KINETIC CRYSTALLIZATION OF GEOPOLYMER

by

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Dissertation submitted in Partial Fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2012

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CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
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Approved by,

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(Dr. Lukman Bin Ismail)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2012

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.

NUR HANIE BINTI ZAMRI

ABSTRACT

Kinetic Crystallization of Geopolymer

The geopolymer was introduced by Davidovits on 1978 to describe inorganic network. Geopolymer is an alternative binders for the Portland Cement (PC) due to many factors such as better chemical and mechanical characteristic concrete and an enviroment issues like emmision of Carbon Dioxide. The aim of this research is to conduct a study on the crystallization kinetic's of geopolymer using the Avrami Kinetic Theory. Tests were carried out using Leatherhead Food Research Association (LFRA) Texture Analyzer to analyze the crystallization profile. This project involved the investigation on different types of alkaline solution and alkaline concentration at different range of temperature. The result indicates that the Potassium Hydroxide at low concentration has better performance in achieving an optimum time for geopolymerization process. Higher temperature is recommended to crystallize the geopolymer as it shorter the setting time. However, the geopolymer still crystallized at room temperature. Based on the kinetic study, the growth rate (K) increased with the concentration of solution and temperature. The Avrami exponent (*n*) trend was increasing as growth rate increases and vice versa.

ACKNOWLEDGEMENT

First and foremost, praise to Allah the Almighty for his guidance and giving me strength to complete this Final Year Project. I believe all of this has been planned carefully by him as He is the best planner.

Heartfelt appreciation is specially made to my Supervisor Dr. Lukman Bin Ismail because his will to guide and support throughout my project. I am very thankful to get assigned to him because he has conveyed a lot of knowledge and information for this project. It has been a great privilege to undergo my project under his supervision. Special thanks to all Lab Technicians in Chemical Engineering Department especially to Mr. Shaharuddin and Mr. Fazli for their hard work and guidance.

Apart from that, I would like to thanks Chemical Engineering Department of Universiti Teknologi PETRONAS who has put a lot of effort towards contributing in making the Final Year Project program a great success. This project has given me vast amount of experience and knowledge in engineering field. Besides, I would like to thank them for their generosity in providing me with all the facilities and technical expertise in making this project successful.

Last but not least, all of these would not materialize without my family and friends who have been supporting me throughout my final year. All of their effort in ensuring the success and completion of this project is really appreciated.

LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENTS

CHAPTER 1

PROJECT BACKGROUND

Basic view on this project will be provided in this chapter. Starting with brief introduction to geopolymer background and the advantages of geopolymer as compare to the portland cement (PC). Then, followed by the problems associated with the Crystalization of Geoplymer, objectives and scope of study for this project that will be refer to also being discuss in this chapter.

1.1 Background Study

One of the fast growing fields worldwide is the construction area. The most widely used construction material in the world is concrete. Annually production of cement is increasing about 3% (McCaffrey, 2002). As per present world static, about 2,600,000,000 tons of cement is required every year. The demand quantity will be higher and increased by 25% within a span of another 10 years. The consumption of concrete is expected to increase due to the increase of infrastructure in all countries especially India and China (Prabir, 2008; Aleem and Arumairaj, 2012). Other than infrastructure, there are other applications of concrete such as in habitation and transportation that lead to development of civilization, economic progress and stability and of the quality of life (Anuar et al., 2011).

Geopolymer is known as a new technology concretes in construction materials that using fly ash-based. According to Aleem and Arumairaj (2012), geopolymer is depend on thermally activated natural materials such as Meta kaolinite or industrial byproducts like fly ash or slag as they are contain silicon (Si) and aluminum (Al). The Si and Al will react with alkaline activating solution to polymerize into molecular chain and become binder. Professor B. Vijaya Rangan (2008) stated that “the polymerization process involves a substantially fast chemical reaction under alkaline conditions on silicon-aluminum minerals that results in three-dimensional polymeric chain and ring structure….”

The geopolymer is first discussed in detailed by Davidovits (1978) to represent networks of inorganic molecule. After that, several research and study on geopolymer using different word for the same type of material such as 'Low-temperature aluminosilicate glass' (Rahier et al. , 1996), 'hydroceramic' (Bao et al., 2005) and 'inorganic polymer concrete' (Sofi et al., 2007) had been done. Basically, the geopolymer are used as one of the alternative product to replace the PC (Nugteren et al., 2008).

1.1.1 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 (CO_2) will be released to atmosphere for every one ton PC produced. About half of CO_2 is produce due to calcinations of limestone and another half is from combustion of fossil fuel (Sreevidyaet al., 2012). The CO_2 is the major threat for the environment and PC is contributes about 7% of the world's CO_2 (Olivia and Nikraz, 2007; Aleem and Arumairaj, 2012). The global warming will occur due to the greenhouse gasses like CO_2 (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). Hydration reaction will occur if the PC is mixed with water which produces primary hydration product calcium silicate hydrate and calcium hydroxide. This will gives 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).

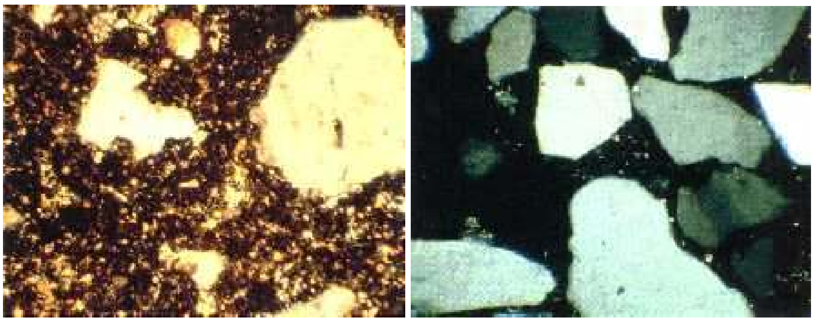


Figure 1.1-Portland Cement (left), Geopolymer (right) (Geopolymer Institute)

Based on the Figure 1.1, 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.

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. However, there are only few researches focusing on the effect of parameters before the setting time. Thus, study on the effect of parameters before setting time of geopolymer will be useful for the designers and engineers especially for construction purpose. Therefore, this study will focus on kinetic crystallization of geopolymer based on the effect of certain parameters only.

1.3 Aim and Objectives

The aim for this project is to conduct a study on the kinetic of crystallization of geopolymer based on type of alkaline solution at different concentration and temperature point. All the variables will be analyzed and related to the Avrami Kinetic Theory.

The following are the objectives of this project:

a) To study the effect of different type of alkaline solution on the crystallization of geopolymer.

b) To study the effect of alkaline concentration on the crystallization of geopolymer.

c) To study the effect of temperature on the crystallization of geopolymer.

1.4 Scope of Study

The parameters tested in this project are type of alkaline solution, concentration of alkaline solution and temperature. 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 and Sodium Silicate or Potassium silicate to forms gel (Aleem and Arumairaj, 2012). The concentration of alkaline solution is varies from 8M to 16 M (Hardjito, 2003; Anuradha et al., 2012). The effect of temperature will be tested by observing the crystallization process of geopolymer at set up temperature range between 25 to 35°C using the LFRA Texture Analyzer. The effect of temperature shall be observed referring to the setting time measurement (Wang and Cheng, 2008). 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 Relevancy and Feasibility of the Project

The significant of this project is to further study and investigate on the kinetic crystallization of geopolymer which will be useful for the designers and engineers especially in the construction field. This study may help for further understanding on the mechanism and kinetic analysis on the crystallization of geopolymer. The project is considered as feasible as all the equipment and material are available at the laboratory in Chemical Engineering Department. The number of parameters tested also within the specific time constraint.

CHAPTER 2

LITERATURE REVIEW

This chapter will cover on the review and study on geopolymer process known as geopolymerization and all the parameter that will be tested in this project such as effect of different types of alkaline solution, effect of alkaline concentration and effect of temperature. The theory of Avrami kinetic theory and LFRA Texture Analyzer also will be included in this chapter.

2.1 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).

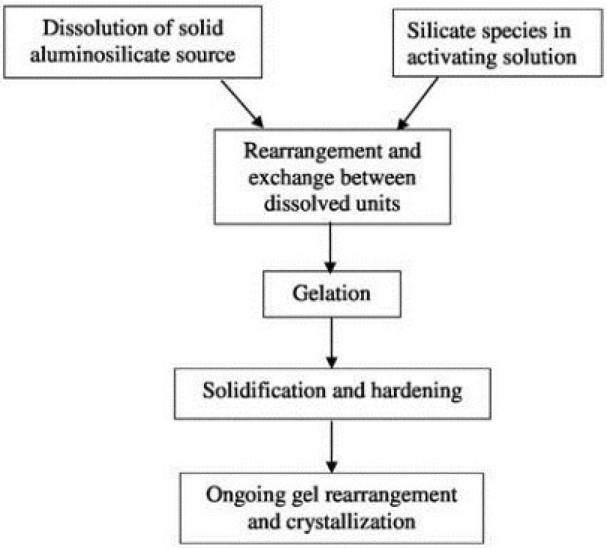
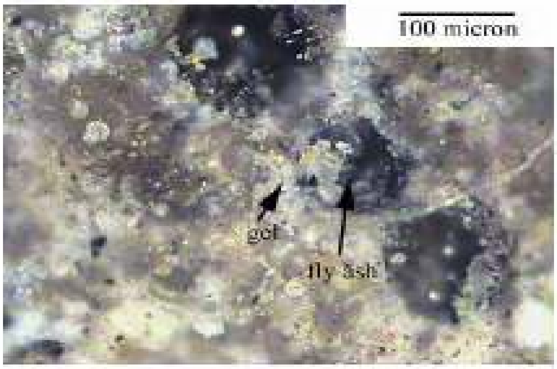


Figure 2.1-Process occurring during geopolymerization **(Xu et al)**

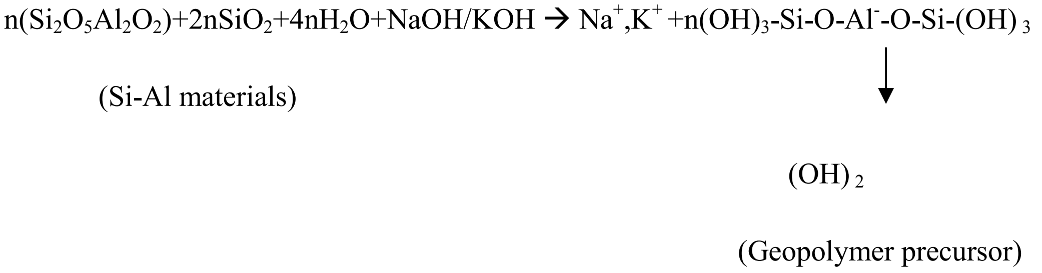


Note: fly ash is black, and gel is white.

Figure 2.2-Optical micrograph of geopolymer (Ubolluk and Prinya, 2009)

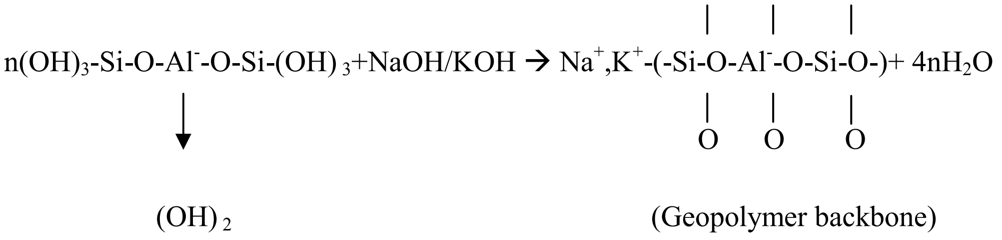
Material with three dimensional polymeric chain and ring structure consisting Si-O-Al-O bonds will appear after the reaction between fly ash and aqueous solution like mixture of Sodium Hydroxide and Sodium Silicate. The equations A and B will be used to describe the schematic formation of geopolymer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

Equation A:



$$\underset{\text{(Si-Al materials)}}{n(Si_2O_5Al_2O_2)+2nSiO_2+4nH_2O+NaOH/KOH} \rightarrow Na^+,K^+ + \underset{\text{(Geopolymer precursor)}}{n(OH)_3\text{-Si-O-Al}^-\text{-O-}\underset{\underset{(OH)_2}{\downarrow}}{\text{Si}}\text{-}(OH)_3}$$

Equation B:



$$\underset{}{n(OH)_3\text{-Si-O-}\underset{\underset{(OH)_2}{\downarrow}}{\text{Al}^-}\text{-O-Si-}(OH)_3}+NaOH/KOH \rightarrow Na^+,K^+\text{-}\underset{\text{(Geopolymer backbone)}}{(\text{-}\overset{|}{\underset{\underset{O}{|}}{Si}}\text{-O-}\overset{|}{\underset{\underset{O}{|}}{Al^-}}\text{-O-}\overset{|}{\underset{\underset{O}{|}}{Si}}\text{-O-})}+4nH_2O$$

According to previous study (Hua et al., 1999; Swanepoel et al, 2002) geopolymerization will occur if chemical reaction between various aluminosilicate oxides with silicate under highly alkaline conditions. The polymerization process involves a substantially fast chemical reaction under alkaline condition on Si-Al minerals (Aleem and Arumairaj, 2012).

2.2 Effect of different type of alkaline solutions

During geopolymerization an alkaline liquid is used (Vijai et al., 2010) as the basic components of geopolymer are fly ash, Sodium Hydroxide or Potassium Hydroxide mixed with Sodium Silicate or Potassium Silicate (Aleem and Arumairaj, 2012). In fly ash-based geopolymer binder, alumino-silicate will be created after fly ash is reacted with the alkaline solution (Prabir, 2008). An alkaline solution is a mixture of base solid dissolves in water. Fly ash will be reacted with the alkaline solution and form a gel which binds the fine and coarse aggregates (Aleem and Arumairaj, 2012). The type and concentration of alkaline solution affect the dissolution of fly ash. By using the Sodium Hydroxide, the leaching of alumina and silicate ions are high as compared to Potassium Hydroxide (Van Jaarsveld and Van Deventer, 1999; Xu and Van Deventer, 1999). The most common combination of alkaline liquid used in geopolymer is Sodium Hydroxide or Potassium Hydroxide and Sodium Silicate or Potassium Silicate (Vijai et al., 2010).

Sodium Hydroxide and Potassium Hydroxide both are caustic bases. However, they are slightly different in chemistry and practical application. The reaction of Sodium Hydroxide and Potassium Hydroxide with water is strongly exothermic that will produce hydrogen and heat. However, the reaction of Potassium Hydroxide with water is slightly less exothermic. In addition, Potassium Hydroxide is more soluble in water as 121g of Potassium Hydroxide will dissolve 100ml of water while 100g of Sodium Hydroxide needed to dissolve same amount of water (Shelly Morgan, 2011).

2.3 Effect of alkaline concentrations

Reaction between aluminosilicate with highly concentrated aqueous alkali hydroxide or silicate solution will produce the geopolymer (Nugteren et al., 2008). The alkaline concentration is varies and usually between from 8M to 16M (Hardjito, 2003; Anuradha et al., 2012). Hardijito and Rangan found that if the Sodium Hydroxide concentration in molar is high, it will result the higher compressive strength. Anuar et al observed that the strength characteristic of geopolymer concrete is influenced by the concentration (molarity) of Sodium Hydroxide (Aleem and Arumairaj, 2012).

The type and concentration of alkaline solution affect the dissolution of fly ash. Ubolluk and Prinya found the result of measuring the silica and alumina ion at different concentration of alkaline. Referring to the Figure 2.3, at 5M of Sodium Hydroxide due to low base condition, the dissolution was low. For 10 M of Sodium Hydroxide the dissolution is increased as the concentration is higher. However, at 15M of Sodium Hydroxide the dissolution decreases due to increase in coagulation of silica (Bergna and Roberts, 2006).

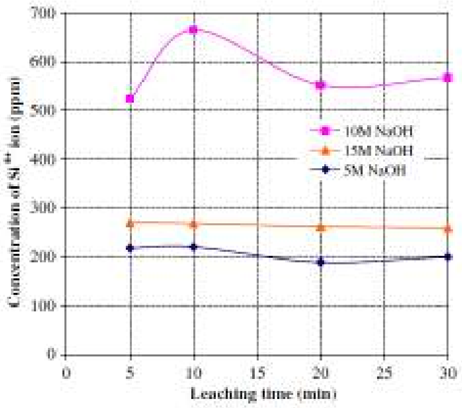


Figure 2.3-Graph of Si^{4+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH.

(Ubolluk and Prinya, 2009)

The silica ion will possess higher dissolution as compared to alumina as alumina content in fly ash is half of silica (Xu and Van Devanter, 2000). Based on Figure 2.4, for higher concentration Sodium Hydroxide which is 10M and 15M, practical amount of alumina ion was identified. Nevertheless, the amount for alumina concentration is smaller at 5M of Sodium Hydroxide (Ubolluk and Prinya, 2009).

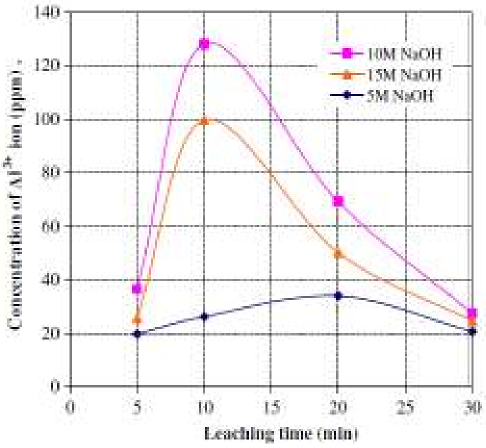
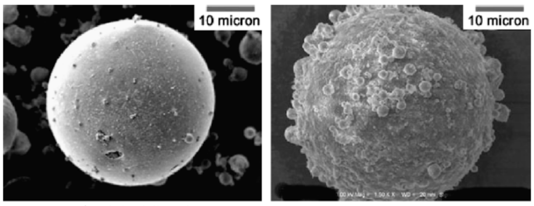


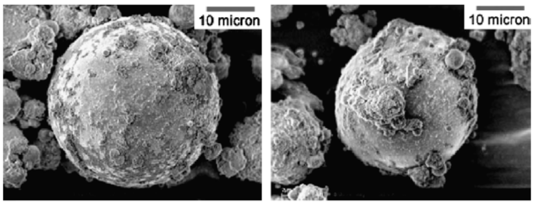
Figure 2.4-Al^{3+} ion concentration with fly ash/NaOH = 3:1 in 5, 10, and 15 M NaOH.

(Ubolluk and Prinya, 2009)

On the other hand, Ubolluk and Prinya also observed the surface of fly ash before and after leaching with different concentration of Sodium Hydroxide. Figure 7a represents the smooth original surface of fly ash. After going through 10 minutes leaching in Sodium Hydroxide, the surface becomes rough depending on the concentration of Sodium Hydroxide. Based on Figure 2.5 (b), (c) and (d), the less sign of attack is show at 5M of Sodium Hydroxide as compared to 10M and 15M of Sodium Hydroxide.



a) original fly ash b) 5M NaOH



c) 10M NaOH d) 15M NaOH

Figure 2.5-SEM of fly ash surfaces leached with NaOH for 10 min. **(Ubolluk and Prinya, 2009)**

Besides, Ubolluk and Prinya define that the compressive strength of geopolymer is also affected by the concentration alkaline. Figure 2.6 show that the compressive strength at high concentration of 10M and 15M for Sodium Hydroxide in separate mixing is high. In contrast, the low strength geopolymer is produce from 5M of Sodium Hydroxide as a result of low leaching of silicate and alumina ions in Sodium Hydroxide solution.

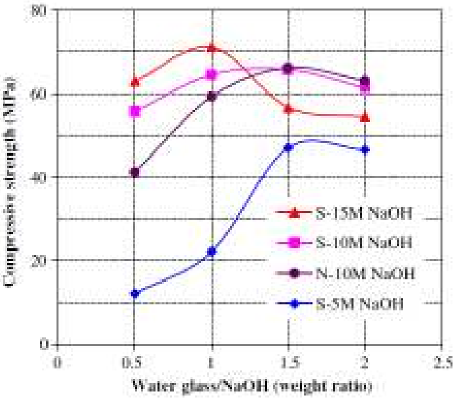


Figure 2.6-Relationship between water glass-to-NaOH ratio (G/N) and strength.

(Ubolluk and Prinya, 2009)

According to Hardijito (2003), referring to Figure 2.7 the compressive strength of geopolymer is proportionate to the alkaline concentration. This condition occurs due to the acceleration in geopolymerization process with increase of the concentration or molarity of Potassium Hydroxide.

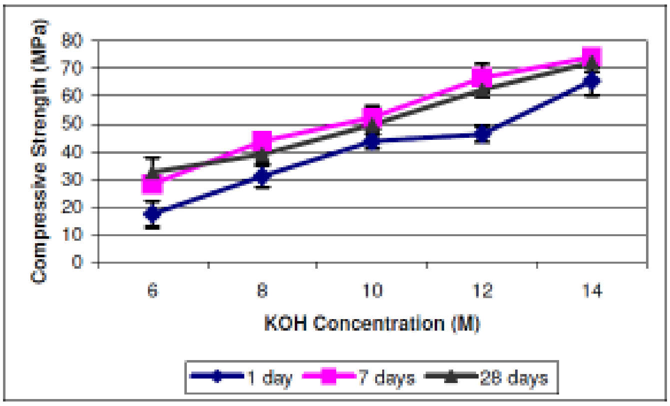


Figure 2.7-The Influence of KOH Concentration on the Compressive Strength (Hardijito, 2003)

2.4 Effect of temperature

Wang and Cheng (2003) defined that high temperature will speed up the geopolymerization process. The effect of temperature on setting time is shown in Figure 2.8. The initial and final setting time for room temperature and 60°C shall be observed and the Figure 2.8 obviously show that geopolymer at setting time 60°C is faster that at the room temperature. This is due to water loss increasing the setting rate. It shows that at room temperature, the time taken for the geopolymer to reach final setting is about 9.5 hours (Wang and Cheng, 2008).

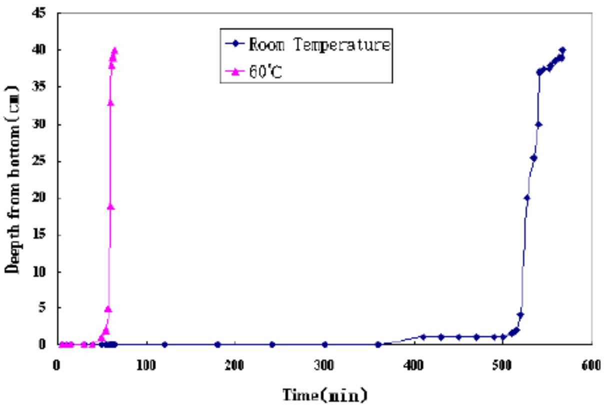
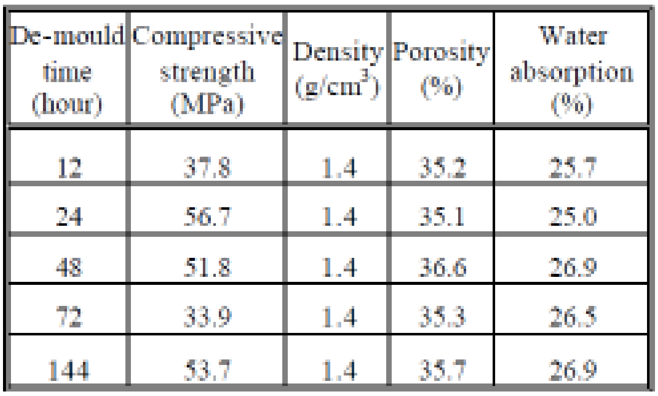


Figure 2.8-The effect of temperature on setting time (Wang and Cheng, 2008)

The effect of de-mould time on geopolymer properties at room temperature and 60°C is shown in Table 2.1 and Table 2.2. Referring to both table, generally can be said that geopolymer have similar characterization. The sample de-mould after 24 hours has the best compressive strength for room temperature and 48 hours for 60°C. However, the compressive strength is decreasing after 24 and 48 hours for respective temperature (Wang and Cheng, 2008).

Table 2.1-Various properties of the geopolymer materials at room temperature

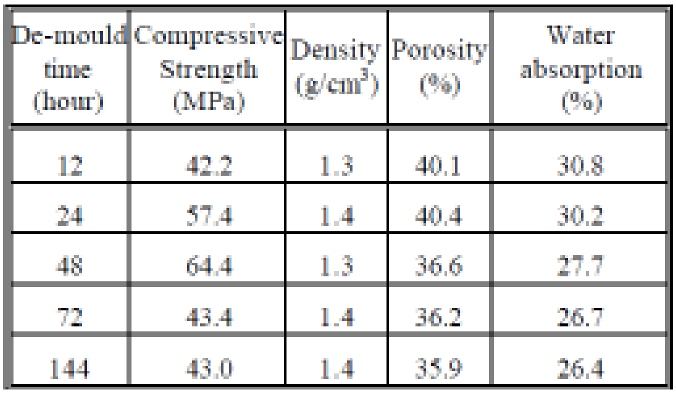
(Wang and Cheng, 2008)



De-mould time (hour)	Compressive strength (MPa)	Density (g/cm^3)	Porosity (%)	Water absorption (%)
12	37.8	1.4	35.2	25.7
24	56.7	1.4	35.1	25.0
48	51.8	1.4	36.6	26.9
72	33.9	1.4	35.3	26.5
144	53.7	1.4	35.7	26.9

Table 2.2-Various properties of the geopolymer materials at 60℃

(Wang and Cheng, 2008)



De-mould time (hour)	Compressive Strength (MPa)	Density (g/cm^3)	Porosity (%)	Water absorption (%)
12	42.2	1.3	40.1	30.8
24	57.4	1.4	40.4	30.2
48	64.4	1.3	36.6	27.7
72	43.4	1.4	36.2	26.7
144	43.0	1.4	35.9	26.4

Based on the result in the table, Wang and Cheng (2008) stated that the trends of the compressive strength can be developed as shown in Figure 2.9. It shows that the compressive strength changing from room temperature to 60°C is similar. The compressive strength of geopolymer at setting time 60°C should be higher that setting room due to high temperature will speed up the geopolymerization process.

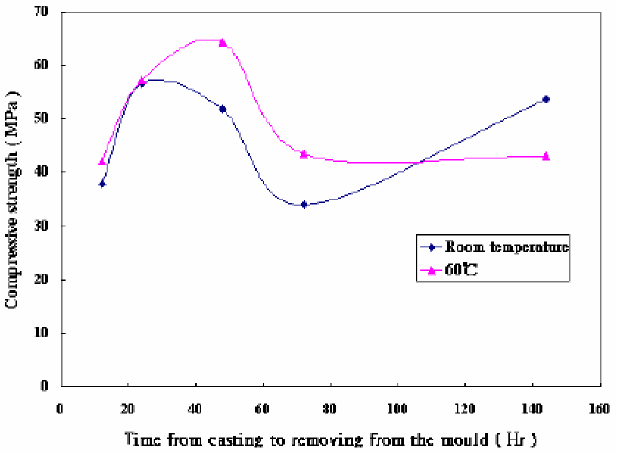


Figure 2.9-The trend of compressive strength changing at different temperatures

(Wang and Cheng, 2008)

2.5 Avrami Kinetic Theory

Kinetic of transformation typically describes as a standard equation known as Kolmogorov-Johnson-Mehl-Avrami (KJMA). This theory is describes how solids transform from one phase to another phase at constant temperature. The theory can be specifically describe the kinetic of crystallization and also generally use to other change of phase in material.

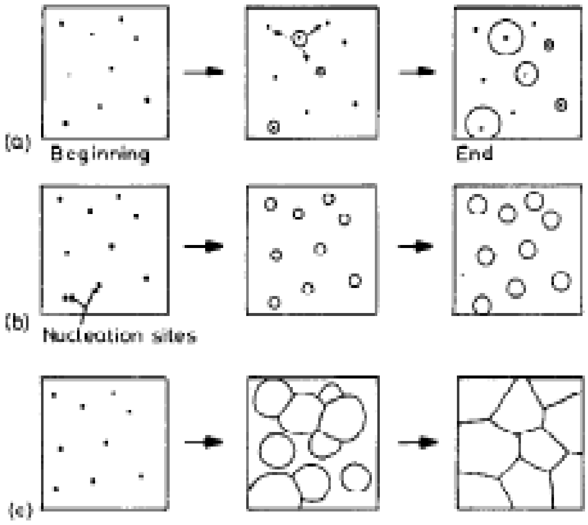


Fig. 5.24 (a) Nucleation at a constant rate during the whole transformation. (b) Site saturation—all nucleation occurs at the beginning of transformation. (c) A cellular transformation.

Figure 2.10-Transformation types

Referring to Lukman et al (2008), the degree of crystallinity is first measured by the geopolymer deposition, δ_r, defined as the mass fraction of the deposition that obtains after cooling process using the Equation 1:

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

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:

$$1 - X =_{\mathrm{e}} -Kt^{n}$$

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

Replacing the X in Equation 2 with δ_r 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 [13, 18].

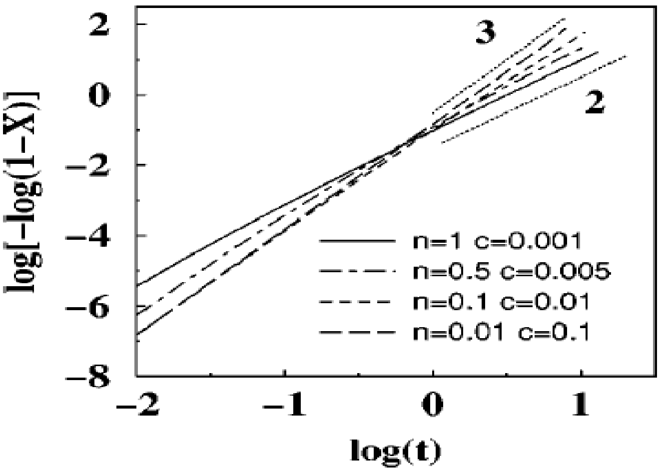


Figure 2.11-KJMA plots for different sets of parameters.

2.6 Leatherhead Food Research Analyzer (LFRA)

LFRA is a type of Universal Testing Machine (UTM) and during the last 20 years it is has become widespread. There are three main components for UTMs such as the drive system, test cells and the puncture (Bourne et al., 1966).

The drive system gives motion to cross-head that hold parts of test cells. The drive system shall be level system, double or single screw, chain or eccentric and hydraulic. A single screw is driven by a standard TA.TX2 Texture Analyzer.

The test cells are holding the food and apply force to it. It is divided into two parts which is lower and upper parts. A lower part is stationary and attached to the base of machine to support or contains the food test while an upper part is attached to crosshead or arm.

The puncture test will measure the force applied to push a probe into food. The test is characterized as follow:

a) A force measuring instrument.
b) Penetration of the probe into the food causing irreversible crushing or flowing of the food.
c) The depth of penetration is usually held constant.

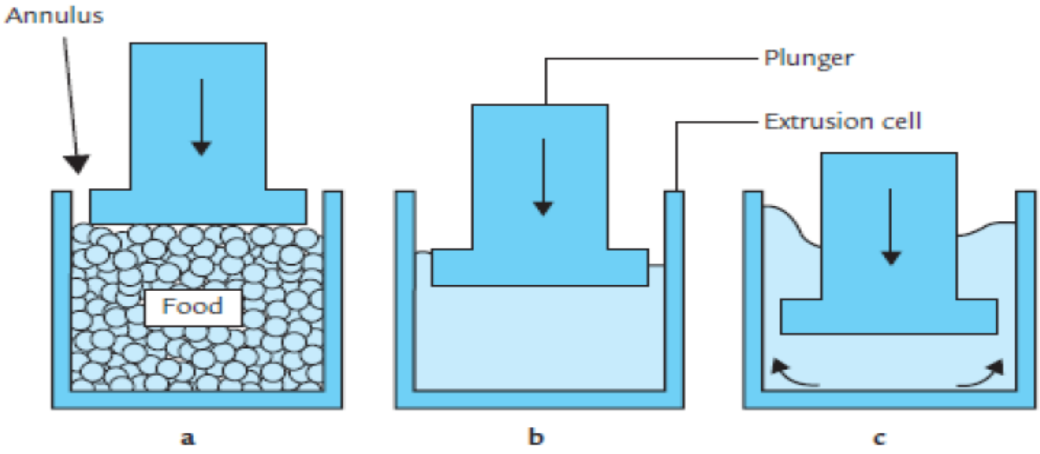


Figure 2.12- Simple cell for back-extrusion tests. (a) The plunger goes down and begins to contact the surface of food; (b) Food is packed down and some liquid may be squeezed out; (c) Food is extruded through annulus. (Bourne, 2002)

Figure 2.13 shows a typical Texture Profile Analysis (TPA) curve from Instron Universal Testing Machine. The force peak for first bite was defined as hardness. The significant break in curve on the first bite is known as fracturability. The cohesiveness was defined by ratio of positive force area under the first and second (A2/A1) compression. The adhesiveness represented by negative force area of first bite (A3) showing the necessary work to pull the compressing plunger from the sample.

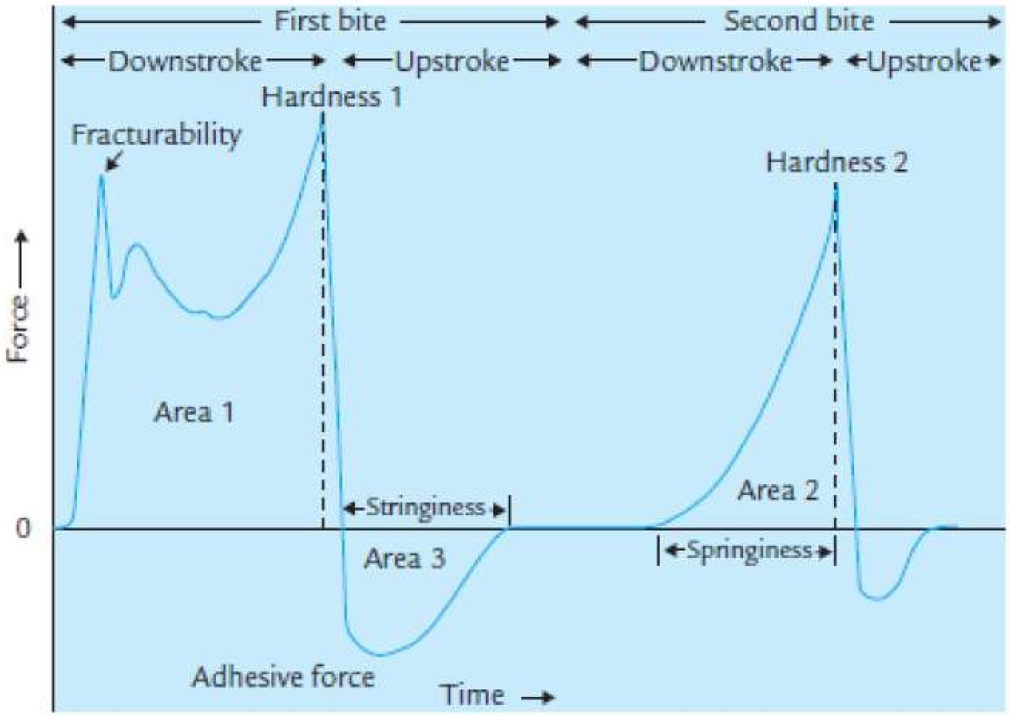


Figure 2.13- A generalized texture profile analysis curve obtained from Instron Universal Testing Machine (Bourne, 2002)

Table 2.3-Dimensional Analysis of TPA Parameters (Bourne,1966a)

Mechanical parameter	Measured variable	Dimension of measured variable
Hardness	Force	mlt^{-2}
Cohesiveness	Ratio	Dimensionless
Springiness	Distance	l
Adhesiveness	Work	ml^2t^{-2}
Fracture-ability (brittleness)	Force	mlt^{-2}
Chewiness	Work	ml^2t^{-2}
Gumminess	Force	mlt^{-2}

Research works done in geopolymer are as listed below:

Table 2.4-List of research works based on chronological order

Year	Reference	Title	Findings
2003	Wang and Cheng	Production geopolymer materials by coal fly ash.	- Compressive strength at high temperature for setting time is higher. - Geopolymer have high fire resistant. - At room temperature, time taken to harden is 9.5 hours but at 60° C 1 hour.
2007	Provis and Devanter	Geopolymerization kinetics. 2. Rection kinetic modeling	- Development of mathematical and computational technique can be applied on geopolymeric aluminosilicate materials.
2008	Prabir SARKER	A constitutive model for fly ash based geopolymer concrete.	- Popovics equation can be used for geopolymer concrete
2008	Djwantoro Hardjito	Strength and thermal stability of fly ash-based geopolymer mortar.	- High concentration alkaline and use ratio silicate to hydroxide 0.8 to 1.5 will produce high compressive strength
2009	Nugteren et al.	High strength geopolymer produced from coal combustion fly ash.	- pH different impact the compressive strength
2009	Thokchom et al.	Performance of fly ash based geopolymer mortar in sulphate solution.	- White depositions appear during exposure to magnesium sulphate
2009	Ubolluk and Prinya	Influence of NaOH solution on the synthesis of fly ash geopolymer.	- Leaching depend on NaOH concentration and leaching time.

2010	Vijai et al.	Effectof types curing on strength of geopolymer concrete.	- Compressive strength test at hot cured higher than at ambient temperature.
2011	Anuar et al.	Strength characteristic of Geopolymer concrete containing recycled concrete aggregate.	- Concentration NaOH influence the strength of geopolymer.
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 Arumairaj	Optimum mix for the Geopolymer concrete.	- Compressive strength increase with optimum increase of aggregate.
2012	Sreevidya et al.	Acid resistance of fly ash based geopolymer mortar under ambient curing and heat curing.	- Geopolymer are highly resistance to sulfuric acid and hydrochloric acid. - Low weight loss
2012	Khater and Zedane	Geopolymerization of industrial by-product and study of their stability upon firing treatment.	- Phosphogypsum affect the geopolymerization
2012	Anuradha et al.	Modified guidelines for geopolymer concrete mix design using Indian standard	- Geopolymer alternative solution for CO_2. - Geopolymer has excellent compressive strength.
2012	Aleem and Arumairaj	Geopolymer concrete-A Review	- High concentration NaOH, high compressive strength. - High curing temperature and longer time, increased compressive strength.

CHAPTER 3

METHODOLOGY

In this section, the process routes and related procedure or methodology throughout the project will be explain and describe in details. Gantt chart and the milestone of the project also will be included. Along with that, the equipment, apparatus and materials used will be listed under this chapter too.

3.1 Research Methodology

Type of research that will be used in this study is performing the experiment in the laboratories using the specific materials and equipments required. Before that, the literature review and study on others and previous paper work need to be done to set the suitable parameter in this study. Parameters selected for this study is types of alkaline, concentration of alkaline and effect of temperature which will be the goal for the experiment. Chart below will summarize the steps and route to achieve the target.

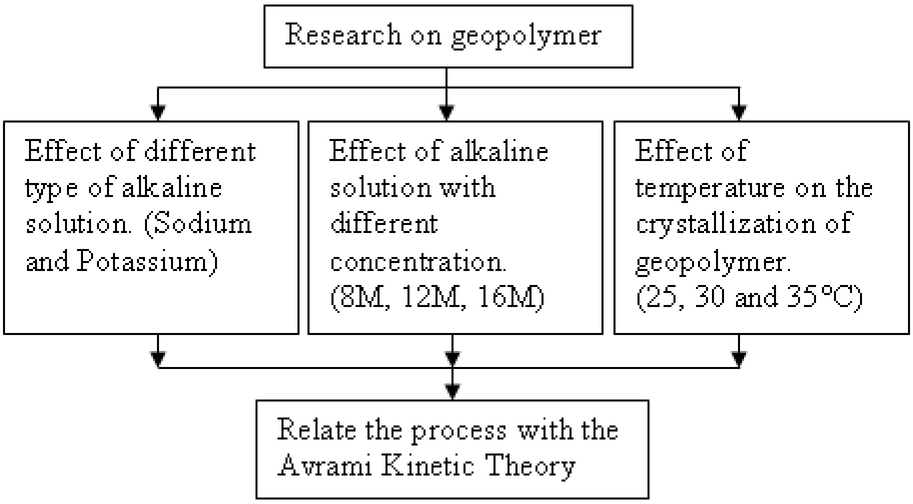


Figure 3.1-Route for test on geopolymer

3.2 Project Activities

Basically the details procedure for the experiment needs to be developed before performing the experiment in the laboratories. There are few steps required in producing geopolymer and achieving the target parameters. The ratio of fly ash to alkaline solution that will be used is 4:1. The general procedure for the crystallization of geopolymer for different types of alkaline solution is as below:

Procedure:

1) The Hydroxide (NaOH/KOH) pellet is weighted depend on concentration required (8M/12M/16M). The pellet is mixed in separate mixture with distillation water in the volumetric flask.
2) The hydroxide/alkaline solution are kept in store for about 24 hours. (to remove heat as the reaction is exothermic)
3) The alkaline solution is mixed with the fly ash depends on the ratio required until well mix.
4) The mixture is molded in the mould and exposed to setting temperature (25/30/35°C).
5) The time is set and the mould is observed. The mould will be tested using LFRA Texture Analyzer for every 30 minutes until it crystallized. The time and data from LFRA Texture Analyzer is recorded.
6) The recorded data from LFRA Texture Analyzer will be related to the Avrami Kinetic Theory.

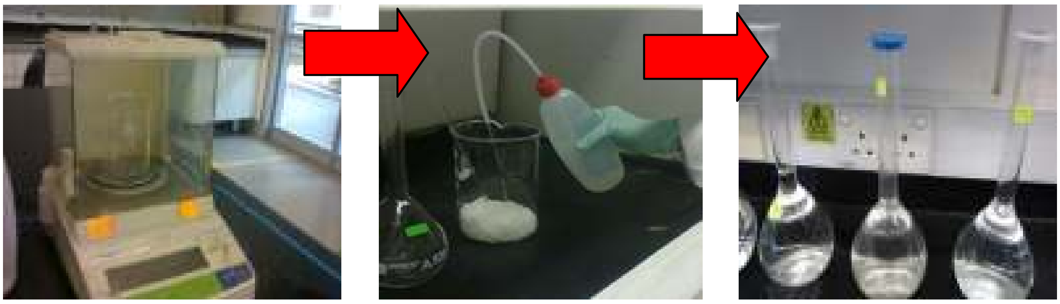

(a) (b) (c)

Figure 3.2-Alkaline preparation (a)Weighing the alkaline pellet, (b)Diluting pellet with distilled water, (c)Alkaline solution

3.2.1 Effect of different types of alkaline

Two types of alkaline solution which is Sodium and Potassium Hydroxide solution at different concentration will be used. The fly ash is mixed with the alkaline solution using 4:1 ratio until well mixed. The mixture is molded in the mould and exposed to setting temperature. The time is set and the mould is observed. The mould will be tested for every 30 minutes using LFRA Texture Analyzer. The time and data from LFRA Texture Analyzer is recorded. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect of different type of alkaline solution is shown in Figure 3.3.

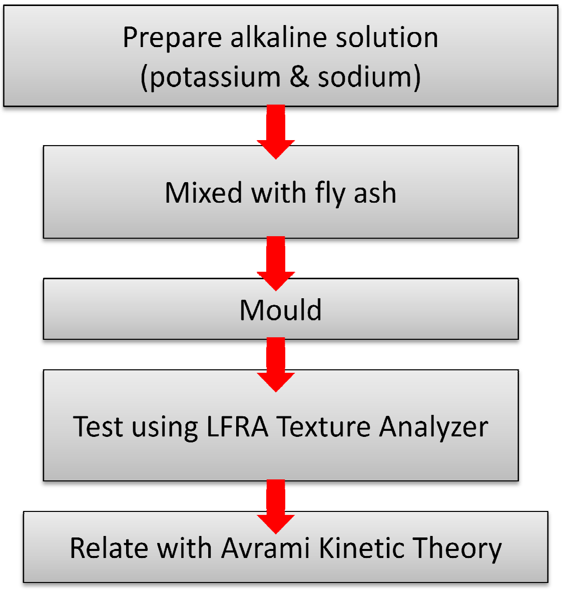


Figure 3.3-Procedure for effect of different type of alkaline

(a) (b)

Figure 3.4-(a)Potassium Hydroxide (b)Sodium Hydroxide

3.2.2 Effect of alkaline concentration

For the experiment on alkaline concentration, the concentration of solution will be varied. The amount of alkaline pellet and distillation water required will be differ depend on the concentration required. The general procedure to test on alkaline concentration is, the fly ash is mixed with the alkaline solution at 8M, 12M or 16M using 4:1 ratio until well mixed. Then, the mixture is molded in the mould and exposed to setting temperature. After that, the time is set and the mould is observed. The mould will be tested for every 30 minutes using LFRA Texture Analyzer. The time and data from LFRA Texture Analyzer is recorded. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect of different concentration of alkaline solution is shown in Figure 3.5.

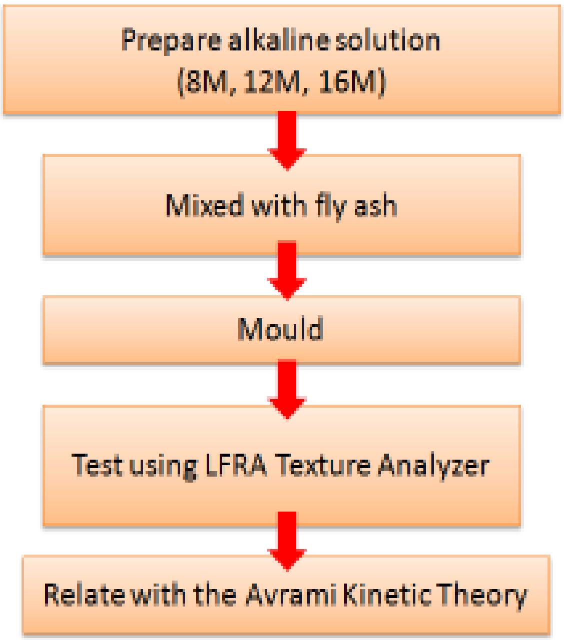


Figure 3.5-Procedure for effect of alkaline concentration

Figure 3.6-Alkaline solution with different concentration

3.2.3 Effect of temperature

The mould geopolymer will be tested at different temperature at 25, 30 and 30°C to observe the optimum temperature for geopolymer to crystallize. Thus, the geopolymer need to be prepared. Firstly, the fly ash is mixed with the alkaline solution at 8M, 12M or 16M using 4:1 ratio until well mixed. Then, the mixture is molded in the mould and exposed to setting temperature 25, 30 or 35°C. After that, the time is set and the mould is observed. The mould will be tested for every 30 minutes using LFRA Texture Analyzer. The time and data from LFRA Texture Analyzer is recorded. The recorded data will be related to the Avrami Kinetic Theory. The simplified procedure for effect of temperature is shown in Figure 3.7.

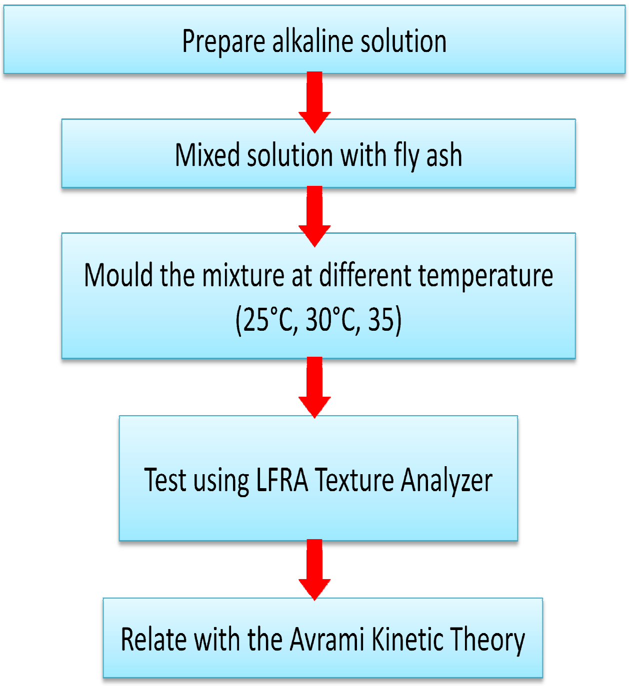


Figure 3.7-Procedure for effect of temperature

Figure 3.8-Water bath for temperature test on geopolymer

3.3 Gantt chart and Key Milestone

To ensure that the project will be according to the dateline that has been issued by the university, I will refer the Gantt chart to make the time period and dateline that I have for every steps of the project. The chart below shows the timeline for every process of the project from FYP I until FYP II.

Table 3.1-Timeline for FYP I

DETAILS/WEEK	1	2	3	4	5	6	7	Mid sem	8	9	10	11	12	13	14
Meeting with Supervisor	🟩	🟩	🟩	🟩	🟩	🟩	🟩		🟩	🟩	🟩	🟩	🟩	🟩	🟩
Preliminary Research Work		🟩	🟩	🟩	🟩										
Submission of Extended Proposal Defense				🟩	🟩	🟩 ●									
Proposal Defense										🟩					
Preliminary Experiment											🟩	🟩	🟩		
Submission of Interim Draft Report											🟩	🟩	🟩	🟩 ●	
Submission of Interim Report															🟩 ●

Table 3.2-Timeline for FYP II

DETAILS/WEEK	1	2	3	4	5	6	7	Mid sem	8	9	10	11	12	13	14	15
Chemicals, materials and equipments preparation	🟩															
Crystallization on different type of alkaline test	🟩	🟩	🟩	🟩	🟩	🟩	🟩		🟩	🟩						
Crystallization on concentration of alkaline test	🟩	🟩	🟩	🟩	🟩	🟩	🟩		🟩	🟩						
Crystallization on temperature test	🟩	🟩	🟩	🟩	🟩	🟩	🟩		🟩	🟩						
Submission of progress report									●							
Pre-SEDEX												●				
Submission of Draft Report													●			
Submission of Dissertation (soft bound)														●		
Submission of Technical Paper														●		
Oral presentation															●	
Submission of Project Dissertation (hard bound)																●

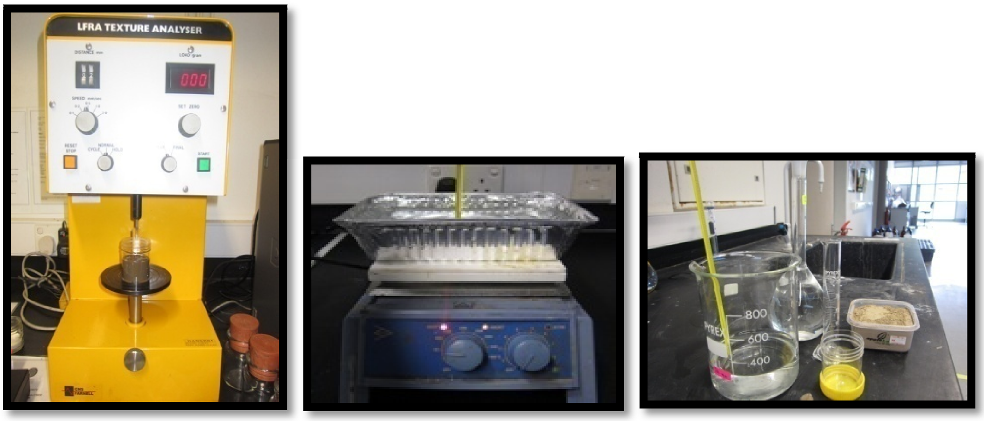
3.4 Equipment, Apparatus and Material Required

The basic tools to conduct an experiment need to be prepared and it must available at the workstation. Most of them are available in the Chemical Engineering Department. They generally can be divided into three main tools t which is equipments, apparatus and material.

There are two main equipments which is LFRA Texture Analyzer and hot plate. They will be used in this experiment depending on their specific purposes. The LFRA Texture Analyzer is used to identify the crystallization point of geopolymer while the hot plate is needed to supply heat for the water in the temperature test.

Basically, the apparatus is needed in order to conduct the experiment from early stages until the end. In this experiment, the beaker and rod glass will be used to dissolve the alkaline pellet with distilled water. After that, it will be diluted in the volumetric flask until desired concentration. Then, measuring cylinder is used to measure the desired amount of alkaline solution before it can be mixed with the fly ash that is weighted using the weighing scale. The mixture will be mixed using the spatula in a beaker. Then, mould will be used to mould the mixture. The thermometer will be used to test the temperature of water while conducting the experiment.

In conducting the experiment, the material also will play the most important role. The Sodium Hydroxide Potassium Hydroxide pellet will be dissolved by the distilled water to be used as alkaline solution. The fly ash is the main ingredient in this experiment.



(a) (b) (c)

Figure 3.9-Basic tools (a) LFRA Texture Analyzer (b) Hot plate (c) Apparatus

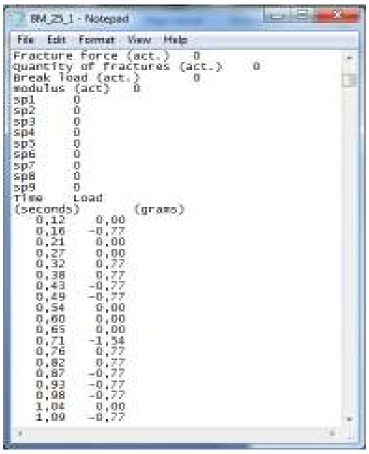
CHAPTER 4

RESULT AND DISCUSSION

The following section discusses the result obtained from the experiment performed so far. The parameters that have been tested include effect of different type of alkaline, effect of alkaline concentration and effect of temperature. The LFRA to quantify the crystallization point is used for all experiment.

4.1 LFRA Texture Analyzer

During the experiment, the LFRA Texture Analyzer test is performed until the geopolymer in solid is formed. Every 30 minutes, the test using LFRA will be performed. Basically, the data for the test will be obtained from the LFRA directly using the software in the form of notepad. Based on the data, the graph of load (g) versus time (sec) will be produced. (Refer *Figure 4.2*)

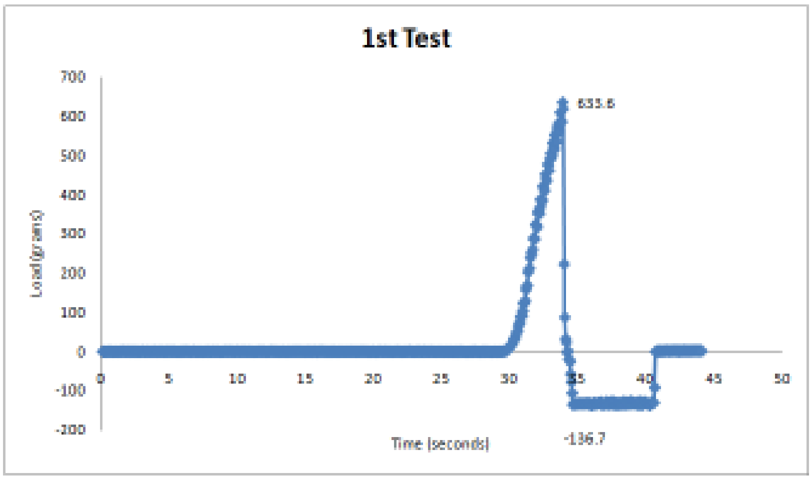


```
Fracture force (act.)    0
quantity of fractures (act.)    0
Break load (act.)        0
modulus (act)    0
sp1      0
sp2      0
sp3      0
sp4      0
sp5      0
sp6      0
sp7      0
sp8      0
sp9      0
Time     Load
(seconds)        (grams)
    0,12     0,00
    0,16    -0,77
    0,21     0,00
    0,27     0,00
    0,32     0,77
    0,38     0,77
    0,43    -0,77
    0,49    -0,77
    0,54     0,00
    0,60     0,00
    0,65     0,00
    0,71    -1,54
    0,76     0,77
    0,82     0,77
    0,87    -0,77
    0,93    -0,77
    0,98    -0,77
    1,04     0,00
    1,09    -0,77
```

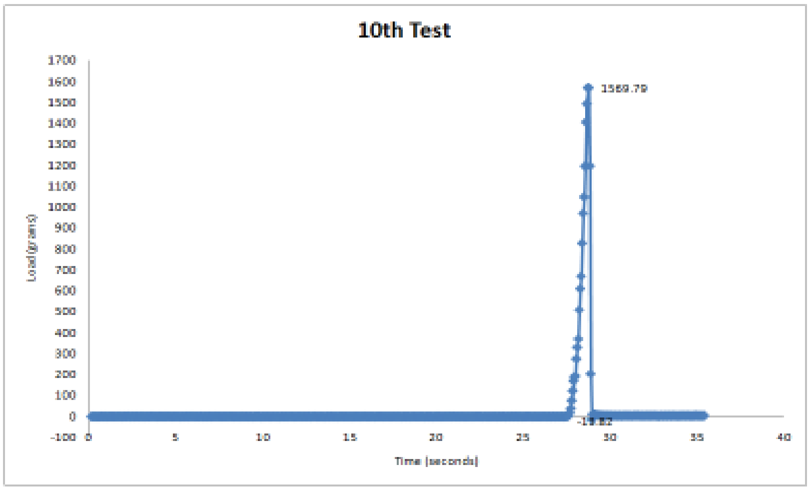
Figure 4.1-Snapshoot from LFRA Texture Analyzer

Here are few sample of graph produced by the LFRA Texture Analyzer for each test. The speed of probe is constant at 0.5 mm/s, probe type is constant same goes to its diameter and depth of penetration is at 2 mm. There are few parameters that can be extracted using the LFRA Texture Analyzer data such as hardness, adhesiveness and springiness.

Figure 4.2 are the graphs from the LFRA for 8M Potassium Hydroxide at 25°C. By the graph, we can assume that the solution is partially solidified or in mixture of solid and liquid. At end of each compression, the curve showed the sharp peak defined as hardness. This situation arises as the machine approaches the end of compression stroke at constant speed, rapidly reverses direction and performs upward stroke at constant speed. In addition, the negative force area is caused by the necessary work to pull the plunger away from the sample that known as adhesiveness. The adhesiveness decreases as geopolymer is going to be crystallize. This is showed by Figure 4.2 (a) and (b).



(a)

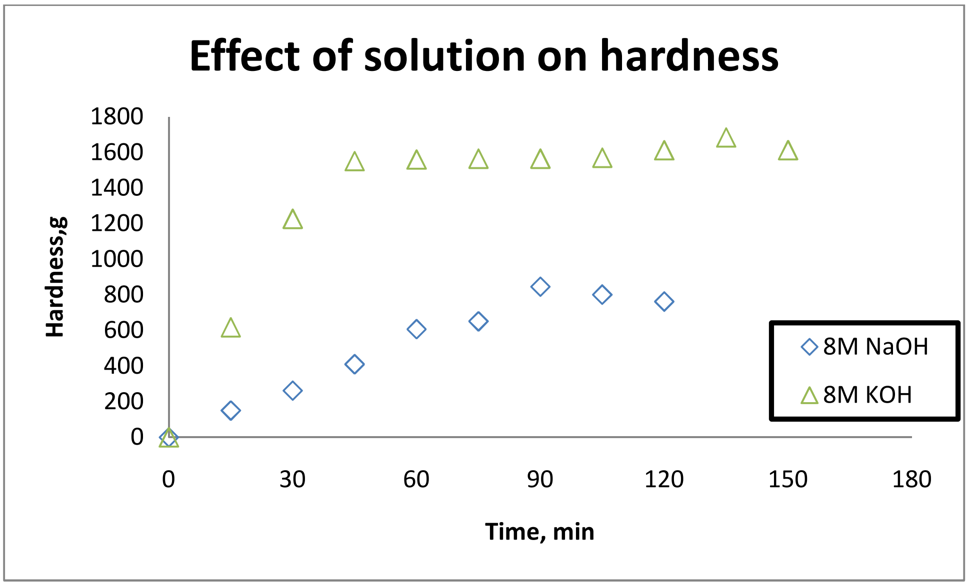


(b)

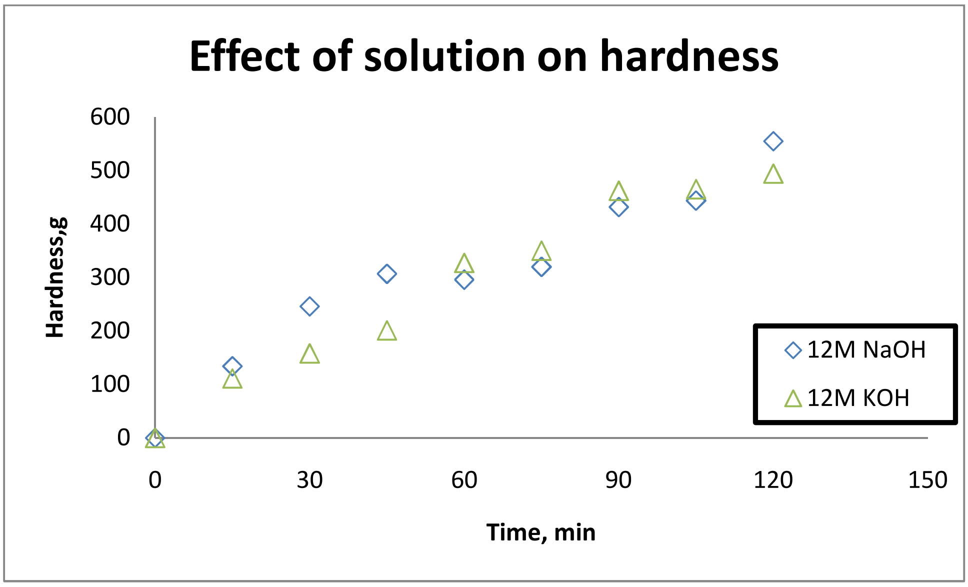
Figure 4.2-Graph from LFRA for 8M KOH at 25°C. (a) First test using LFRA; (b) Tenth test using LFRA

4.1.1 Effect of different types of alkaline

Figure 4.3 until 4.5 indicate the optimum time required by each solution to reach maximum hardness. Based on the graph, the Potassium Hydroxide performed well at low concentration while Sodium Hydroxide is vice versa. Throughout the graph, at 8M Potassium Hydroxide reach its maximum hardness faster but it is became slower at 16M compared to Sodium Hydroxide. This situation will be discussed further under effect of concentration.



(a)



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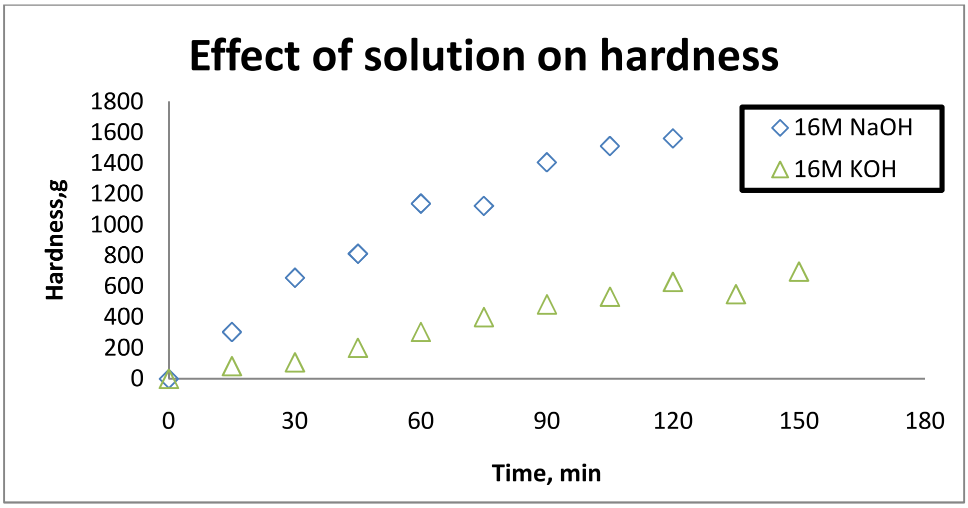
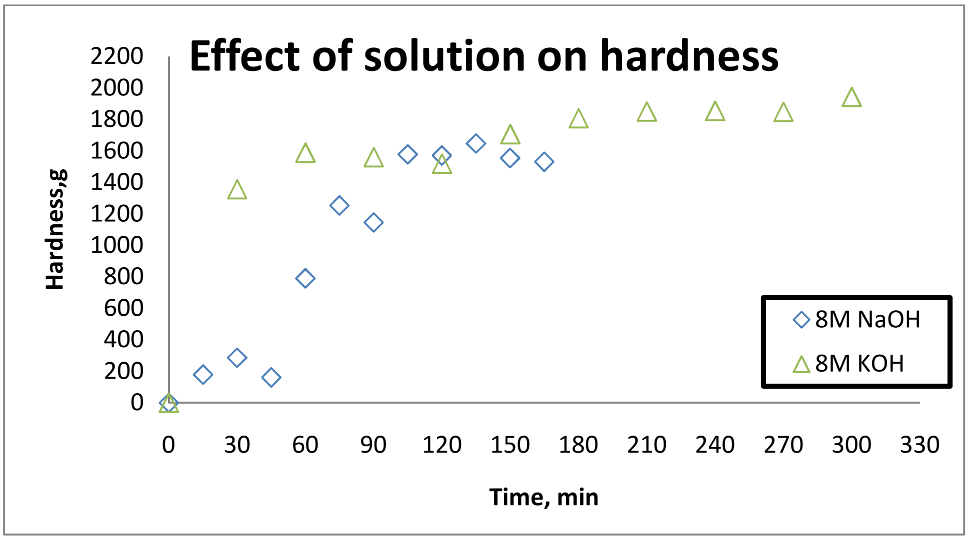
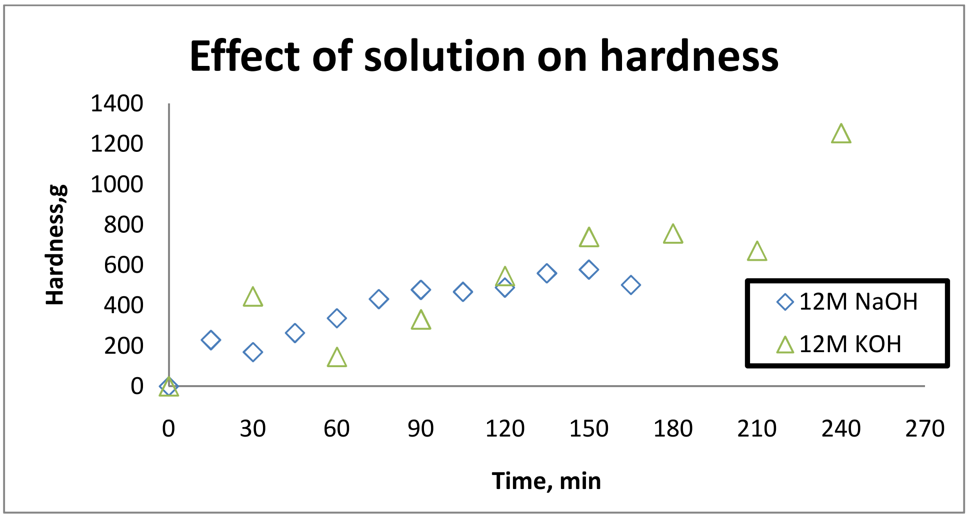


(c)

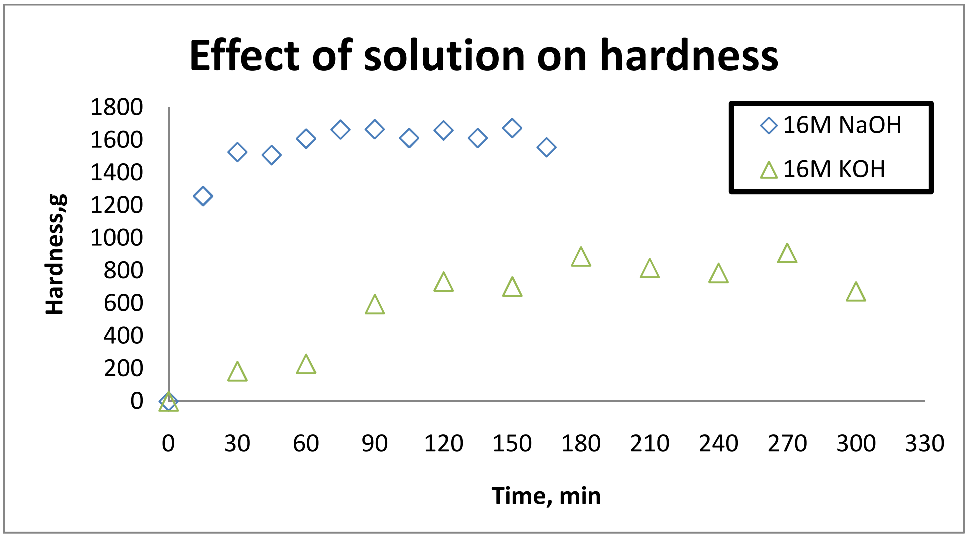
Figure 4.3-Effect of solution on hardness at 25°C. (a)8M; (b) 12M; (c)16M



(a)

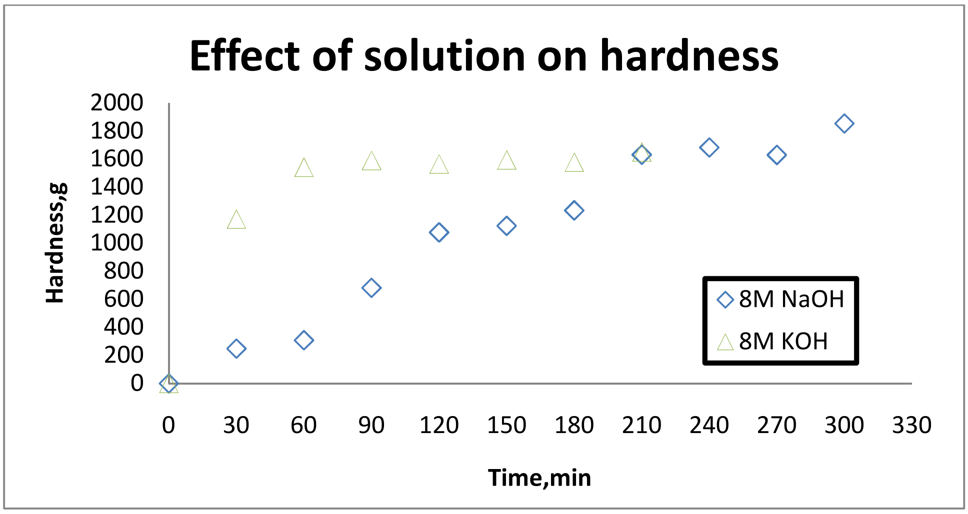


(b)

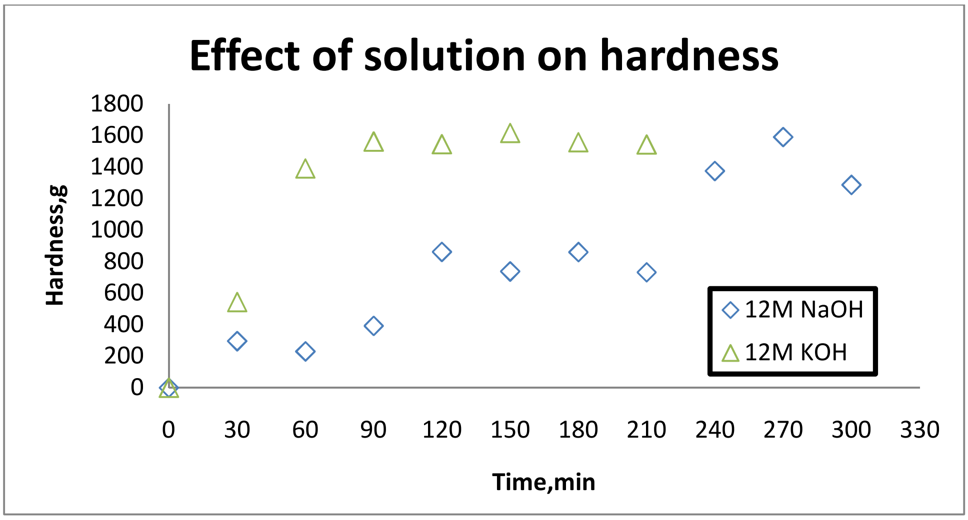


(c)

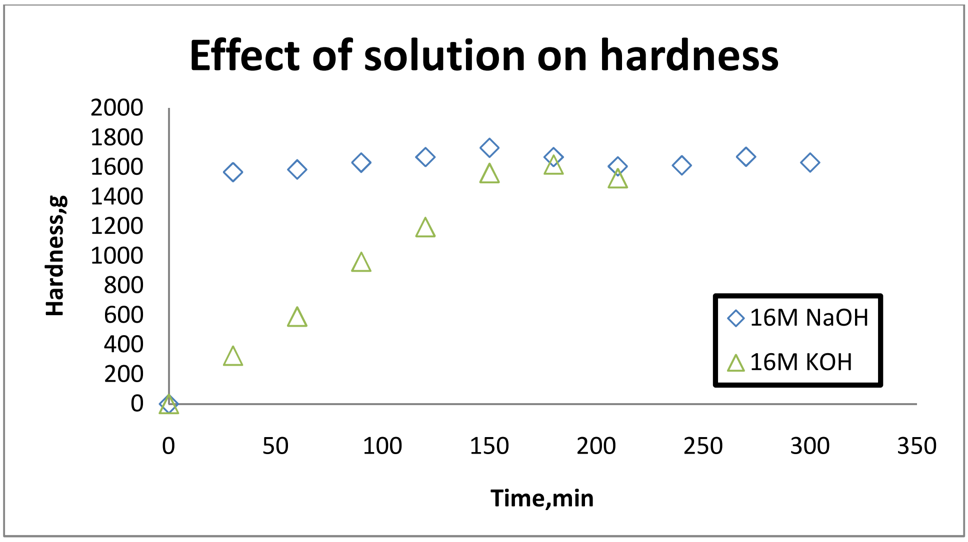
Figure 4.4-Effect of solution on hardness at 30°C. (a)8M; (b) 12M; (c)16M



(a)



(b)

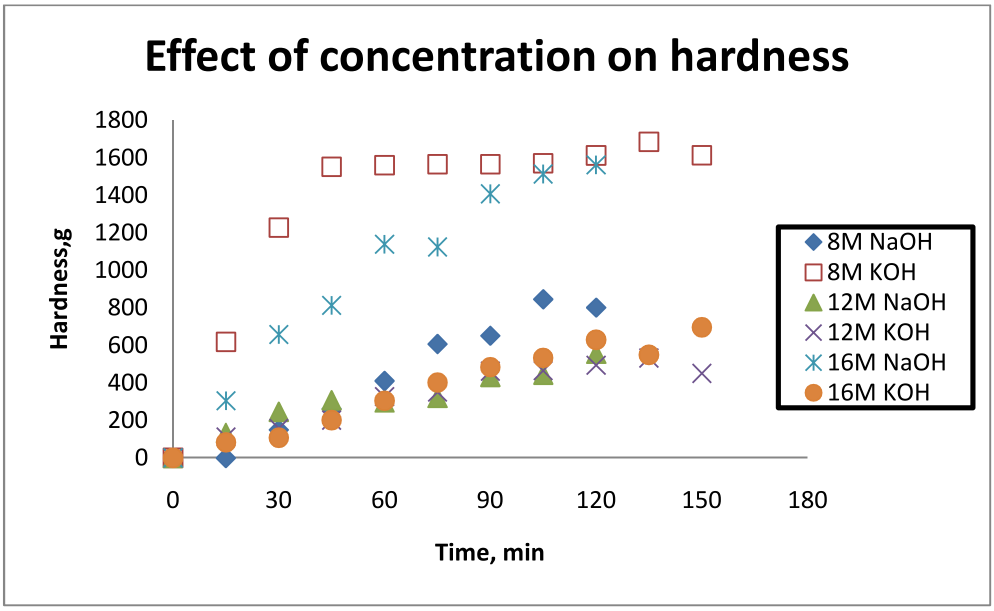


(c)

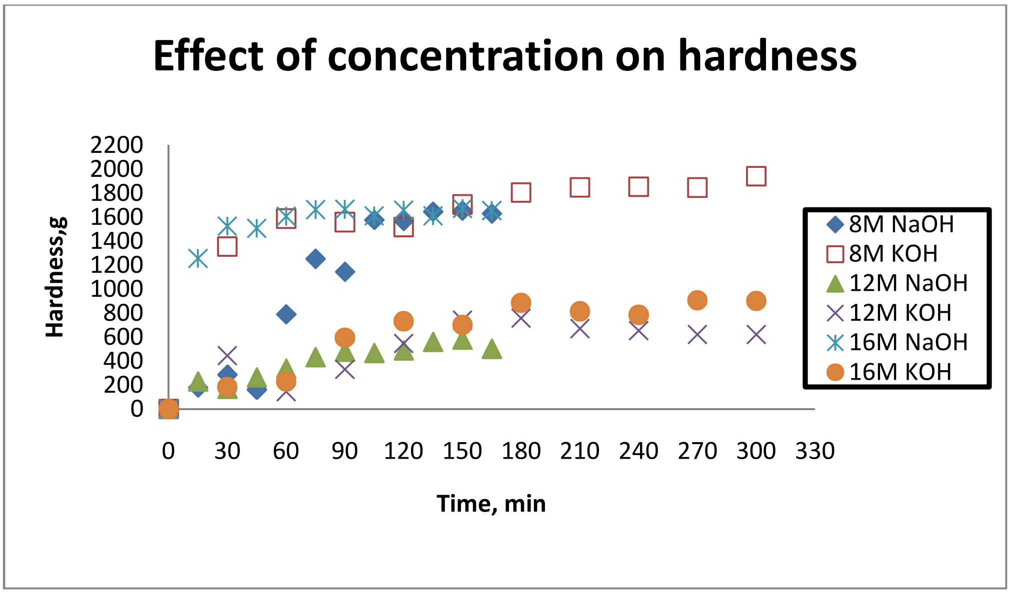
Figure 4.5-Effect of solution on hardness at 35°C. (a)8M; (b) 12M; (c)16M

4.1.2 Effect of alkaline concentrations

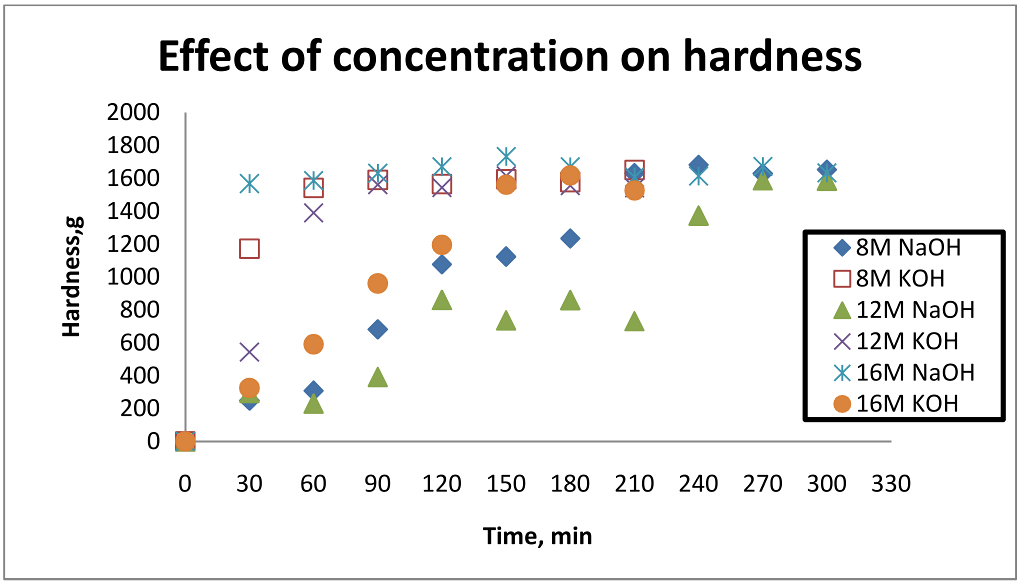
Figure 4.6 show that the 8M of Potassium Hydroxide achieved maximum concentration earlier than other samples while Sodium Hydroxide at 16M present as the best concentration. Based on the literature review, at more than 15M of Sodium Hydroxide, the dissolution supposed to be decreasing due to increase in coagulation of silica. This is due to acceleration of geopolymerization as the concentration is increased.



(a)



(b)

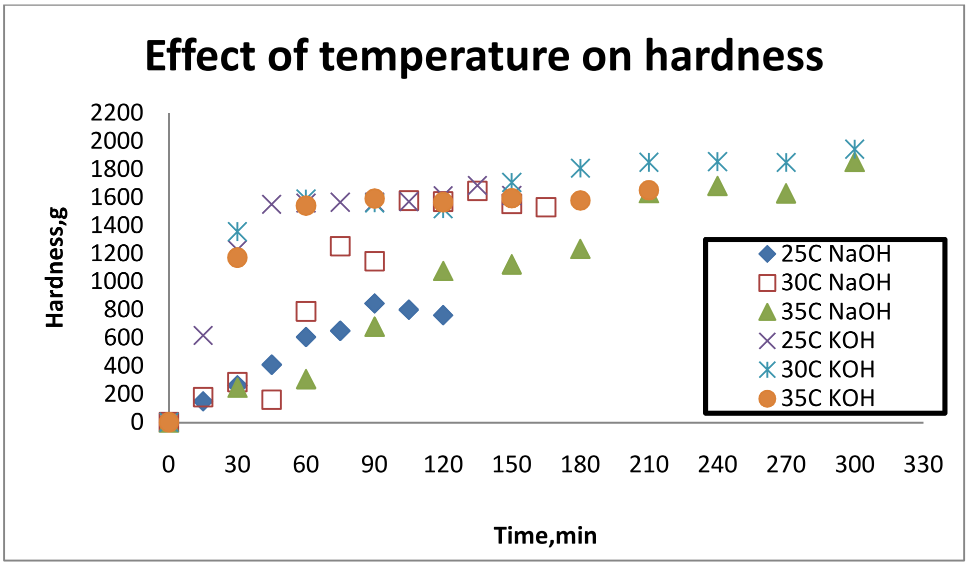


(c)

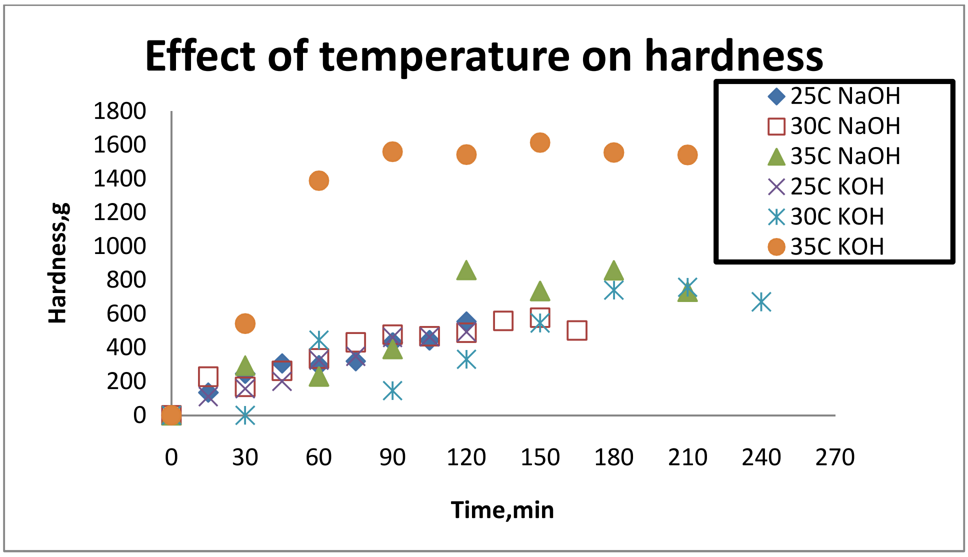
Figure 4.6-Effect of concentration on hardness. (a) 25C; (b) 30C; (c) 35C

4.1.3 Effect of temperature

Figure 4.7 shows that hardness increase linearly as the temperature is increasing. It is obvious that most of the samples are rapidly achieved maximum hardness at 35°C. The geopolymer setting time at 35°C is faster than others due to water loss will increase the setting rate.



(a)



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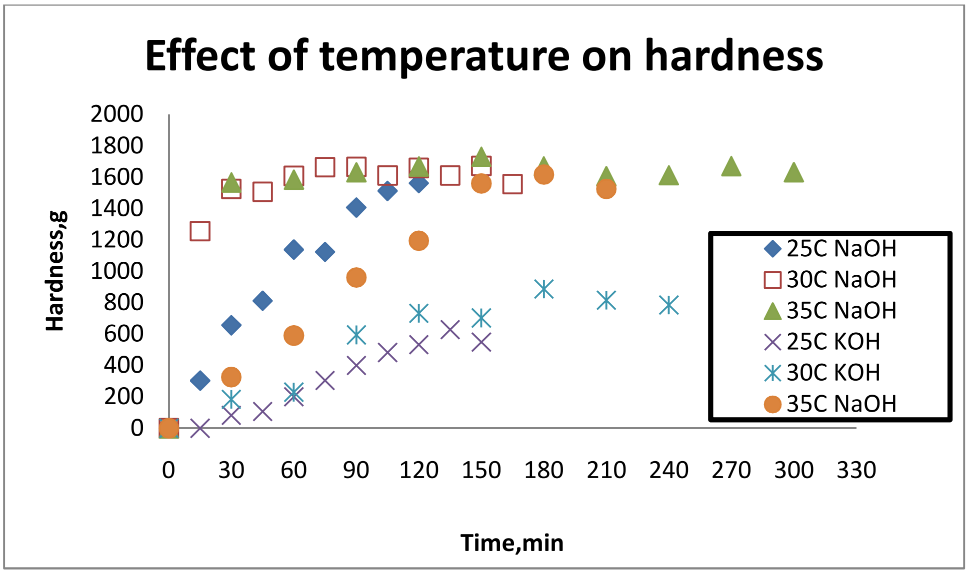
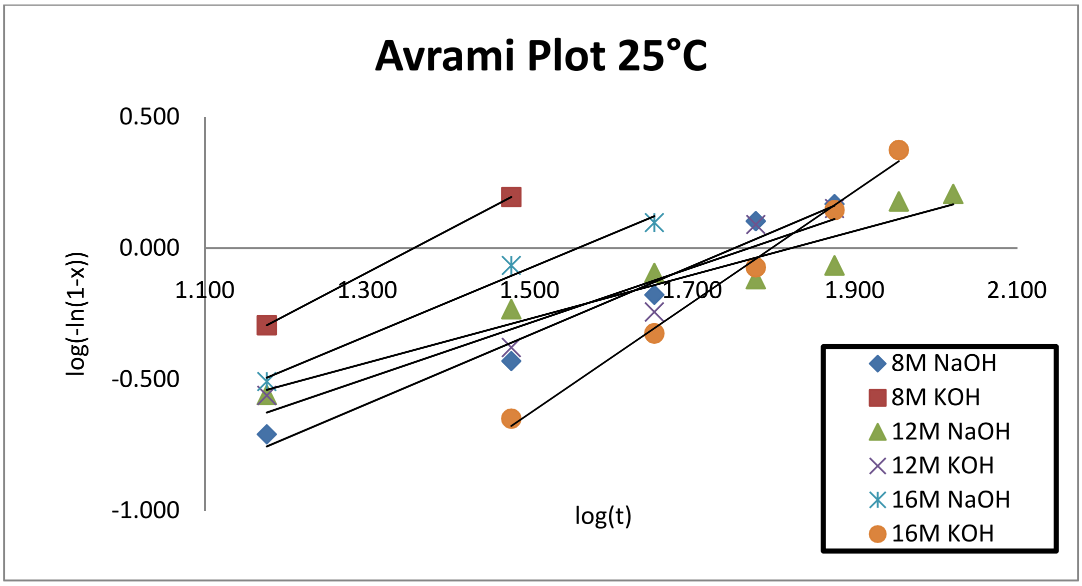


(c)

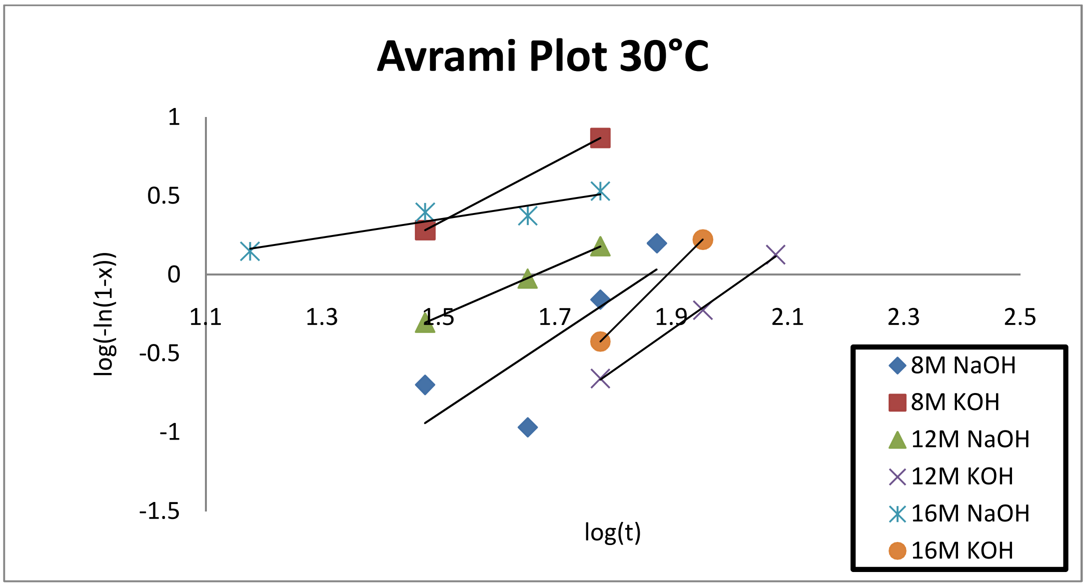
Figure 4.7-Effect of temperature on hardness. (a) 8M; (b) 12M; (c) 16M

4.2 Kinetic Analysis

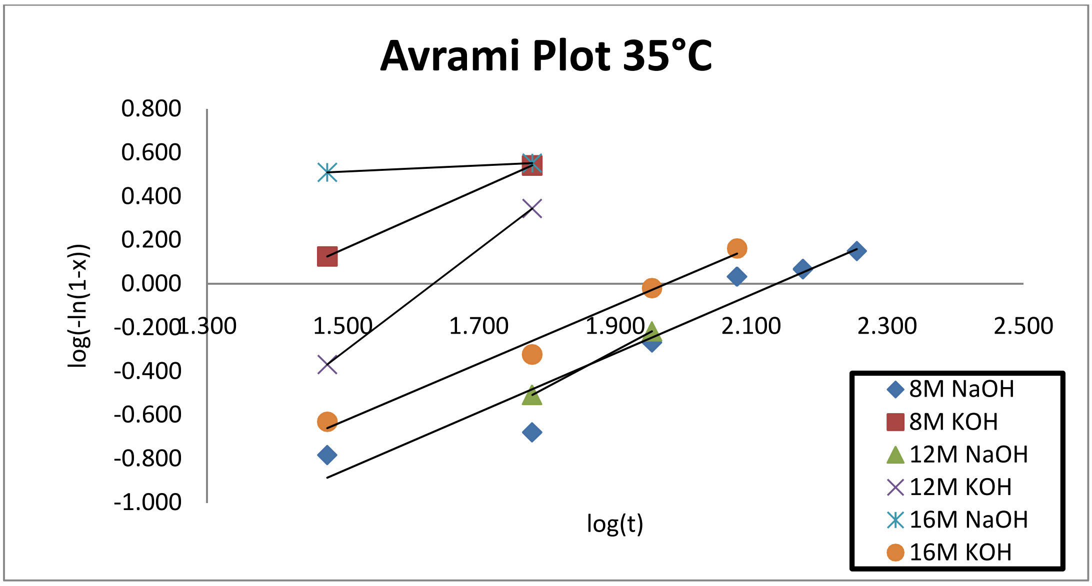
According to the graph of hardness represent earlier, the curve shall be analyzed using the Avrami Theory to extract the kinetic of crystallization. Figures 4.8 are plot log |-ln (1-x)| versus log (t) for the effect of solution, concentration and temperature on the hardness of geopolymer. From the plot, the Avrami exponent (*n*) and rate constant (K) are extracted and tabulated in the Table 4.1, 4.2 and 4.3.



(a)



(b)



(c)

Figure4. 8-Avrami Plot. (a) 25C; (b) 30C; (c) 35C

Based on the Tables, the obvious trend shall be observed from the value of growth rate (K). The K values for both solutions are opposed each other. The most accurate result is tabulated in Table 4.2 at 30°C. It shows that the K value for Potassium Hydroxide is increases with the concentration and temperature while the K value for Sodium Hydroxide is gradually decreases as the concentration and temperature increases. The expected value for the growth rate is increases as the concentration increases since geopolymerization process will accelerate as reported by Hardjito. Thus, the experiments need to be repeated at least three times to obtain more accurate result.

Besides, the Avrami exponent (*n*) also will be against the K value. The values will decreases as the K value is increases and vice versa. This specifies the variety of growth form at different concentration and temperature. Referring to the Avrami parameters developed by Hay in Table 4.4, a model of Spheres, Discs and Rods shall represented the three, two or one dimensional forms of growth. The growth form for the geopolymer shall be concluded as one, two and three dimension as some of the *n* values from the Table 4.1 until 4.3 is more than three.

Table 5-Extracted Avrami Parameters from Figure 29 (a)

Concentration	n	K (min^{-1})	Concentration	n	K (min^{-1})
8M NaOH	1.312	2.299	8M KOH	1.632	2.203
12M NaOH	0.835	1.521	12M KOH	1.054	1.867
16M NaOH	1. 290	2.010	16M KOH	2.112	3.797

Table 6-Extracted Avrami Parameters from Figure 29 (b)

Concentration	n	K (min^{-1})	Concentration	n	K (min^{-1})
8M NaOH	2.449	4.560	8M KOH	1.943	2.588
12M NaOH	1.608	2.680	12M KOH	2.600	5.290
16M NaOH	0.572	0.508	16M KOH	3.673	6.956

Table 4.3-Extracted Avrami Parameters from Figure 29 (c)

Concentration	n	K (min^{-1})	Concentration	n	K (min^{-1})
8M NaOH	1.342	2.869	8M KOH	1.383	1.917
12M NaOH	1.653	3.446	12M KOH	2.371	3.871
16M NaOH	0.140	0.303	16M KOH	1.324	2.615

Table 4.4-Avrami Parameters for crystallization of polymer (J. N. Hay)

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

CHAPTER 5
CONCLUSION AND RECOMENDATION

5.1 CONCLUSION

In conclusion, the result that obtained from the LFRA Texture Analyzer based on hardness showed that;

- The best concentration for Potassium Hydroxide is 8M as the time taken to crystallize is shorter compared to other concentration.
- Meanwhile, for the Sodium Hydroxide, the best concentration is 16M.
- The best alkaline solution is Potassium Hydroxide as at low concentration it takes shorter time to crystallize compare with Sodium Hydroxide.
- The high temperature is highly recommended to crystallize the geopolymer in shorter time. However, the geopolymer still can be crystallized at room temperature.

Besides, based on Avrami Theory;

- The growth rate (K) of Potassium Hydroxide is increases with the concentration and temperature while the growth rate for Sodium Hydroxide decreases as concentration and temperature increases. The geopolymerization will accelerate with the concentration. Thus, the expected value for growth rate is increases with concentration.
- The Avrami exponent trend will increases as growth rate increases and vice versa. Thus, the growth form for the geopolymer shall be concluded as one, two and three dimensions as the Avrami exponent values is more than three.

5.2 RECOMMENDATION

In future work plan, few recommendations are suggested to expand and improve this project.

- The ratio between alkaline solution and solid shall be considered in order to get the best mixing time for geopolymer to crystallize.
- Furthermore, the silicate solution shall be added into the mixture while preparing the geopolymer as it will influence the silica ratio in the geopolymer then affect the geopolymerization rate.
- Besides hardness, there are others LFRA Texture Analyzer parameters such as adhesiveness and resilience. The study on the trending of these parameters shall give wider scope for this project.

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7 APPENDICES

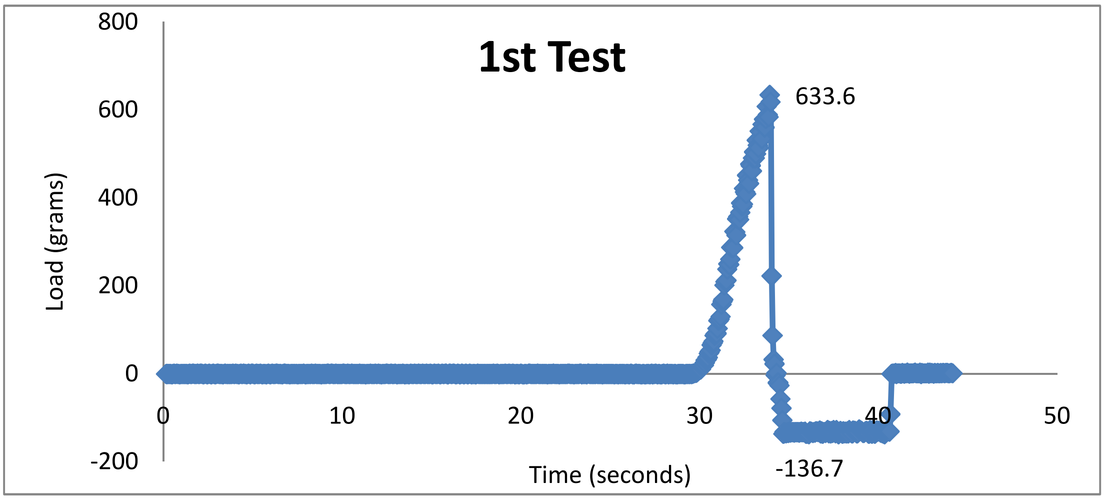

Figure 7.1- 1st test graph from LFRA for 8M KOH at 25C

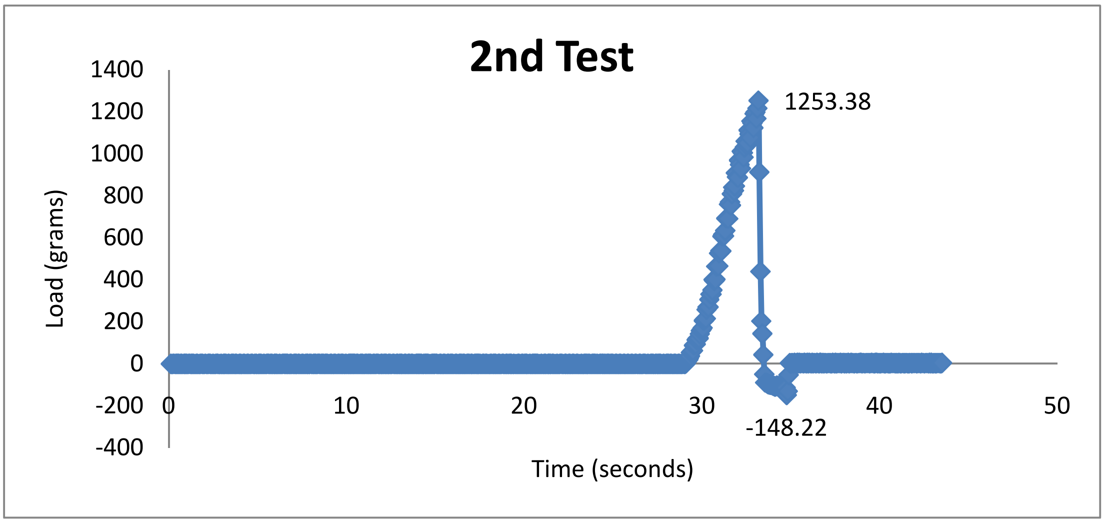

Figure 7.2- 2rd test graph from LFRA for 8M KOH at 25C

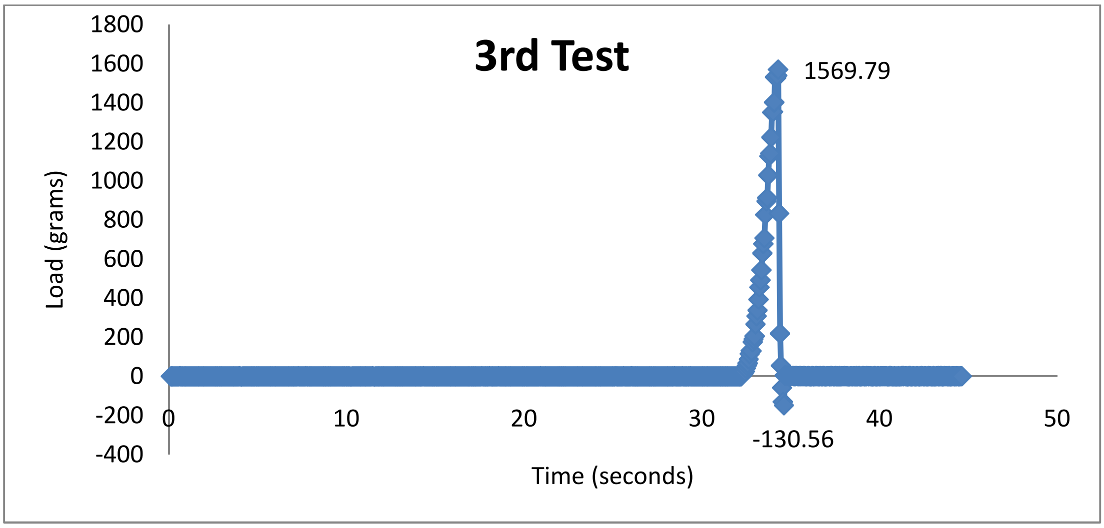

Figure 7.3- 3rd test graph from LFRA for 8M KOH at 25C

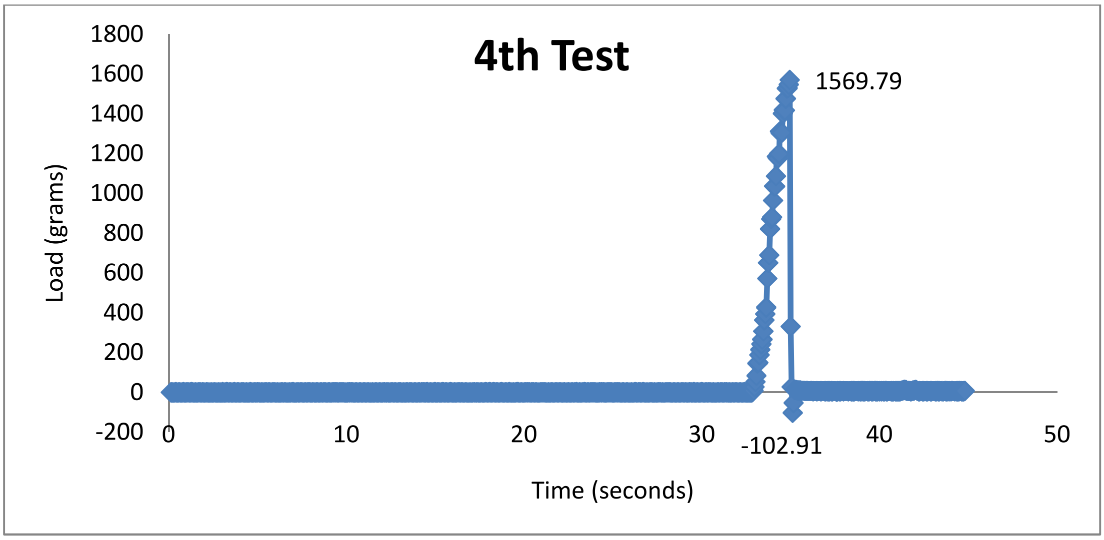

Figure 7.4- 4th test graph from LFRA for 8M KOH at 25C

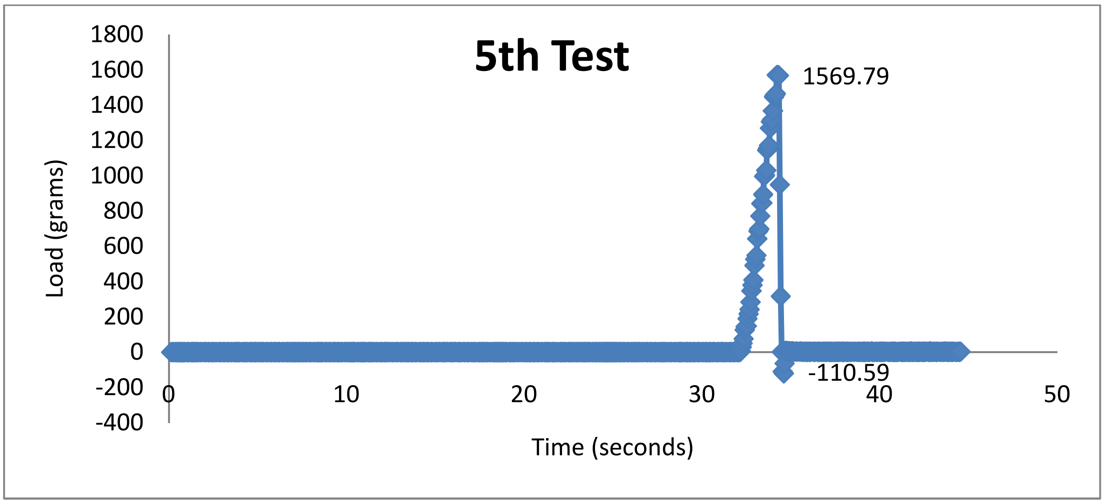

Figure 7.5- 5th test graph from LFRA for 8M KOH at 25C

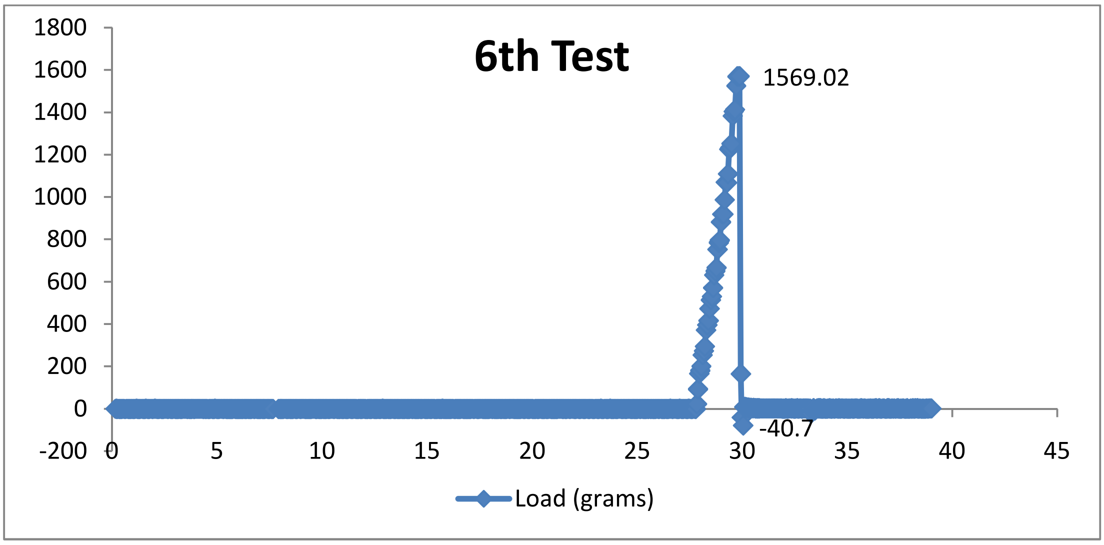

Figure 7.6- 6th test graph from LFRA for 8M KOH at 25C

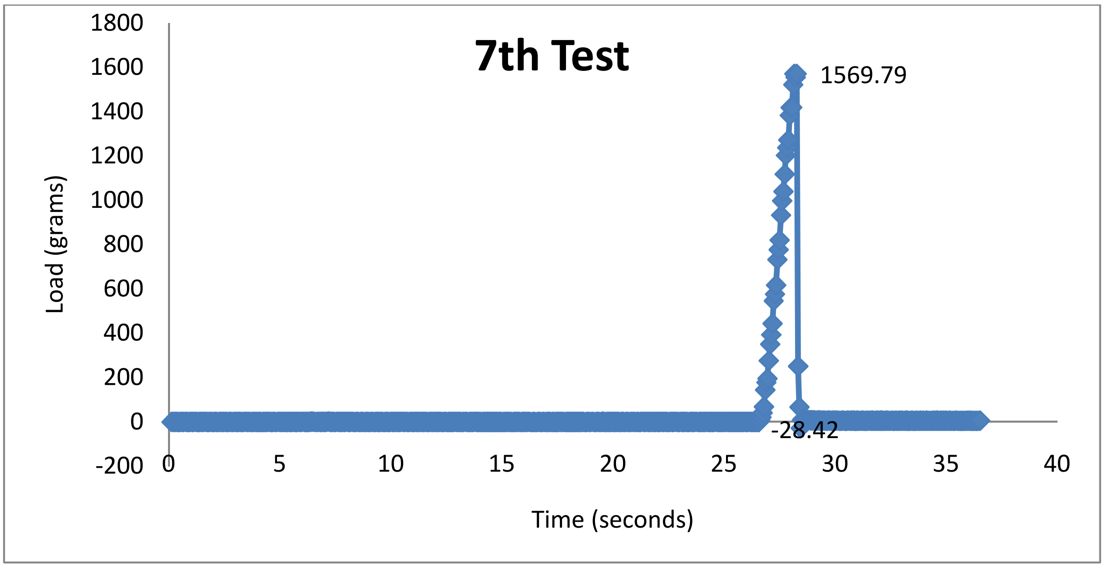

Figure 7.7- 7th test graph from LFRA for 8M KOH at 25C

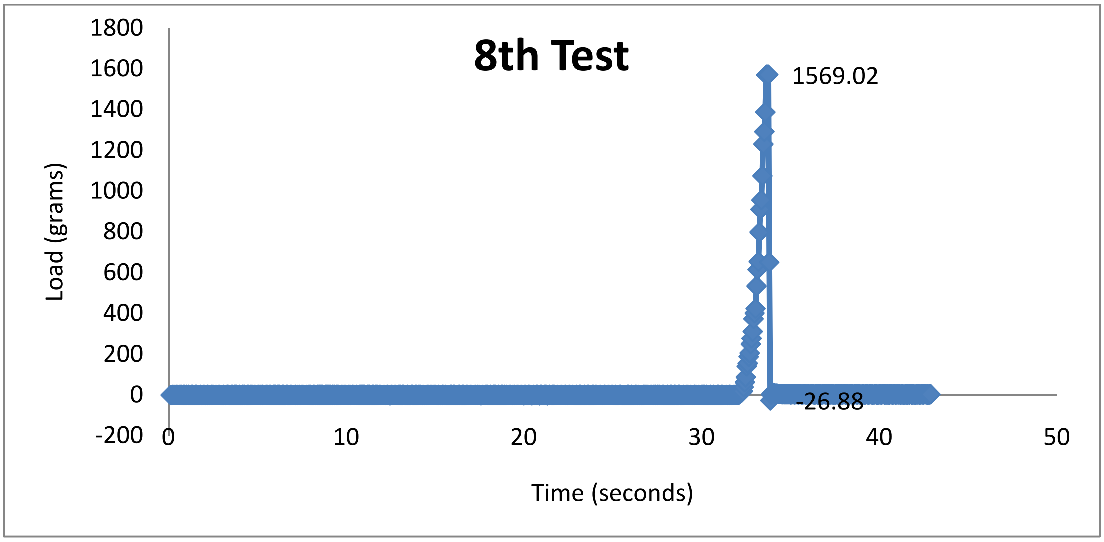

Figure 7.8- 8th test graph from LFRA for 8M KOH at 25C

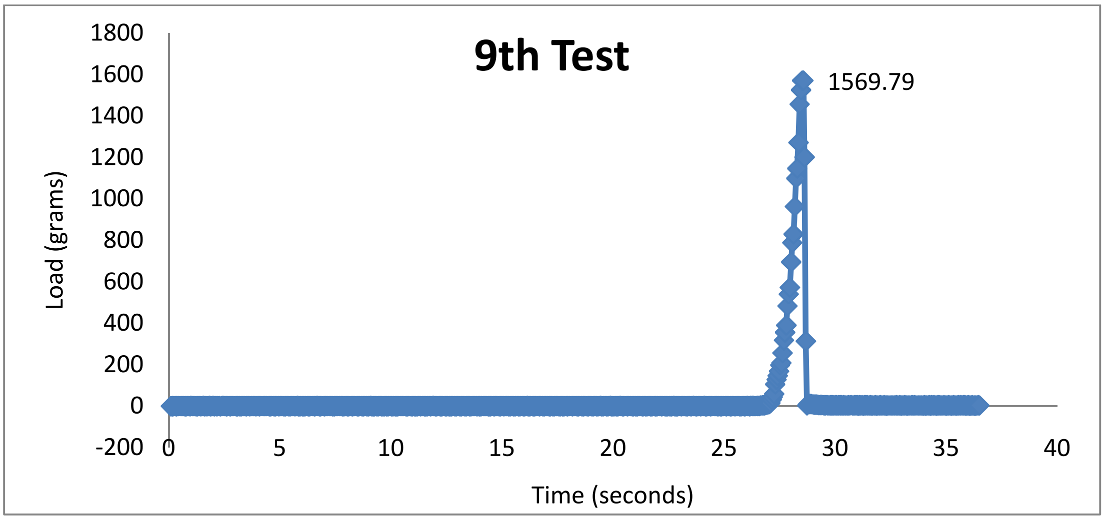

Figure 7.9- 9th test graph from LFRA for 8M KOH at 25C

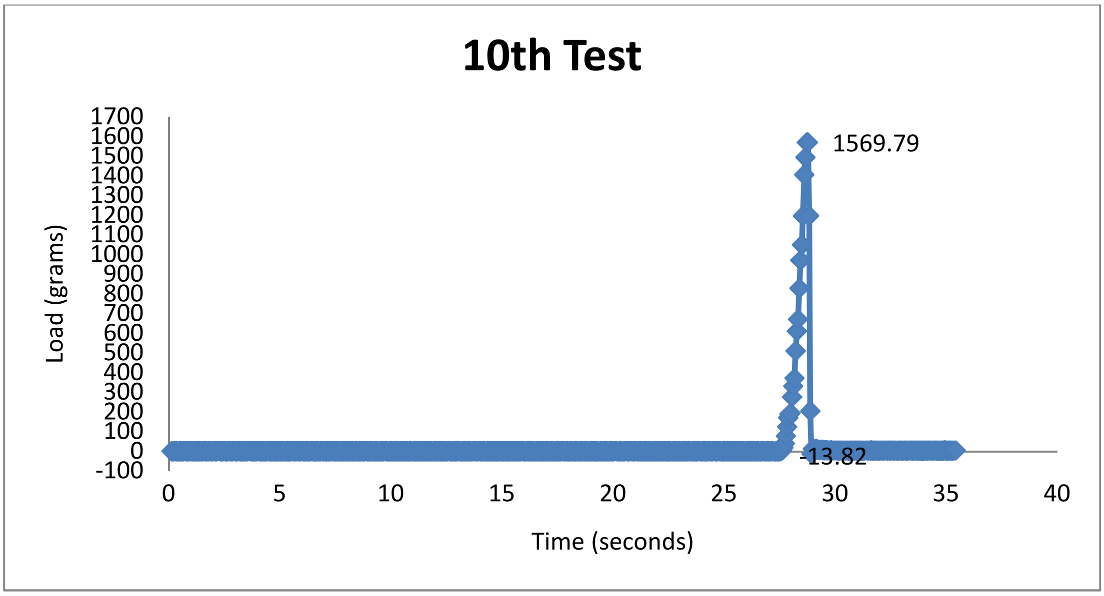

Figure 7.10- 10th test graph from LFRA for 8M KOH at 25C