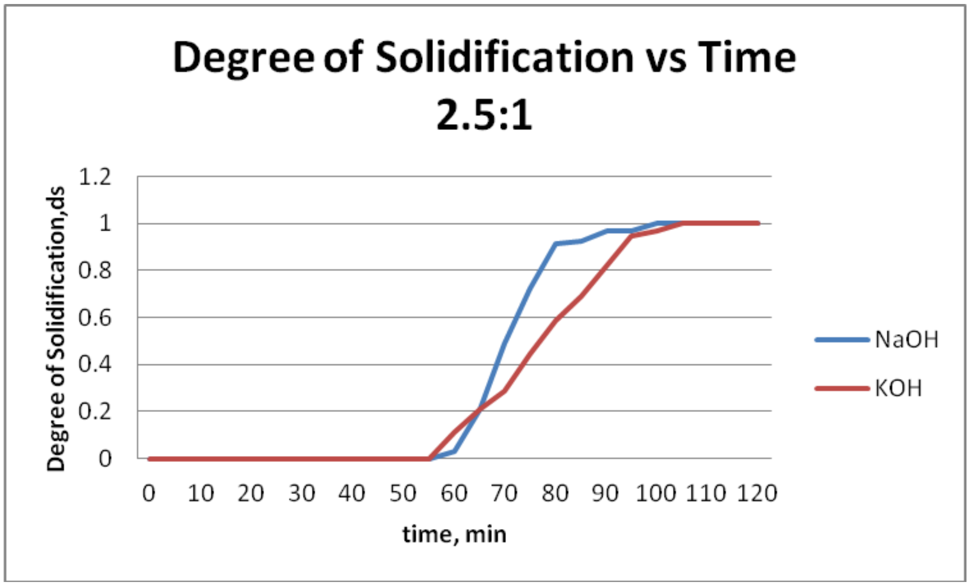

Figure 17: Graph of degree of solidification (2.5:1 ratio)

The degree of solidification is better with NaOH compared to KOH in 2.5:1 solid to liquid ratio.

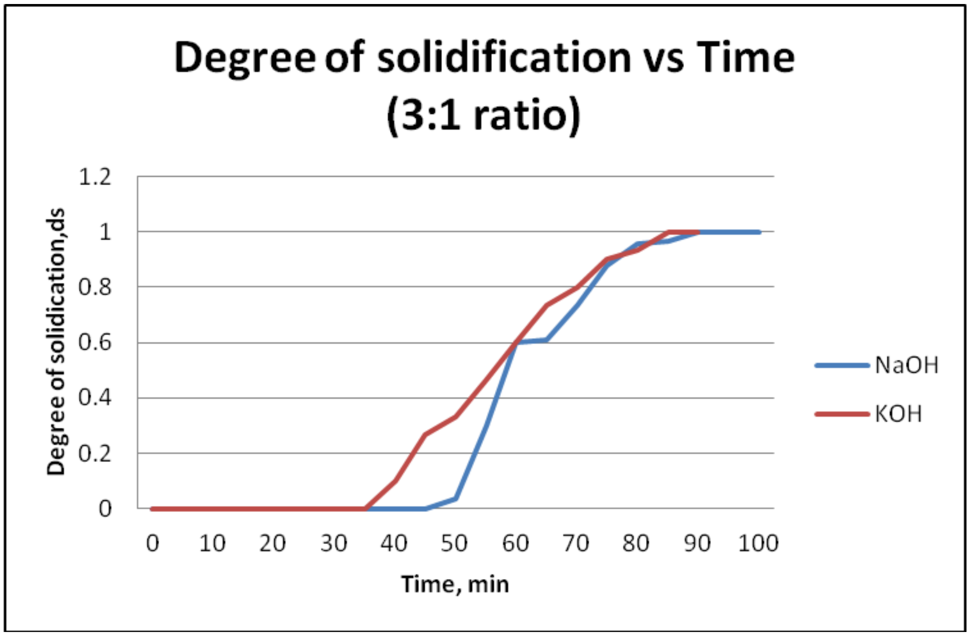

Figure 18: Graph of degree of solidification (3:1 ratio)

The degree of solidification is better with KOH compared to NaOH in 3:1 solid to liquid ratio.This shows that optimum mixture for KOH is with higher solid value than alkaline value

4.2.2 Fly-ash with 10% kaolin

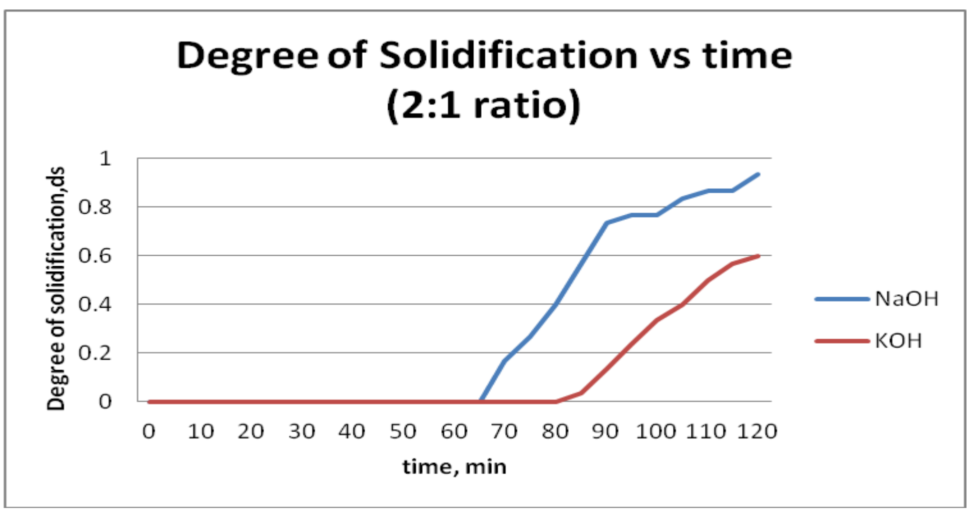

Figure 19: Graph of degree of solidification (2:1 ratio)

The degree of solidification is better with NaOH compared to KOH in 2:1 solid to liquid ratio.

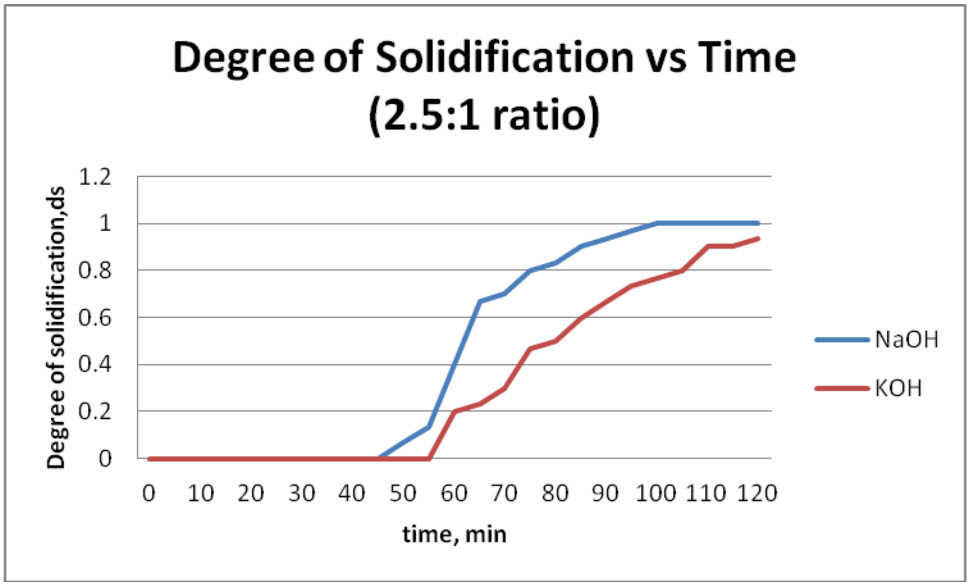

Figure 20: Graph of degree of solidification (2.5:1 ratio)

The degree of solidification is better with NaOH compared to KOH in 2.5:1 solid to liquid ratio.

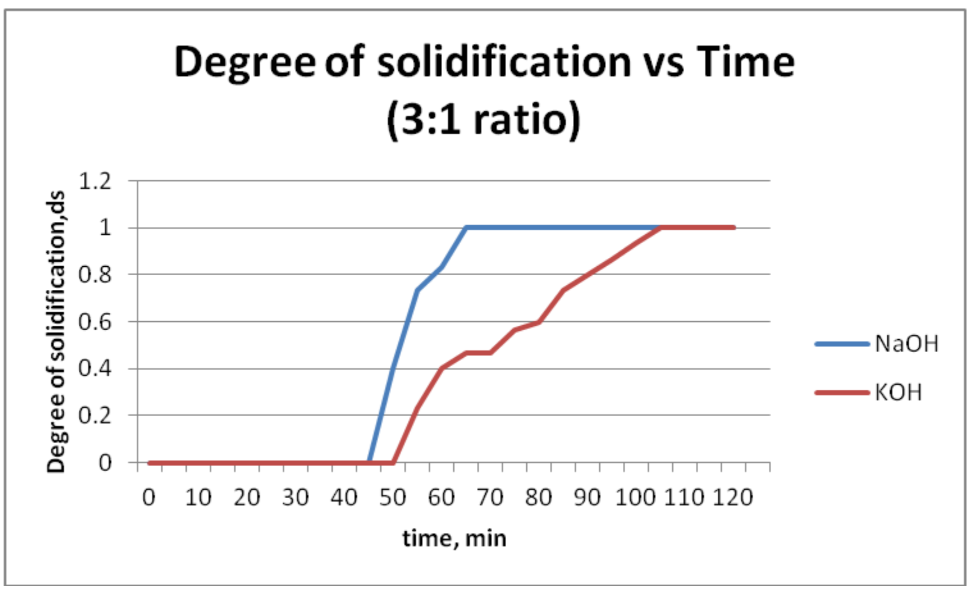

Figure 21: Graph of degree of solidification (3:1 ratio)

Performance of geopolymer mixture containing 10% of kaolin is better with NaOH than KOH in all solid ratio. The presence of Kaolin alters the reaction of fly-ash with alkaline, causing different performance of solidification at all mixture.

4.3 The effect of variation of solid loading value in geopolymer formation

Graphs below show that using different solid loading value, the solidification is faster at highest solid value. This is due to process of removing water is faster and the reaction for geopolymerization is also faster.

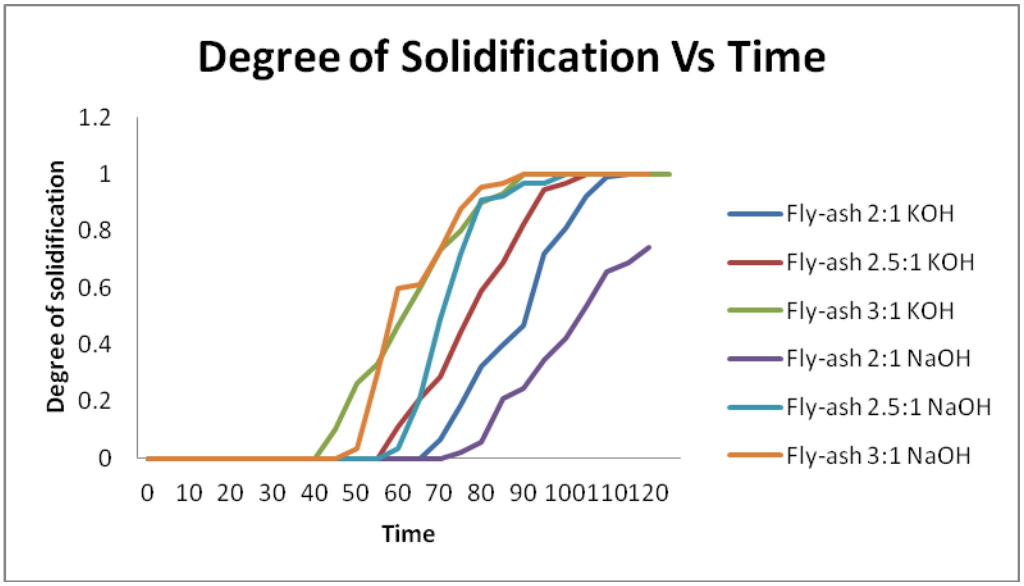

Figure 22: Degree of solidification using different alkaline activator

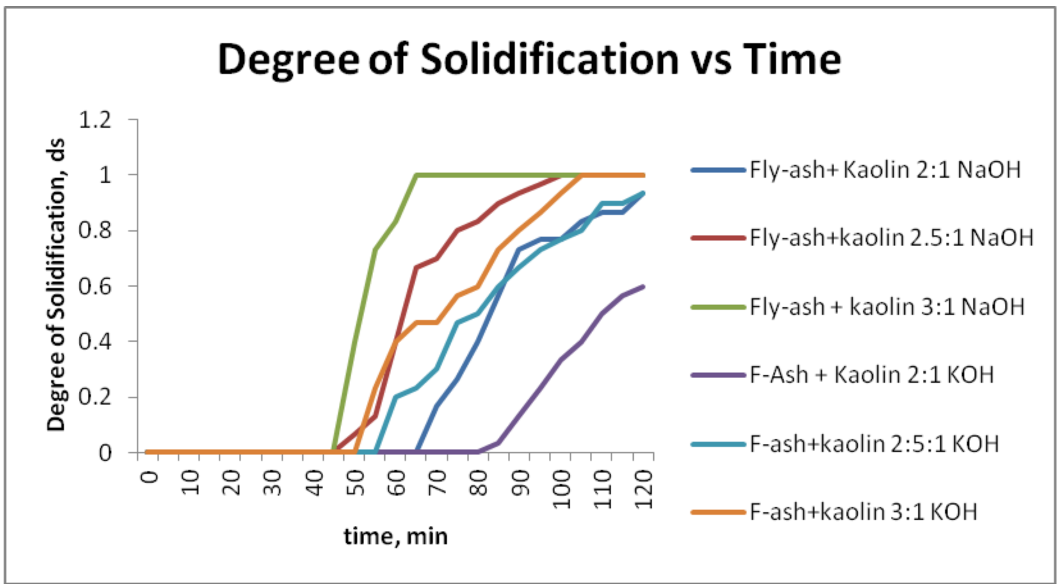

Figure 23: Degree of solidification using different alkaline activator

4.4 Kinetic Analysis

According to the graphs of degree of solidification represent earlier, the curve shall be analyzed using the Avrami Theory to extract the kinetic of solidification. The figure are plot log | -ln (1-ds)| versus log (t) for the all parameters in this research. From the plot, the Avrami exponent (n) and rate constant (K) are extracted and tabulated in table.

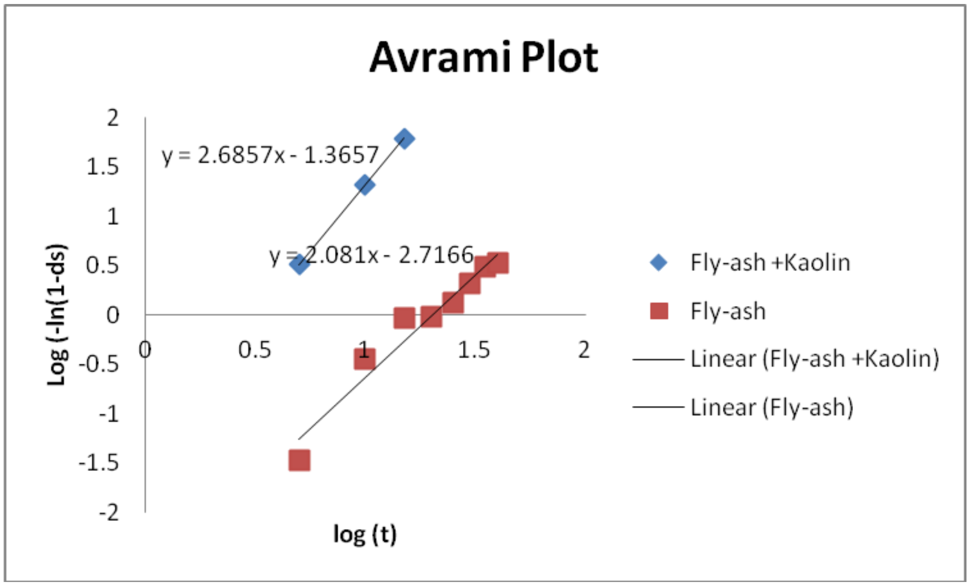

Figure 24: Avrami plot for experiment 1 (addition of additives)

Table 2: Extracted parameter from figure 23

Parameter	**n**	**K (min^{-1})**
Fly-ash + Kaolin	2.6857	0.043
Fly-ash	2.0881	0.00192

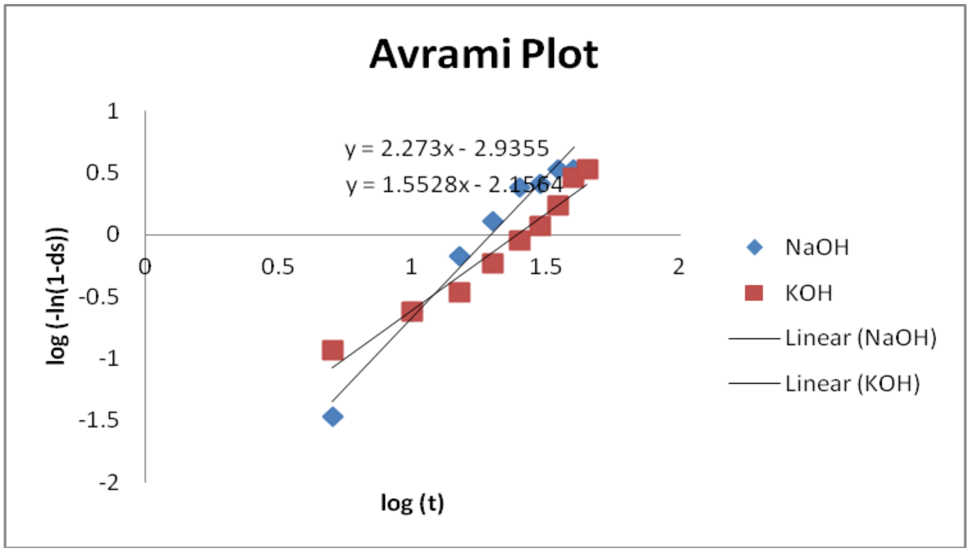

Figure 25: Avrami plot experiment 2 (different alkaline activator)

Table 3: Extracted parameter from figure 24

Parameter	**n**	**K (min^{-1})**
NaOH	2.273	$1.15x10^{-3}$
KOH	1.5528	$6.98x10^{-3}$

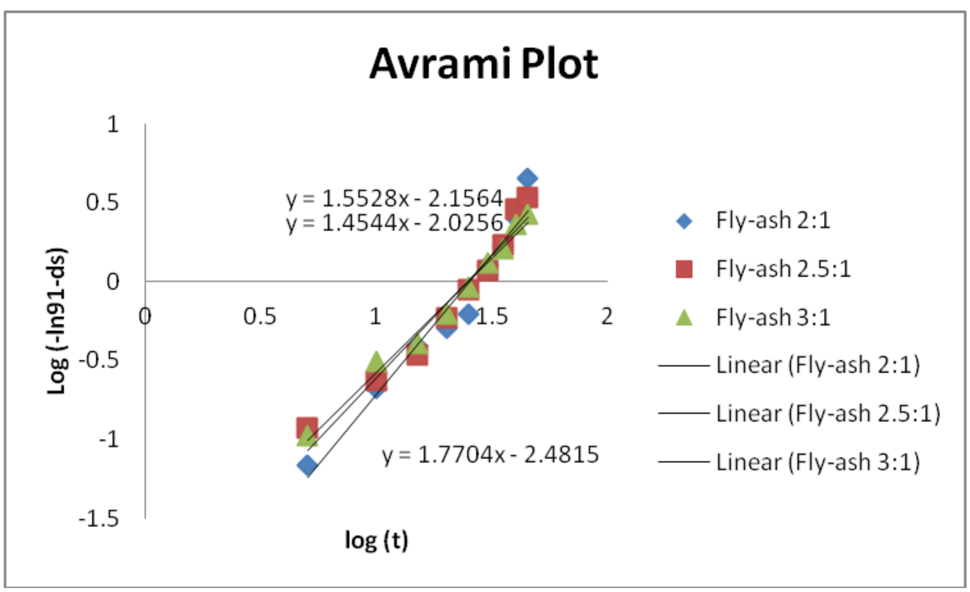

Figure 26: Avrami plot for experiment 3 (solid loading)

Table 4: Extracted parameter from figure 25

Parameter	**n**	**K (min^{-1})**
Fly ash 2:1	1.7704	3.30×10^{-3}
Fly ash 2.5:1	1.5528	6.98×10^{-3}
Fly ash 3:1	1.4544	9.43×10^{-3}

Based on the tables, the obvious trend can be observed from the value of growth rate (K). The growth rate shows the value for each experiments conduct as the higher growth rate can be seen in fly-ash with kaolin, in solid loading value of 3:1. While in experiment two show KOH has better growth rate as discussed above, performance of KOH is optimum in 8M concentration. The growth form for the geopolymer shall be concluded as one, two and three dimension as the value of n tabulated is one and two.

Table 5: Avrami Parameters for Crystallization of polymer (J.N.Hay)

Crystallization Mechanism	**n**	**Growth form**
Spheres		
• **Sporadic**	4	Three Dimension
• **Instantaneous**	3	Three dimension
Discs		
• **Sporadic**	3	Two Dimension
• **Instantaneous**	2	Two Dimension
Rods		
• **Sporadic**	2	One Dimension
• **Instantaneous**	1	One Dimension

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In conlusion, the result obtain from the research conducted showed that

- The best mixture for geopolymer is with addition of additives which is 10% of kaolin, and the setting time is a lot shorter compared to fly ash alone.
- The addition of additive is at best performance in Sodium Hydroxide.
- The alkaline activator KOH shows better performance in fly-ash but not with the addition of additives.
- The solid loading value shows shorter time of solidification with the increase of solid amount.

Based on Avrami Theory

- The growth rate (K) increases with the addition of additives, and at highest at highest solid loading ratio (3:1). The growth rate also higher in KOH than NaOH in fly-ash geopolymer experiment.
- The avrami exponent trend will decrease with the growth rate except for fly-ash with addition of kaolin,Thus the growth form can be concluded in dimensions.

5.2 Recommendation

For future research work, few recommendation are suggested to improve the related project

1. The concentration of alkaline solution should be taken to consideration because different alkaline have different optimum mixture with geopolymer
2. The addition of sodium silicate will helps the process of geopolymerization and will improve the result of the experiments as it will influence the silica ratio in the geopolymer then will affect the geopolymerization rate
3. The products of each experiment should be tested will strength test to prove it hardness and advantage than the other type of geopolymer.

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