EXPERIMENTAL STUDY ON THE EFFECT OF ADDITIVES IN GEOPOLYMER'S KINETIC FORMATION

By

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CERTIFICATION OF APROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

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Approved by,

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(Dr. Lukman Bin Ismail)

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ABSTRACT

Geopolymer is a novel material produced from the reaction between silica and alumina as the main raw material with an alkaline solution as an activator to the process so called as geopolymerization process. On top of that, most of the raw materials used in geopolymerization especially for the aluminosilicate materials are taken from the waste product such as fly ash, slag, volcanic ashes and wastewater from industry. Recently, there is an initiative in utilizing waste product from agricultural waste such as palm oil fuel ash (POFA), microwave incinerated rice husk ash (MIRHA) and sugarcane bagasse ash (SCBA) as the new raw materials for geopolymerization due to high composition of silica and fairly composition of alumina and other minerals. However, in geopolymer's field of study, there is a lack of initiative in investigate the effects of setting time for the geopolymer to solidify with the manipulation of some important parameters and explained it by using Avrami's Kinetic Theory and presented the concept connected to the nucleation of new crystal particles and growth rate of crystal particles into spherical shaped. Basically, this project is to determine the effect of additives in geopolymer's kinetic formation. The manipulation of parameter in this study is the manipulation of the composition of the main aluminosilicate material. Tentatively, the main raw aluminosilicate material for this project is fly ash Class F with some additional percentage of agricultural waste ashes (POFA, RHA and SCBA) as the additives. Furthermore, this project also focuses on the growth of crystal in geopolymerization and explained it by using Avrami's Kinetic Theory. From the sample characterization study in literature review, it is highly noticed that the amount of silica composition in the additives samples are the highest and fairly composition of alumina and other minerals are detected in the samples. From the experimental result, the increase composition of silica in the starting material of the geopolymerization hindered the time to solidify. Based on the Avrami's Kinetic Theory, the transformation form of crystal in the geopolymerization process features two and three dimensional structures while some samples exhibits the existence of secondary nucleation in geopolymer's growth.

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Mohamad Zulfarid Khalid.

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ABBREVIATIONS AND NOMENCLATURES

ASTM	American Society for Testing and Materials
Al_2O_3	Alumina
CO^2	Carbon Dioxide
BFS	Blast Furnace Slag
FESEM	Field Emission Scanning Electron Microscopy
K	Growth Value
LFRA	Leatherhead Food Research Association
LFSU	Lab Facilities Service Unit
MIRHA	Microwave Incinerated Rice Husk Ash
M	Alkaline Element
m	Avrami's exponent
mm	Milimeter
MPa	Mega Pascal
MSDS	Material Safety Datasheets
NaOH	Sodium Hydroxide
n	Degree of Polymerization
OPC	Ordinary Portland Cement
POFA	Palm Oil Fuel Ash

POC	Palm Oil Clinker
RHA	Rice Husk Ash
SCBA	Sugarcane Bagasse Ash
SiO_2	Silica
Si:Al	Silica to Alumina ratio
SEM	Scanning Electron Microscopy
UTP	Universiti Teknologi PETRONAS
V_t	Volume of Crystallization Material
XRD	X-ray Diffraction Spectroscopy
X	Degree of Crystallization
^oC	Degree Celsius
δ_r	Geopolymer Deposition
$\delta\infty$	Maximum Deposition From Deposition Curve
δo	Initial Mass Of Geopolymer Content In Liquid

CHAPTER 1
INTRODUCTION

1.1 Project Background

Geopolymer or also known as inorganic geopolymer is a class of cementitious aluminosilicates binder resources which gaining the reputation as an alternative to Ordinary Portland Cement (OPC) due to its low carbon dioxide emission. Considered as the most stable material in the earth and a good alternative to replace OPC, geopolymer utilized the alumino-silicate containing industrial wastes as its raw materials such as fly ash, waste glass and slags. Generally the main constituents for the geopolymer are alkaline solution and alumino silicate containing materials.

The applications of geopolymers are widely used in the production of concrete, substance for coating, adhesives and fiber composites, fire resistant materials, decorative stone artifacts, thermal insulation, low-tech building materials, low cost ceramic tiles, refractory items, thermal shock refractories, bio-technologies (material for medicinal applications), and composites.

In producing a geopolymer concrete, there are some aspects need to be understood especially in the solidification phase during geopolymerization process. The study of the hardening phase or setting time of geopolymer is vital in producing a high quality of geopolymer concrete. The factors that affected the setting time includes of curing temperature, water content, concentration of alkaline solution and also the composition of the aluminosilicates activator. In this research, the purpose of the research is to introduce a form of additives that produced from the agricultural waste such as palm oil fuel ash (POFA), microwave incinerated rice husk ash (MIRHA) and sugarcane bagasse ash (SCBA) and its effect on the setting time of the geopolymer resin. The compositions of these ashes are predominantly containing a high weight percentage of silica and less amount of alumina. Thus, the focus of this research is to study the effect of manipulating the silica and alumina composition inside the geopolymer resin and the effect towards the final setting time required for the geopolymer solidification. The main constituents

used in this research are Class F Fly Ash as the main alumino silicate material in this research, sodium hydroxide solution as the alkaline activator and POFA, MIRHA and SCBA as the source of additives in this experiment. The Vicat needle is used to measuring the solidification phase of the geopolymer. Later, the data obtained from the solidification test will be analyzed and presented based on the Avrami's Kinetic Theory.

1.2 Problem Statement

Over the years, many researches regarding the geopolymer physical properties are well-documented by various researchers especially on the compressive strength (Duxson et al., 2007), effect of the ambient curing condition (Nath & Sarker, 2012), water resistance lightweight geopolymer (Nazari et al., 2012) and etc. However, the mechanism in monitoring and controlling the formation of geopolymer and alkali activation as a whole are not well understood. This is due to most of the studies only focusing on the geopolymer's chemical and physical properties after setting time such as compressive strength, acid resistance, water absorptivity and steadiness of geopolymer (Nurhanie *et al.*, 2012). Conversely, there are only a few researchers were focused to study the effect of setting time especially on the hardening of the geopolymerization process and deduced it by using Avrami's Kinetic Theory's perspective. There is also abundance research on the usage of agricultural waste such as POFA, MIRHA and SCBA as the replacement material for fly ash as the main aluminosilicates material for the geopolymerization process. However, due to the fact that the three waste materials are containing high amount of silica and low amount of alumina (Ganesan, Rajagopal, & Thangavel, 2007; He, Jie, Zhang, Yu, & Zhang, 2013; Zarina, Al Bakri, Kamarudin, Nizar, & Rafiza, 2013), thus in this research these three materials will only be used as the additive to the basic geopolymer recipe. Therefore in this research, it is focusing more on the effect of additive in geopolymer solidification process where the additives are composedly produced from agricultural wastes materials such as POFA, MIRHA and SCBA The transformation of crystal from nucleation phase until the crystal formation will be explained based on the Avrami's Kinetic Theory.

1.3 Objectives

In this research, the main focus is to study the effect of additives in geopolymer solidification where the types of additives used are mainly form the agricultural waste product. The size of the additives is remaining constant throughout the experiments. Later, by using Avrami's Kinetic Theory, the phase transition of this geopolymer will be explained briefly after all the data is obtained for the solidification of the geopolymer.

The objectives that have been recognized for this research are:

I. To study the effect of palm oil fuel ash (POFA) as an additive in the geopolymer solidification process
II. To investigate the effect of microwave incinerated rice husk ash (MIRHA) as an additive in the geopolymer solidification process
III. To determine the effect of sugarcane bagasse ash (SCBA) as an additive in the geopolymer solidification process

1.4 Scope of Study

The scope of study in this research is to analyze the formation of crystal based on several additives added into the geopolymer resins. The additives used are palm oil fuel ash (POFA), microwave incinerated rice husk ash (MIRHA) and sugarcane bagasse ash (SCBA). These additives are rich in silica and have some potential in acting as a pozzolan in geopolymer mixtures. Main aluminosilicates used in this research is Class F Fly Ash, while the alkaline activator will be sodium hydroxide (NaOH) solution. The concentration of the sodium hydroxide solution used is 14M, and process temperature are set at 25^{o}C and 60^{o}C respectively. The solidification phase will be measured by using Vicat needle and later the data obtained will be analyzed by using Avrami's Kinetic Theory.

CHAPTER 2

LITERATURE REVIEW

2.1 Geopolymer

Due to some setbacks experienced by the Ordinary Portland Cement (OPC) especially in carbon dioxide management(Damilola, 2013), the reputation of geopolymer is tentatively increase as an alternative to the OPC in a variety of applications in industry (Duxson et al., 2007). Considered as a group of inorganic polymer, geopolymer is obtained by low-temperature alkali activation of alumina (Al_2O_3) and silica (SiO_2) containing materials (De Silva & Sagoe-Crenstil, 2009) . This cement-like material can be composed by reacting the alumino-silicates materials such as calcined clays, blast furnace slags and coal fly ashes with the alkaline solution (Duxson et al., 2007).

Geopolymer is an incipient family of construction materials that used mainly as a new substance for coatings, adhesives, and for fiber composites (Damilola, 2013). Application wise, J. Davidovits (2011) claims that geopolymer is basically a new material that used for coatings and adhesives, new binders for composites, waste encapsulation and new cement for concrete. The wide variety of potential applications includes: fire resistant materials, decorative stone artifacts, thermal insulation, low-tech building materials, low energy ceramic tiles, refractory items, thermal shock refractories, bio-technologies (materials for medicinal applications), cement and concretes, composites for infrastructures repair and strengthening, high-tech composites for aircraft interior and automobile, high-tech resins system, radioactive and toxic waste containment, arts and decoration, cultural heritage, archeology and history of sciences. Table 1 shows the application of geometric material based on Si:Al ratio.

Table 1.Application of Geometric Material Based on Si:Al Ratio (J. Davidovits, 2011)

Si:Al	Applications
1:1	• Bricks, Ceramics, Fire Protection
2:1	• Low CO_2 cements and concretes
	• Radioactive and toxic waste encapsulation
3:1	• Fire protection fiber glass composite
	• Foundry equipment
	• Heat resistant composite from 200^{o}C to 1000^{o}C
	• Tooling for titanium process
>3:1	• Sealants for industry from 200^{o}C to 600^{o}C
	• Tooling for SPF aluminum
20-35:1	• Fire resistant and heat resistant fiber composites

Based on the Table 1, it summarize that the higher the Si:Al ratio, the more sophisticated applications the geopolymer can achieved from a basic commodity usage as bricks and ceramics to the advanced engineering applications such as fire resistant and heat resistance fiber composites.

2.1.1 Geopolymerization Process

Generally, the process of geopolymerization requires two main components which are alkaline solution as an activator and alumino-silicates material as the source material. It is an intricate multiphase process, involving a series of dissolution–reorientation-solidification reactions analogous to those observed in zeolite synthesis from solid precursors (Provis, Duxson, Van Deventer, & Lukey, 2005). The statement from Provis et al. (2005) is accepted by Komnitsas and Zaharaki (2007) who described geopolymerization as the analogue of zeolites synthesis since the chemistry involved is homogenous, albeit the resulting products are different in composition and structure. Although the chemical composition of geopolymers are likely similar to zeolites, but the levels of matrix phase crystallinity are different from each other (De Silva, 2009).

The structure of the geopolymer is comprises mainly of Si-O-AL and Si-O-Si tetrahedral bonds arranged in a solid x-ray amorphous aluminosilicates network (Rees, Provis, Lukey, & van Deventer, 2008) . Damilola (2013) described the yielding of the polymeric Si-O-Al-O bonds in geopolymer as follows:

$M_n[-(SiO_2)_z\text{-}Al\text{-}O]_n \cdot wH_2O$

(Where M is an alkaline element, the symbol "-"indicate presence of a bond, z is 1, 2 or 3, and n is degree of polymerization) Geopolymer product formed may be amorphous orsemi-crystalline in structure depending on the temperature of geopolymerization (Damilola, 2013; Pacheco-Torgal, Castro-Gomes, & Jalali, 2008).

In expounding the geopolymerization process, Provis et al. (2005) presented the summarization of the process as in Figure 1 where the model was originally applied to the geopolymerization of metakaolin, but its applicability is opportune to be used as a concise explication in general geopolymerization process (van Deventer, Provis, Duxson, & Lukey, 2007).

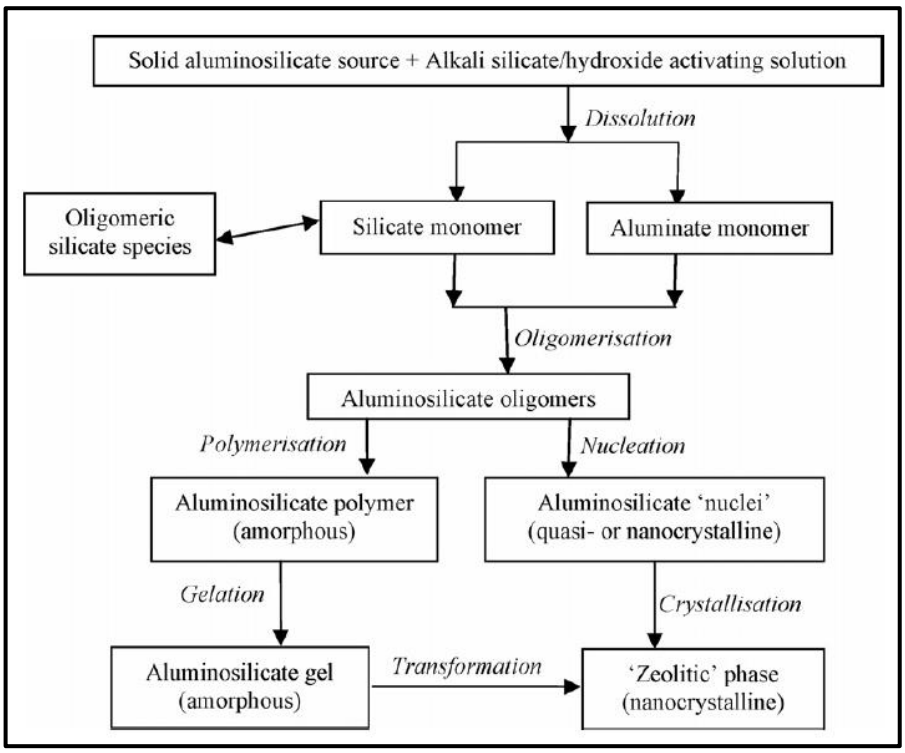


Figure 1. Schematic outline of the reaction process involved in geopolymerization (Provis et al., 2005; van Deventer et al., 2007)

Fundamentally, the geopolymerization process commences with the dissolution of the alkaline solution together with the solid aluminosilicates sources such as fly ash, metakaolin, slags and etc. (Duxson et al., 2007; Muñiz-Villarreal et al., 2011; Rees et al., 2008). At very high pH, the dissolution of the aluminosilicates engenders a supersaturated aluminosilicates solution. Through condensation, the oligomers in the

aqueous phase form large networks as the results of formation of gel in the concentrated solutions. Water which consumed during the dissolution process is released during this stage (Duxson et al., 2007). Depending on the raw material processing conditions, solution composition and synthesis condition, the time for the supersaturated aluminosilicates solution to form a continuous gel varies considerably. Via the reorganization and rearrangement of the gel network from the gel formed, the increment of the connectivity between the gel networks resulting in the three-dimensional aluminosilicates network or Poly(sialates) that are commonly attributed to geopolymers (Duxson et al., 2007; Muñiz-Villarreal et al., 2011; Pacheco-Torgal et al., 2008). Figure 2shows the structures of poly(sialates) according to Joseph Davidovits (2005).

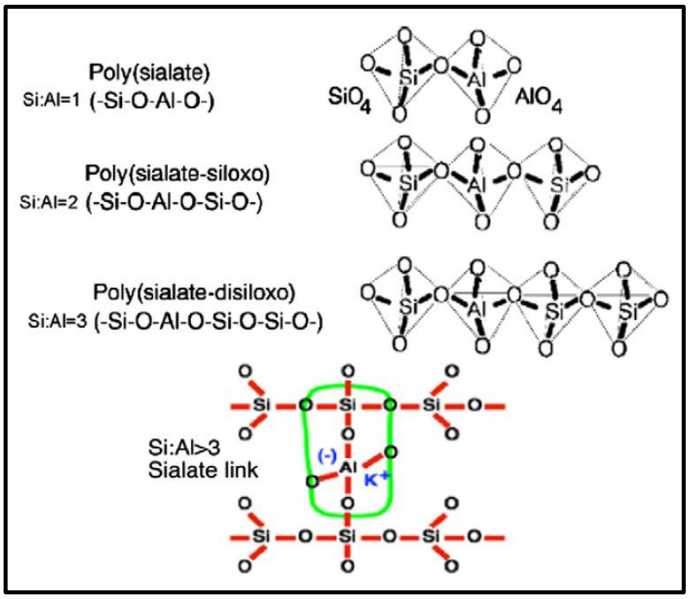


Figure 2. Poly(sialates) structures (Joseph Davidovits, 2005; Pacheco-Torgal et al., 2008)

2.2 Development of Research in Geopolymer

Geopolymer research findings increasing throughout the years where various findings related to geopolymer have being published worldwide. Most findings are focusing on the geopolymer's properties, application, and mix-design recipe for geopolymerization and very limited findings in solidification of geopolymer.

2.2.1 Research in Geopolymer's Properties and Applications

Various researches have been done by scientist all over the world in order to produce a workable geopolymer that has extensive set of properties and applications so that it can be very useful to mankind. This is important so that there is a need to utilize geopolymer as an alternative to multiple applications. For an example in production of geopolymer cement to replace the Ordinary Portland Cement (OPC), the researches not only focusing on the way the geopolymer cement can compete with the OPC in term of physical properties (such as in compressive strength), but also the researches introduced some of the new properties and applications that might be useful as an added values such as acid and alkali resistivity (Duxson et al., 2007), water resistant lightweight geopolymers cement (Nazari, Riahi, & Bagheri, 2012) and suitability to be used as adhesives and coatings.

In term of utilization of agricultural waste in geopolymer's technology, findings from Kusbiantoro, Nuruddin, Shafiq, and Qazi (2012) that utilized the microwave incinerated rice husk ash (MIRHA) shows the effect in compressive strength and bonding strength by introducing the addition of the MIRHA as a part of the raw starting material in geopolymerization process. Due to MIRHA's pozzolanic characteristic, the addition of MIRHA and Fly Ash in the geopolymer mould lead to high geopolymer matrix quality with denser gel structure, improving the overall performance of fly ash geopolymer concrete. Figure 3 shows the FESEM images of geopolymer concrete cured in ambient condition.

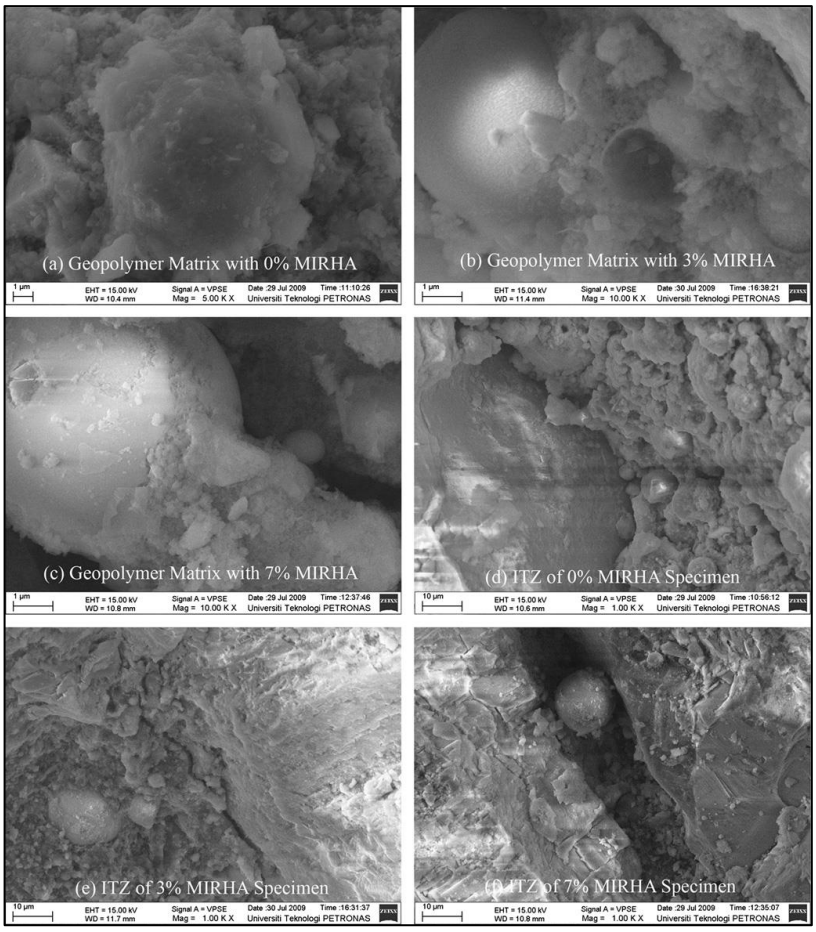


Figure 3.FESEM images of geopolymer concrete cured in ambient condition (Kusbiantoro et al., 2012)

From Figure 3, the FESEM images show that with the increasing addition of MIRHA into the geopolymer matrix, the gel structure become denser and lead to a high quality of geopolymer matrix thus improving an overall performance of the fly ash geopolymer concrete.

Islam, Alengaram, Jumaat, and Bashar (2014) utilizing palm oil fuel ash (POFA) as an additive in studying the effect of addition of percentage of POFA in fly ash and slag paste in the development of compressive strength of the geopolymer mortar. This research is vital in studying the feasibility of geopolymer in producing a high compressive strength mortar that can be used later as a concrete block for buildings and etc. From the study, Islam et al. (2014) deduce that the addition of POFA up to 30% into fly ash and slag paste increasing the compressive strength of the mortar up to 70% which

is more than 60 MPa. Figure 4 shows the effect of POFA on the compressive strength of mortar mixed with slag and fly ash at the age of 28-day.

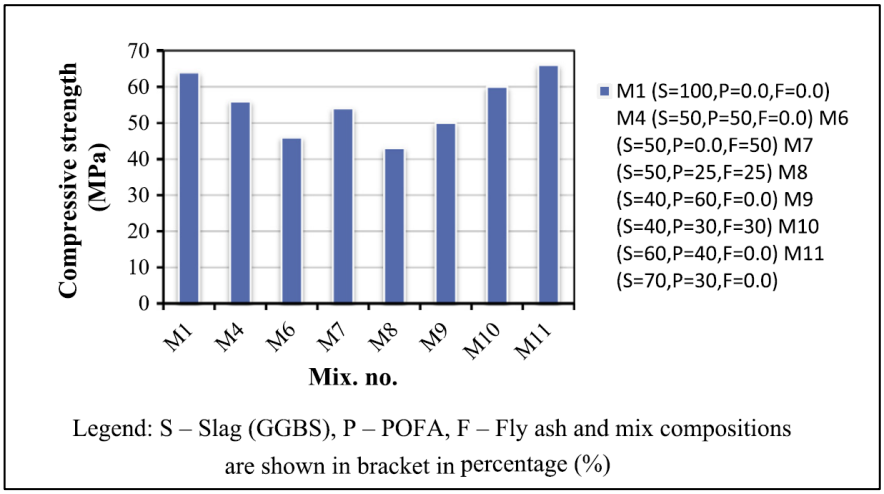


Figure 4. The effect of POFA on the compressive strength of mortar mixed with slag and fly ash at the age of 28-day (Islam et al., 2014)

Sugarcane bagasse ash or SCBA also has the characteristic as the pozzolanic material. It has been used as the admixture in the Ordinary Portland Cement (OPC) just like reported by Cordeiro, Toledo Filho, Tavares, and Fairbairn (2009) where the addition of the SCBA into the OPC mould will increase the rheology of the mould to flow. Although there is no quantifiable change in the mechanical performance of the cement, the addition of 10, 15 and 20% by mass of SCBA into OPC mould mixture provides a resistance to penetration of chloride ions. The high amount of silica concentration and others composition such as aluminum, iron, and some small amount of alkalis and alkaline earth oxide in the composition of SCBA shown that SCBA also has a potential as the raw material for geopolymer (Sivakumar, Hariharan, & Barathan, 2013). There is a report by Castaldelli et al. (2013) that using SCBA as an additive in a blast furnace slag (BFS) as a starting material for the production of alkali-activated material or known as geopolymer. The additive is added in four different mixtures ratio, and the compressive test is done in order to know the workability of the geopolymer as the replacement of cement concrete. The highest compressive strength recorded in 3 days curing period is 53.5 MPa for the 85/15 ratio of BFS:SCBA. Table 2 below shows the result from the mechanical strength of geopolymer mortar cured at 65^{o}C.

Table2. Mechanical strength of geopolymer mortars cured at 65 ^{o}C (Castaldelli et al., 2013)

Mixtures	R_c (MPa)		R_f (MPa)	
	3 days	7 days	3 days	7 days
100/0	45.5 ± 2.9	62.2 ± 2.6	5.80 ± 0.3	5.39 ± 1.1
85/15	53.5 ± 2.0	51.2 ± 0.4	5.31 ± 0.4	2.94 ± 0.6
75/25	49.0 ± 2.7	52.8 ± 1.9	5.31 ± 0.6	4.00 ± 0.4
60/40	42.8 ± 0.9	43.2 ± 0.3	3.84 ± 0.5	3.19 ± 0.4

As a summarization, Table 3 below shows the summary of the research works done in geopolymer in term of its applications, properties and mix-design. The summarization is a part of the research done worldwide in order to explore the possibility and workability of geopolymer especially in producing green technology products.

Table3. Summary of the research done in geopolymer in term of its applications, properties and mix-design

Properties and Application		
Reference	**Title**	**Findings**
Joseph Davidovits (2002)	30 years of successes and failures in geopolymer applications. Market trends and potential breakthroughs	• The origin of geopolymer initiator in 1978 • Geopolymer potential application in the construction field
Duxson et al. (2007)	Geopolymer technology: the current state of the art	• Geopolymer potential use in adhesives and coatings • Strength against fire and acid resistance • High compressive strength in geopolymer concrete (60-70 MPa)
Cordeiro et al. (2009)	Ultrafine grinding of sugar cane bagasse ash for	• Rheology of the concrete paste to flow increase with the

	application as pozzolanic admixture in concrete	addition of ultrafine grinding of SCBA as admixture in concrete paste
Nazari et al. (2012)	Designing water resistant lightweight geopolymers produced from waste materials	• Production of water resistant lightweight geopolymer cement from waste product like fly ash, rice husk bark ash and palm oil clinker (POC)
Kusbiantoro et al. (2012)	The effect of microwave incinerated rice husk ash on the compressive and bond strength of fly ash based geopolymer concrete	• Addition of MIRHA to fly ash lead to high geopolymer matrix quality with denser gel structure, improve the performance of fly ash geopolymer concrete.
Castaldelli et al. (2013)	Use of Slag/Sugar Cane Bagasse Ash (SCBA) Blends in the Production of Alkali-Activated Materials	• The highest compressive strength recorded in 3 days curing period is 53.5 MPa for the 85/15 ratio of BFS:SCBA
Islam et al. (2014)	The development of compressive strength of ground granulated blast furnace slag-palm oil fuel ash-fly ash based geopolymer mortar	• Compressive strength increased up to 30% when added POFA into fly ash + slag paste (>60 MPa) • Highest recorded compressive strength during the test is between 60-66 MPa
	Mix Design	
Reference	**Title**	**Findings**
De Silva and Sagoe-Crenstil (2009)	The Role of Al2O3, sio2 and Na2O on the Amorphous → Crystalline Phase Transformation	• Initial mixtures appeared to be critical factors in observing amorphous→crystalline

	In Geopolymer Systems	transformation. • High content of silica, increased the setting time of solidification
Aleem and Arumairaj (2012)	Optimum mix for the geopolymer concrete	• Fly ash as the optimum mix for the main raw material for the geopolymerization
Zarina et al. (2013)	Review on the various ash from palm oil waste as geopolymer material	• Potential of agricultural wastes as pozzolanic material in geopolymer and concrete material

From the various results from previous research journals, it is clearly shown that geopolymer has a very bright potential in reproduce many green, environmental friendly products especially in production of concrete and cement. It is proven that in term of comprehensive strength, the addition of POFA, MIRHA and SCBA improving the strength of the cement paste. The usage of waste products like slag, fly ash and even agricultural wastes such as POFA, MIRHA and SCBA provides a very good platform in utilizing the waste products into a new novel invention. POFA, MIRHA and SCBA have the potential as pozzolan material and thus it can be utilize in the production of geopolymer. However, by having a good characteristic as the raw material for the production of geopolymer is not good enough since the workability of the geopolymer is also depending on the time taken for the geopolymer to solidify. If the geopolymer itself could not solidify within the desired period, the workability of the geopolymer can be questioned. Thus, in this research by introducing the appropriate amount of additives from POFA, MIRHA and SCBA into the fly ash as the main raw material mixture of the geopolymer, the time taken for the geopolymer to solidify will be the main parameter monitored throughout the experiments. The results will be further analyzed by using Avrami's Kinetic Theory.

2.3 Solidification of Geopolymer

The composition of the silica and alumina plays a very vital role in the geopolymerization process since aluminosilicates material is considered as the important material in the geopolymerization process (De Silva & Sagoe-Crenstil, 2009). By adding variations ratio of additives containing silica and alumina into the geopolymerization process, the setting time of the process can be measured and quantified thus makes this research as an important research in study the effect of additional additives containing silica/alumina composition in geopolymerization process. In the previous research done by De Silva and Sagoe-Crenstil (2009) shows that by decreasing the silica amount in the initial mixture formulation accelerated the amorphous to crystalline transformation. The focus on this research is the solidification of the geopolymer with addition of several waste materials from agricultural industries:

I. Effect of Palm Oil Fuel Ash (POFA) as an additive in geopolymer solidification
II. Effect of Microwave Incinerated Rice Husk Ash (MIRHA) as an additive in geopolymer solidification
III. Effect of Sugarcane Bagasse Ash (SCBA) as an additive in geopolymer solidification

2.3.1 Palm Oil Fuel Ash (POFA)

In 2010, Malaysia is known as the second largest oil palm producer in the world due to its large production domestically where 18.6 million metric tons production has been made through the year (Zarina et al., 2013). This large production of oil palm leads to uncontrolled waste product released from this industry and received many criticism and complaint. The wastes include such as empty fruit brunches (EFB), kernels, palm fibers, and nut shells. Later, these wastes were incinerated in boilers and produce two type of palm ashes known as boiler ash and palm oil fuel ash (POFA)(Zarina et al., 2013). In Malaysia only, a thousand tons of POFA are produced per annum by the 200 palm oil mills all over the country, and most of it is simply discarded into ponds without any commercial value(Karim, Zain, Jamil, & Lai, 2013). POFA is used in various applications such as cement replacement in production concrete, raw material for

geopolymer composite, air purifier and wastewater treatment in cleaning atmospheric contaminants (Karim et al., 2013). Figure 5 shows the original POFA obtained from the palm oil mills which incinerated in the temperature of 800^{o}C.

Figure 5. Original POFA obtained from the palm oil mills (Zarina et al., 2013)

Zarina et al. (2013) reported the chemical composition of silica (SiO_2) is rich in POFA. This is accepted by Chandara, Sakai, Azizli, Ahmad, and Hashim (2010) as the result of the composition test by using X-ray Diffraction shows that the composition of SiO_2 is greater than alumina (Al_2O_3) in POFA. Table 4 below shows the chemical composition of POFA for 5 samples as reported by (Zarina et al., 2013).

Table 4. Chemical composition of POFA from 5 samples (Zarina et al., 2013)

Chemical Components	Palm Ash Composition (wt, %)				
	Malaysia[23]	Thailand[26]	Thailand[27]	Thailand[28]	Malaysia[29]
SiO_2	51.18	65.3	63.6	57.7	43.6
Al_2O_3	4.61	2.5	1.6	4.5	11.4
Fe_2O_3	3.42	1.9	1.4	3.3	8.4
CaO	6.93	6.4	7.6	6.5	4.8
MgO	4.02	3.0	3.9	4.2	0.4
SO_3	0.36	0.4	0.2	0.2	2.8
K_2O	5.52	5.7	6.9	8.2	3.5
Na_2O	0.06	0.3	0.1	0.5	4.7
LOI	21.6	10.0	9.6	10.5	18.0

As reported in Table 4, from 5 samples stated, it is clearly shown that the composition of SiO_2 is abundance in every POFA samples. Meanwhile the composition of Al_2O_3 is not dominant in the samples.

The utilization of POFA in geopolymer really affected the properties of the geopolymer itself. Various research shows that the usage of POFA as an additive into the geopolymer resin enhance the compressive strength, tensile strength, modulus of elasticity and expansion (Chandara et al., 2010; Kupaei, Alengaram, Jumaat, & Nikraz, 2013; Yahya et al., 2013; Zarina et al., 2013). For the study of the setting time in POFA as an additive in geopolymer, there is not enough data to be compared since most of the research focusing on the physical properties of the geopolymer itself such as compressive strength, acid resistance and etc. In the case of OPC, higher content of silica increases the strength of the cement, but its setting time is lengthy (Karim et al., 2013). However, alumina rich OPC will faster the setting time of the cement but the cement strength is deteriorate. This is due to the cements sample where the absorption of water is reduced and thus reduces the strength of the cement paste.

2.3.2 Sugarcane Bagasse Ash (SCBA)

Sugarcane bagasse is a waste product produced from the agricultural activity mainly in the sugarcane production. Some of the sugarcane bagasse is treated and used as soil amendment and the others is used for the power generation activity (Sivakumar et al., 2013).The sugarcane bagasse ash (SCBA) is burnt at temperature varying from 700^{o}C-900^{o}C through the incinerated process of the sugarcane bagasse during the power generation activity. Cordeiro et al. (2009) suggest that due to the high content of silica, SBCA has the potential to be used as the pozzolan in admixture of geopolymer concrete. The same result also found in the composition of SCBA as Cordeiro et al. (2009) reported by Sivakumar et al. (2013) that the amount of SiO_2 is higher than the Al_2O_3in SCBA. The composition of the SCBA is presented as in Table 5.

Table 5. Composition of the BFS and SCBA (Castaldelli et al., 2013)

Oxide	BFS	SCBA
SiO_2	30.19	31.41
Al_2O_3	10.66	7.57
Fe_2O_3	1.31	6.02
CaO	39.53	16.06
MgO	7.50	1.07
Na_2O	0.87	0.14
K_2O	0.58	1.58
SO_3	1.95	0.78
TiO_2	0.51	2.09
MnO	0.40	0.10
Chloride	0.44	0.14
LOI	5.62	32.20

In the table above, the composition of silica for SCBA show that the amount of silica is the highest (31.41%), slightly higher than the composition of silica in BFS. The fair composition of Si:Al gives the SCBA the opportunity to be utilized as a pozzolanic admixture in geopolymerization. De Silva and Sagoe-Crenstil (2009) claim that in geopolymerization process, the increase amount of silica composition inside the resin will delay the solidification duration of that particular geopolymer. This is agreed by Karim et al. (2013) where the research use another pozzolanic material such as POFA which also consist of high silica content rather than alumina and from the result it shows that the setting time for the solidification of the geopolymer is longer.

2.3.3 Microwave Incinerated Rice Husk Ash (MIRHA)

Categorized as one of the pozzolanic material, rice husk ash is produced through the combustion process of rice husk (Kusbiantoro et al., 2012) and used predominantly for the generation of electricity (He et al., 2013). According to Karim et al. (2013) approximately 16-22 million tons of rice husk ash are produced worldwide. Considered as the waste material in the rice mills industry, the composition of the rice husk ash as reported by He et al. (2013) is mainly compose of silica (around 90 – 95 wt.%). The high content of silica inside the rice husk ash causes the disposal process difficult. In this research, the rice husk ash is acquired from the burning process of rice husk by using UTP-Microwave Incinerator at 800^{o}C incineration temperature. This incinerated rice husk ash also is known as Microwave Incinerated Rice Husk Ash (MIRHA). Figure6 shows the SEM image of MIRHA particles.

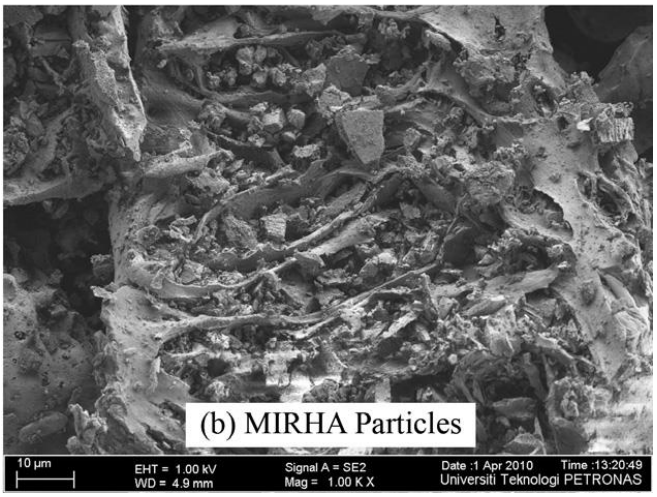


Figure 6.SEM image of MIRHA particles (Karim et al., 2013)

In addition, for MIRHA, as claimed by (He et al., 2013; Karim et al., 2013; Kusbiantoro et al., 2012)its chemical composition shows that the composition of SiO_2also is higher than Al_2O_3. The alumina content in MIRHA shows less than 1% rather than silica content which is around 89 – 90 % from total composition as reported by Karim et al. (2013).Table5 shows the oxide composition of fly ash and MIRHA particle as reported by Karim et al. (2013)

Table 6. Oxide composition of fly ash and MIRHA particle (Karim et al., 2013)

Oxide composition percentage of fly ash and MIRHA particle.

Oxide	Percentage (%)	
	Fly ash	MIRHA
Al_2O_3	29.1	0.45
SiO_2	51.7	89.34
P_2O_5	1.7	2.58
SO_3	1.5	0.90
K_2O	1.6	4.98
CaO	8.84	0.76
TiO_2	0.702	0.02
Fe_2O_3	4.76	0.40
SrO	0.109	–
Mn_2O_3	–	–
MgO	–	0.49

As in the table above, the composition of silica for both fly ash and MIRHA shows the highest percentages which are 51.7% and 89.34% respectively. However, the composition of alumina in MIRHA is significantly lesser than in the fly ash. The composition of alumina in MIRHA is 0.45% where in fly ash the composition is around 29.1%.

2.4 Avrami's Kinetics Theory

Avrami's Kinetic Theory is a well-known explanation of crystallization kinetics through the heuristic Avrami phase transition (Yang, 2006). The theory aim is to explain the isothermal solid transformation from one phase to another phase through nucleation of particles. Basically, the kinetics of solidification for the geopolymer can be defined specifically through this theory. The crystallization kinetics of the bulk crystallization of polymers can be explained as,

$$1-X=e^{-Vt} \qquad \textbf{Equation 1}$$

Where X is the degree of crystallization, and V_t is the volume of crystallization material. Contrary, for the case of instantaneous nucleation, the Avrami exponent, *m*, is introduced as the exponent not only depend on the structure of the crystal but also on the nature of nucleation (Yang, 2006)

$$1-X=e^{-Ktm} \qquad \textbf{Equation 2}$$

Where K is the growth rate and *m* is Avrami's exponent. Sensitive to the dimensionality of growth, the Avrami's exponent, *m,* is also sensitive to the time of nucleation and growth (Ramirez, Ni, & Lee, 2006). Conversely, (Ismail, Westacott, & Ni, 2008) claim that the degree of crystallinity is measured through the geopolymer deposition (δ_r) where the mass fractions of the crystal deposited on the wall during the cooling process is taken as the important parameter in measuring the degree of crystallinity. The geopolymer deposition, δ_r can be expressed as

$$\delta r = \frac{\delta t - \delta o}{\delta \infty - \delta o} \qquad \textbf{Equation 3}$$

Where,

δt – the total deposition at time (min)

$\delta \infty$ - the maximum or asymptotic deposition from deposition curve

δo – initial mass of geopolymer content in liquid

By replacing the X in the Equation 2 with δ_r in Equation 3, and taking log twice in Equation 2 can be written as

$$\log [-\ln(1-\delta_r)] = \log K + m \log (t) \qquad \textbf{Equation 4}$$

Above equation signifies the equation of straight line Y=mX+c if the graph of log [-ln(1-δ_r)] vs. log(t) is plotted. Figure 7 below shows the graph of log [-ln(1-δ_r)] vs. log(t).

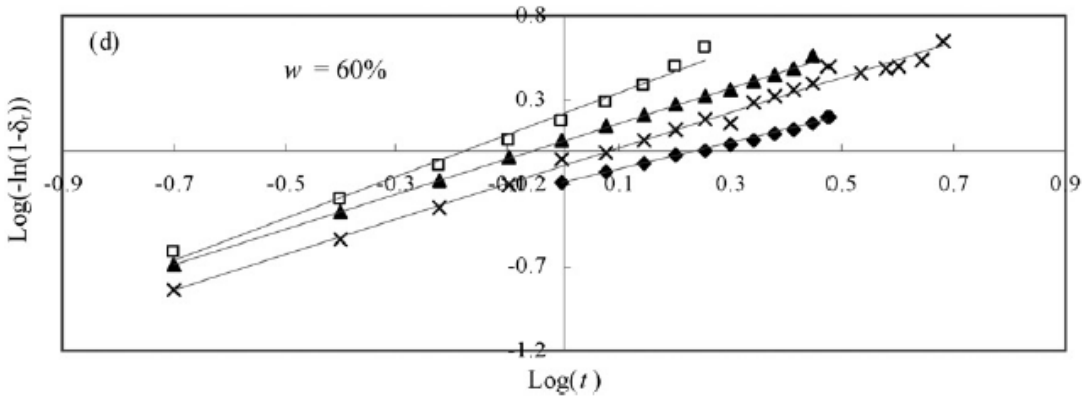


Figure 7. Graph of log [-ln(1-δr)] vs. log(t) (Ismail et al., 2008)

The value of the Avrami's exponent (*m*) is denotes as the gradient of the straight line in the graph, while the growth value (*K*) of geopolymer's particle is represents as the y-intercept of the graphs. In determining the microstructure of geopolymer by the value of exponent (*m*) in the equation, the modified Avrami's Kinetic Theory is explicitly chosen. The Avrami's parameter for solidification of polymer by (Ismail et al., 2008) is summarized as in Figure 8.

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

[a] Constant thickness.
[b] Constant radius.

Figure 8. Avrami's parameter for solidification of polymer (Ismail et al., 2008)

2.5 Vicat Needle

In the study of plastic and cement solidification, the most common instrument used is by using Vicat Needle. In addition, in this research the solidification of geopolymer also will be determined and measured by using the Vicat Needle. The Vicat needle is used in determining the setting time for the geopolymer to curing from liquid into solid form (Pauzi, 2013). Measuring in millimeter, Vicat Needle shows the depth of penetration on the sample in order to know the material's hardness.

The Vicat needle of working fundamental is quite straightforward. It starting with tested the material with the depth of 40mm, which will be located at the center of the specimen under the 10mm end of Vicat needle. Then, the needle end will make contact with the material phase by lowering the movable rod. After that, the movable rod will be permitted to free fall for penetration of needle after the indicator of measurement is set at zero. Until the material is solidified, the depth of penetration will be recorded and repeated every five minutes. Once the Vicat needle incapable to penetrate the material, the solidification of material can be determined.

According to the ASTM C191-04, the Vicat needle is used in measuring the geopolymer's hardening with the needle's diameter of 1.00±0.05mm and 10.00±0.05mm.Nath and Sarker (2012) claim that the optimum needle's diameter to be used in determining the setting time is 1.00±0.05mm. From the feasibility point of view, Pauzi (2013) suggests that in the process to determine the setting time for the geopolymer's hardening, between Vicat needle and LFRA Texture Analyzer, the Vicat needle shows the most feasible result.

CHAPTER 3
METHODOLOGY

3.1 Project Flow Chart

The methodology applied in this project is through finding and experimental works. In early stage, the process involved are comprises of collecting all the fundamental information about geopolymer from past journals, paper work and engineering book and compiled it as literature review. Next the samples are prepared according to the objectives stated earlier in this project works. Then, the process continues to the experiments to determine the effects of agricultural wastes as an additive in solidification of geopolymer. The types of agricultural wastes chosen in this research are Palm Oil Fuel Ash (POFA), Microwave Incinerated Rice Husk Ash (MIRHA) and Sugarcane Bagasse Ash (SCBA). Lastly, the results gained from the experimental works will be analyzed and synthesized based on the Avrami's Kinetic Theory.

3.2 Project Activities

Before conducting the experiment, the details of procedures are very important in order to minimize error in the result and also to control the hazards around the laboratory. During handling the chemicals such as high concentration of sodium hydroxide solution, the safety measures should be taken seriously in order to prevent from any incident. The Material Safety Datasheets (MSDs) of the chemicals used must be read before handling the chemicals so that the personnel will aware about the hazardous properties of that material.

There are three sets of experiments that need to be completed in order to fulfill all the objectives of this research. The experiments started with the preparation of the ashes from the agricultural wastes. Then, the experiments continue with the process of

preparing the alkaline solution at concentration of 6M and 14M respectively before the dissolution process between the aluminosilicates ashes and alkaline solution took place.

3.2.1 Effect of Palm Oil Fuel Ash (POFA) as an additive in geopolymer solidification

First, a 300μm sieve is used to sieve the incomplete combusted fibers and nutshells from the POFA (Chandara et al., 2010). Next, by using ball mill, the POFA sample is ground for 45 minutes to obtain more particles. After that, the ground POFA was heated for an hour in an electric furnace at 500^{o}C to increase the pozzolanic properties and removing the unburned carbon in the sample (Zarina et al., 2013). Then, the POFA is ready to be used as the activator material in this experiment. The preparation of the POFA sample is summarized as Figure 10 below.

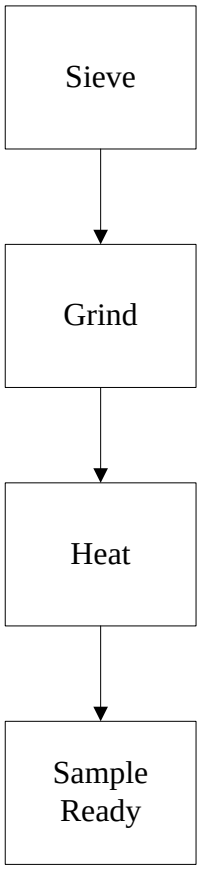


Figure 9. Summarization of the procedures in preparing the POFA sample

3.2.2 Effect of Microwave Incinerated Rice Husk Ash (MIRHA) as an additive in geopolymer solidification

Firstly, the sample of the MIRHA is obtained from the incineration process of rice husk with UTP-Microwace Incinerator in 800^{o}C incineration temperature (Kusbiantoro et al., 2012). Next, by using a 300μm sieve, the MIRHA is sieved in order to remove any incomplete combusted rice husk from the sample. After that, the MIRHA is then ground in a ball mill for 2000 cycles (Kusbiantoro et al., 2012). Next, the ground MIRHA was heated for an hour in an electric furnace at 500^{o}C to increase the pozzolanic properties and removing the unburned carbon in the sample. Then, the MIRHA is ready to be used as the activator material in this experiment. The preparation of the MIRHA sample is summarized as Figure 11.

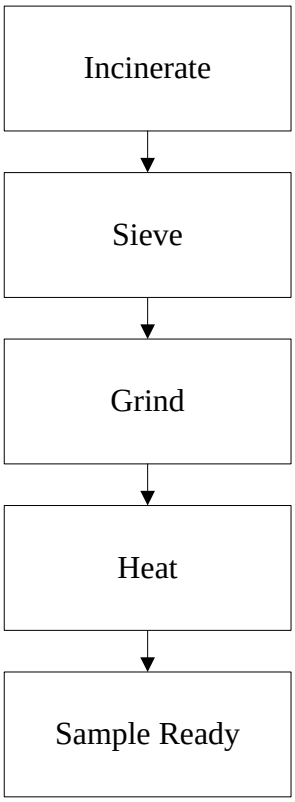


Figure 10. Summarization of the procedures in preparing the MIRHA sample

3.2.3 Effect of Sugarcane Bagasse Ash (SCBA) as an additive in geopolymer solidification

First of all, the sugarcane bagasse collected need to be naturally dried under the sun and make sure the water content is below 10% moisture. Next, the sugarcane bagasse is incinerated by using the UTP-Microwave Incinerator at 800^{o}C for an hour (Cordeiro et al., 2009). After that, by using a 300μm sieve, the SCBA is sieved in order to remove any incomplete combusted sugarcane bagasse and ground by using a ball mill for 2000 cycles. Then, the ground SCBA was heated for an hour in an electric furnace at 500^{o}C to increase the pozzolanic properties and removing the unburned carbon in the sample. Then, the SCBA is ready to be used as the activator material in this experiment. The preparation of the SBCA sample is summarized as Figure 12 below.

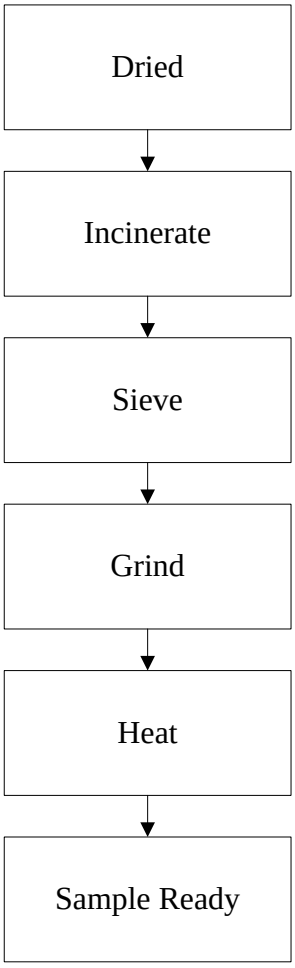


Figure 11. Summarization of the procedures in preparing the SCBA sample

3.2.4 Step by step procedures in conducting the experiment in geopolymerization process

After all the preparations of ashes are completed, the experiments continue with the geopolymerization process. The first step to conduct the geopolymerization process is the sodium hydroxide solution is prepared by diluting the distilled water with the sodium hydroxide (NaOH) pellets in a volumetric flask on selected concentration (14M of NaOH solution). Since geopolymerization is exothermic reaction, the alkaline solution is kept in a store at room temperature for 24 hours to remove excess heat. After that, fly ash powder and selected agricultural waste ash are mixed together with NaOH solution depending on ratio required. Table 6 shows the simplified mix proportions for these experiments, where **X** can be denote as type of

additives (POFA or RHA or SCBA). Figure 13 illustrates the step by step procedure in preparing geopolymer mould.

Table 7. Mix Proportions for the Geopolymerization Process

Mix Proportion Ratio	**(Fly Ash:X) 100:0**	**(Fly Ash:X) 70:30**	**(Fly Ash:X) 50:50**	**(Fly Ash:X) 0:100**
Liquid: Solid	0.4	0.4	0.4	0.4
Molarity of NaOH	14M	14M	14M	14M
Process temperature	25^{o}C & 60^{o}C	25^{o}C & 60^{o}C	25^{o}C & 60^{o}C	25^{o}C & 60^{o}C

Next, the fresh mixture of fly ash, additives and NaOH solution is rapidly poured into plastic mould for moulding process and exposed it into desired process temperature (25^{o}C and 60^{o}C)(Pauzi, 2013). Time is set and the mould is tested and observed every 5 minutes interval by using Vicat needle until it solidified. Then, the results obtained from this experiment will be analyzed and discuss based on the Avrami's Kinetic Theory. Figure 14 shows the summarization of procedures to test the solidification of geopolymer.

Figure 12. Summarization of the procedures in preparing the geopolymer mould

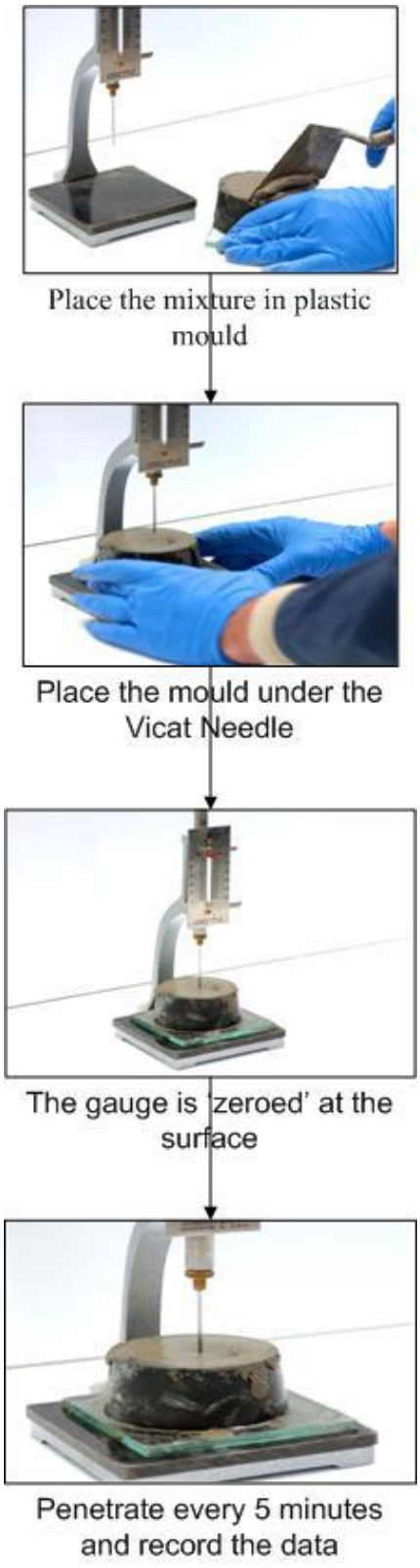
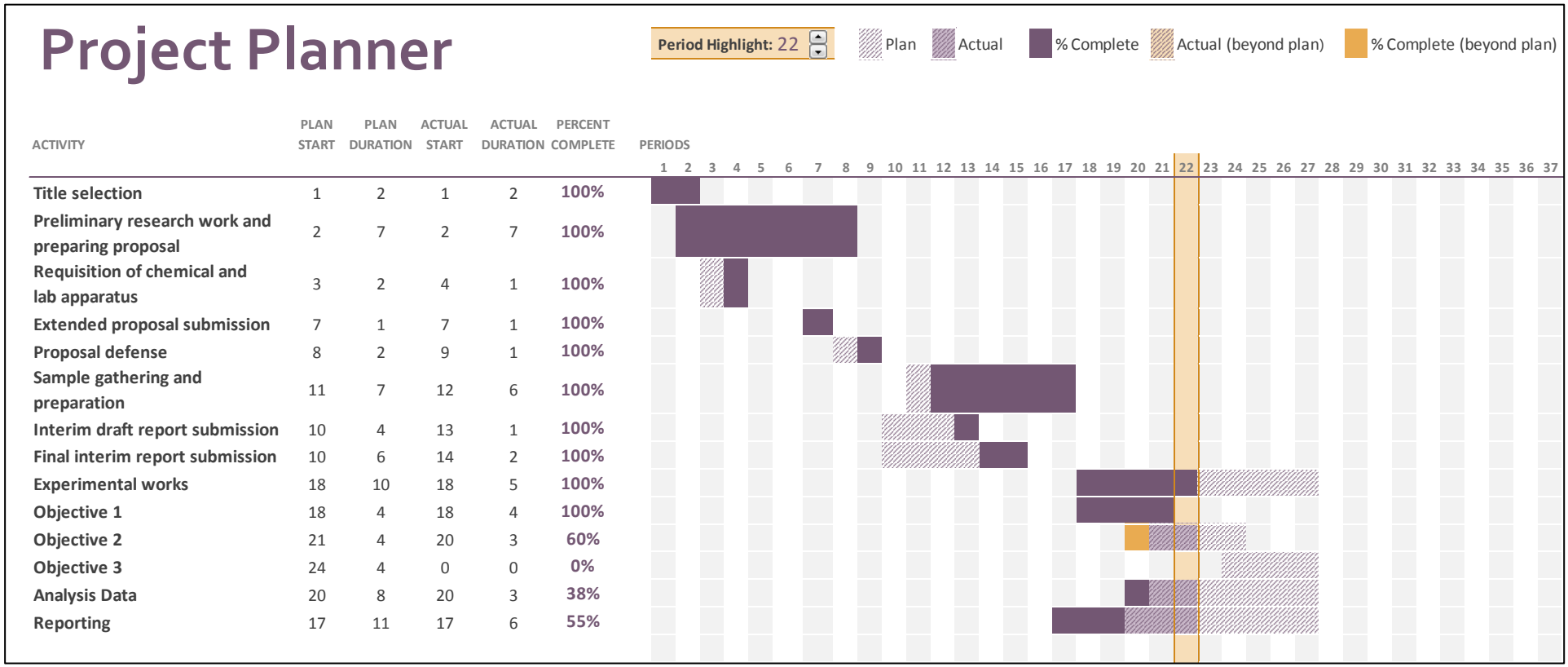


Figure 13. Summarization of procedures to test the solidification of geopolymers

3.2 Gantt Chart And Key Milestones

Basically the project will kick off in week 15 where it starts with sample preparation for the additives (POFA/MIRHA/SCBA). Next, experimental works will be commencing started from week 18 until week 27 and the distribution of the experimental works are based on the objectives planned earlier. At the end of every experimental works according to the objectives, the data gain from the experiment will be analyzed and compile into a report. The data will be analyzed by using Avrami's Kinetic Theory. The analysis of data and reporting section are estimated completed at week 28. The Table 8 below shows the Gantt chart for this project.

Table 8. Gantt chart for the Project



ACTIVITY	PLAN START	PLAN DURATION	ACTUAL START	ACTUAL DURATION	PERCENT COMPLETE
Title selection	1	2	1	2	100%
Preliminary research work and preparing proposal	2	7	2	7	100%
Requisition of chemical and lab apparatus	3	2	4	1	100%
Extended proposal submission	7	1	7	1	100%
Proposal defense	8	2	9	1	100%
Sample gathering and preparation	11	7	12	6	100%
Interim draft report submission	10	4	13	1	100%
Final interim report submission	10	6	14	2	100%
Experimental works	18	10	18	5	100%
Objective 1	18	4	18	4	100%
Objective 2	21	4	20	3	60%
Objective 3	24	4	0	0	0%
Analysis Data	20	8	20	3	38%
Reporting	17	11	17	6	55%

3.3 Equipment, Apparatus And Material Required

In completing this experiment, there are some equipment, apparatus and material required. Most of the elements are available in Chemical Engineering Laboratory in Universiti Teknologi PETRONAS (UTP). For basic equipment used in this experiment, the Vicat needle is the equipment used to measure the solidification of the geopolymer resin and this equipment is available in Block 5, UTP Chemical Engineering Laboratory. Next, ball mill grinder is important in grinding the ashes sample (POFA/MIRHA/SCBA) and this equipment is also available at Block 5, UTP Chemical Engineering Laboratory. For MIRHA sample, the sample will be taken directly from UTP very own Microwave Incinerator where the sample will be incinerate at temperature of 800^{o}C. For sieving purposes, a sieve machine is required in order to sieve the additive sample so that the particle size is kept constant at 300μm. Figure 14 below shows the sieving machine used for this experiment.

Figure 14. Sieving machine used for sieving the additives

Besides equipment, suitable apparatus also is important in ensure the experiments are conducted in a proper manner. In this research, the apparatus required are beaker, volumetric flask, glass rod, measuring cylinder, spatula, weighing scale and 300μm sieve. The glass rod and beaker is used as early preparation of NaOH solution as the NaOH pellets are required to be dissolved in the distilled water. Then, volumetric flask

is used in diluting the dissolved NaOH solution until the desired concentration is achieved. Weighing scale is utilized to weight the sample ratio of fly ash powder and any selected agricultural ashes prepared earlier with the ratio as stated in Table 3.1. Later, measuring cylinder is used to measure the correct amount of NaOH solution that should be mixed together with the fly ash plus the additives from the agricultural ashes prepared earlier and the mixture will be place in a mould before the solidification test by Vicat needle is tested. Figure 15 shows the volumetric flask used for storing sodium hydroxide solution.

Figure 15. Volumetric flask used in this experiment

In these experiments, fly ash Class F is used as the main alumino-silicate material for the geopolymerization process. Sodium hydroxide and distilled water are used in preparing the alkaline activator for these experiments. For the agricultural wastes, POFA and MIRHA will be obtained directly from the palm oil mill and UTP Microwave Incinerator respectively, and the SCBA will be synthesized manually.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 The Experimental Results

Three experiments are conducted in this project in order to determine the effect of additives in the geopolymer's kinetic formation. Basically for one particular experiment, there will be four subsections where the operating condition such as concentration of the precursor solution and the operating temperature is varying throughout the experiment. The concentration of the precursor solution is set at 14M and the operating temperatures are set for both room temperature (25^{o}C) and at 60^{o}C. The solidification of the geopolymer mould will be measure by using Vicat Needle instrument. The data will collected covered until recent date only, thus some of the data might not available due to insufficient time for the mould to solidify. The data will be analyzed based on the theory claimed in journals paper and books.

4.1.1 Experiment 1: Effect of Palm Oil Fuel Ash (POFA) In Solidification of Geopolymer

The main objective for this experiment is to study the effect of palm oil fuel ash or POFA in solidification of geopolymer. The main aluminosilicates raw material is fly ash Class F and alkaline activator is sodium hydroxide solution. The mix proportions between main aluminosilicates material with the additive from POFA is discussed as in the Chapter 3 earlier. In this experiment the concentration of the precursor solution is set at 14M and the operating temperatures are set for both room temperature 25^{o}C and at 60^{o}C. Figure 16 shows the result for this experiment where the graph of Vicat Needle penetration's depth vs. time is plotted to represent the effect of POFA in solidification of geopolymer for 14M concentration of NaOH solution.

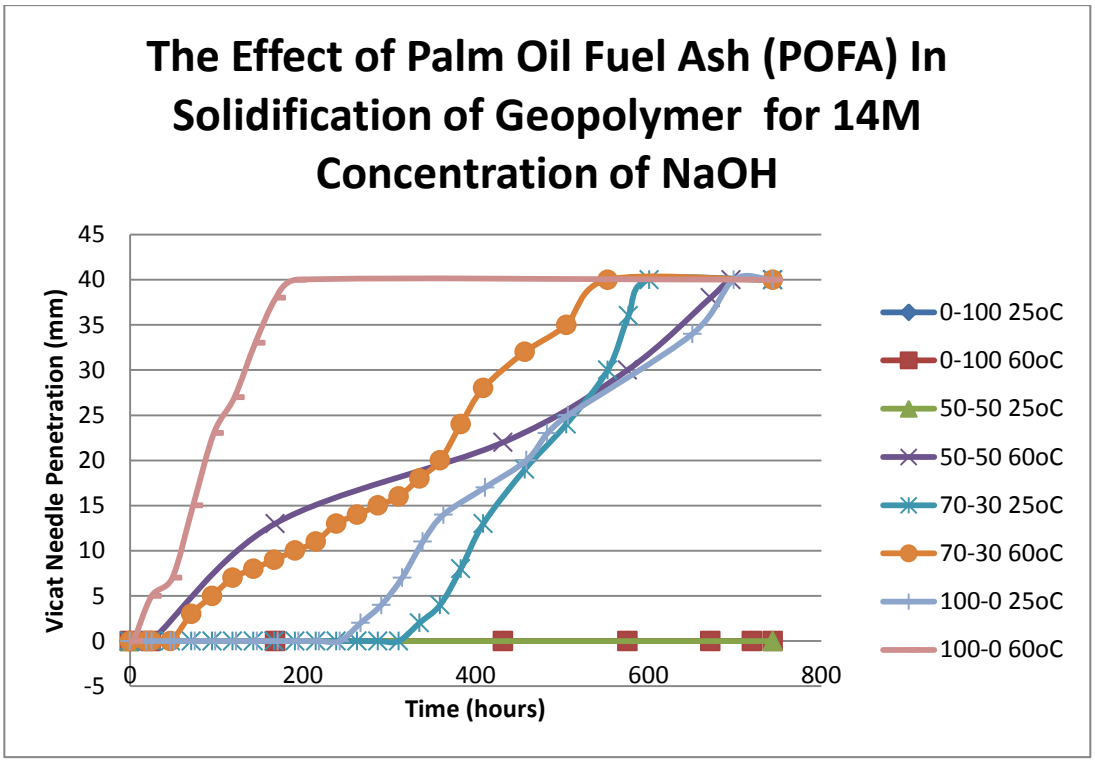


Figure 16. The effect of palm oil fuel ash (POFA) in solidification of geopolymer for 14M concentration of NaOH

The graph above shows the effect of multiple proportions of POFA as additive in the geopolymerization process. The mix proportion is in ratio of Fly Ash:POFA ratio as discussed earlier in Chapter 3. The data gained from the penetration of the Vicat needle into the geopolymer mould is translated into an S-curve where the maximum value of penetration is set at 40mm. From the graph, it is clearly shows that at temperature of 60^{o}C with the ratio of 100:0 (Fly Ash:POFA) where there is no additive is added, the time taken to solidify is the fastest at 193 hours. Since there is no addition of the additive into the fly ash during the sample preparation process, the composition of the aluminosilicate is not altered. As reported by (Kupaei et al., 2013; Phair & van Deventer, 2002) the composition of fly ash is mainly silica and alumina and traces percentage of other minerals such as calcium oxide, magnesium oxide and etc. The percentage of silica is usually around 42.4% up to 57.60%, where the percentage of alumina is around 27.1% to 28.90% (Kupaei et al., 2013; Phair & van Deventer, 2002). The figuratively balance composition between silica and alumina do not affected the

setting time for the geopolymer to solidify prominently, only when the composition of the aluminosilicate material is altered, the setting time for the geopolymer to solidify will be affected. The addition of POFA into the fly ash sample will change the chemical composition of the initial aluminosilicate material used for geopolymerization process. POFA is known to have a high content of silica rather than alumina as reported by (Zarina et al., 2013) where silica content can be more than 50% in a certain sample of POFA and the composition of alumina can be as low as 1.6% to 11.4%.

The addition of POFA as an additive into the fly ash sample promotes the alteration of the chemical composition of fly ash. Since both of the compounds have a high composition of silica, logically the final composition of POFA and fly ash will have a high percentage of silica too. The high amount of silica in the composition of main aluminosilicate for geopolymerization process will hindered the setting time for the geopolymer to solidify. This is shown at the Figure 16 where the increasing amount of POFA additive into the fly ash will hindered the setting time for the geopolymer to solidify. The prominent result that matches this claimed is shown in Figure 16 for the ratio of Fly Ash:POFA of 50:50, at temperature of 60^{o}C where the time taken for the geopolymer mould to solidify is at 696 hours. Since the alkaline activator used in this experiment is only sodium hydroxide without any other addition of modulus alkali silicate, the process of geopolymerization subsequently require a longer time for the geopolymer to solidify. The modulus alkali silicate likes sodium silicate accelerates the geopolymerization process due to the presence of Si^{4+} ion that vital for the leaching process in the polycondensation of geopolymer (Xu & Van Deventer, 2000).

However, from this S-curve, the kinetics of the reaction cannot be assumed directly from the graph itself. This series of data need to be analyzed by using Avrami's Kinetic Theory and translated from sigmoidal curve into a linear graph. From this graph, the gradient of the graph represent the Avrami's exponent that will give the hypothetical view on how the crystal growth during the geopolymerization. The intercept of the vertical axis of the linear graph will indicate the growth value of the graphs thus represent the actual kinetics for the reaction. This will be covered further in subsection 4.2 where the data will be analyzed by using Avrami's Kinetic Theory.

4.1.2 Experiment 2: Effect of Rice Husk Ash (RHA) In Solidification of Geopolymer

The main objective for this experiment is to study the effect of rice husk ash or RHA in solidification of geopolymer. The main aluminosilicates raw material is fly ash Class F and alkaline activator is sodium hydroxide solution. The mix proportions between main aluminosilicates material with the additive from RHA is discussed as in the Chapter 3 earlier. In this experiment the concentration of the precursor solution is set at 14M and the operating temperatures are set for both room temperature 25oC and at 60oC. Figure 17 shows the result for this experiment where the graph of Vicat Needle penetration's depth vs. time is plotted to represent the effect of RHA in solidification of geopolymer for 14M concentration of NaOH solution. For this experiment, in ratio of Fly Ash:RHA for 100:0 ratio, the result is kept constant as in subsection 4.1.1 for both operating temperature of 25^{o}C and 60^{o}C as it is considered as the constant set for geopolymer mould without any additives added.

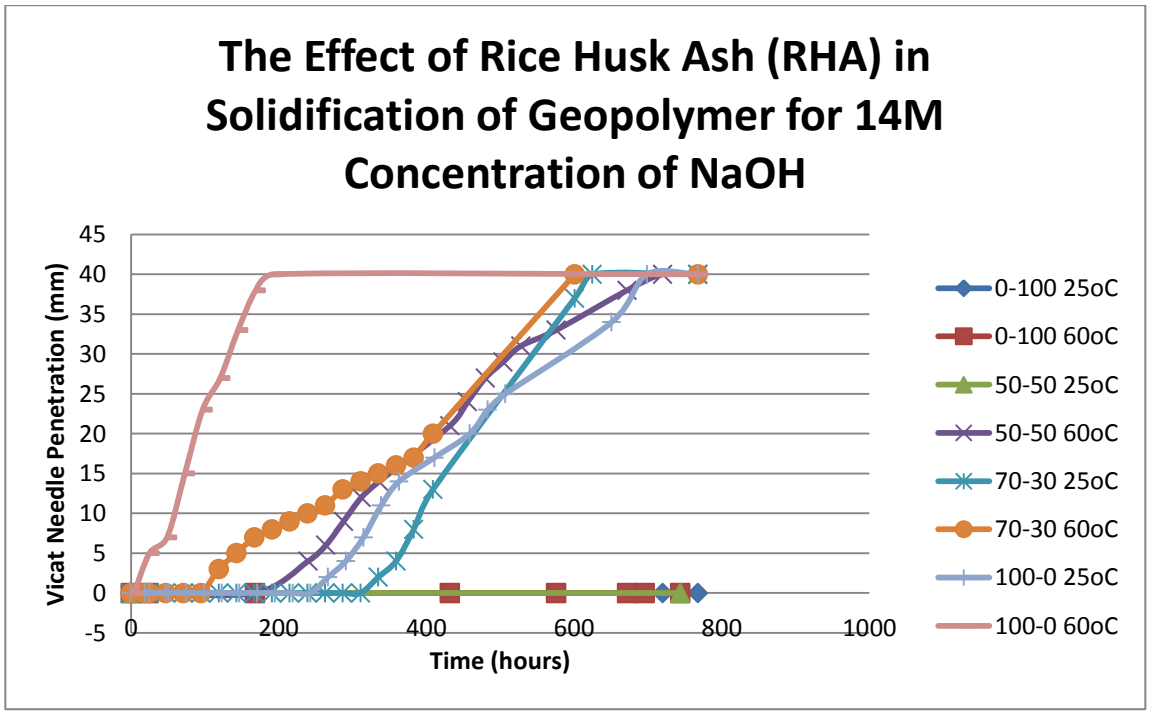


Figure 17. The effect of rice husk ash (RHA) in solidification of geopolymer for 14M concentration of NaOH

Figuratively, the S-curve as in Figure 17 shows that as the amount of additive increase in the geopolymer mixture, the time taken for the geopolymer to solidify is also increase. The composition of RHA is mainly silica and less alumina and traces of some others minerals. The presence of high composition of silica in the geopolymer mould promotes the setting time to be slower than usual. Comparing the time taken for geopolymer mould to solidify as in ratio (Fly Ash:RHA) of 70:30 at 60^{o}C and ratio 50:50 at 60^{o}C, the result show that the mould is solidify at a faster duration in the ratio of 70:30 rather than the ratio of 50:50. For ratio of 70:30, the time taken for the geopolymer to solidify is 601 hours while for ratio of 50:50 the solidification time measured is 720 hours. This is mainly due to the effect of alteration of main aluminosilicate by adding up additive into the initial mixture. The silica-rich RHA hindered the setting time of the geopolymer mould to solidify. Contradict to the mix proportion ratio which not has any addition of additive in the mixture, the time recorded for the mould to solidify is fastest among all. In 193 hours, the mould solidifies at working temperature of 60^{o}C.

Indeed, the temperature plays a vital role in the solidification of geopolymer. The polycondensation process occurred during the geopolymerization releases water as by-product. By increasing the operating temperature for the geopolymerization process, the water from the polycondensation process can be removed at a faster rate and thus speed up the setting time for the geopolymer to solidify. Based on claims by (Muñiz-Villarreal et al., 2011), the optimum temperature for the geopolymerization is 60^{o}C. One of the examples that replicate this case is for the ratio of 50:50 and working temperature is 25^{o}C. The observation for this geopolymer mould is shown as in Figure 18.

Figure 18. Observation for geopolymer mould at ratio of 50:50 with working temperature of 25^{o}C

Based on the observation made for this ratio, the geopolymer itself do not solidify completely due to the excessive water released from the geopolymerization process. A thick layer of water is present at the surface of geopolymer. This might be due to the leaching of Si, Al and traces of other ions phenomenon happened as the fly ash and the RHA reacts with the sodium hydroxide solution during the dissolution stage of geopolymerization. This process releases water as by-product. Since the working temperature is quite low (at 25^{o}C), the process of removing water is slow thus preventing the mould from solidify completely.

Nevertheless, from this S-curve, the kinetics of the reaction cannot be presumed directly from the graph itself. This series of data need to be evaluated by using Avrami's Kinetic Theory and translated from sigmoidal curve into a linear graph. From this graph, the gradient of the graph symbolize the Avrami's exponent that will give the hypothetical view on how the crystal growth during the geopolymerization. The intercept of the vertical axis of the linear graph will indicate the growth value of the graphs thus represent the actual kinetics for the reaction. This will be covered further in subsection 4.2 where the data will be analyzed by using Avrami's Kinetic Theory.

4.1.3 Experiment 3: Effect of Sugarcane Bagasse Ash (SCBA) In Solidification of Geopolymer

The main objective for this experiment is to study the effect of sugarcane bagasse ash or SCBA in solidification of geopolymer. The main aluminosilicates raw material is fly ash Class F and alkaline activator is sodium hydroxide solution. The mix proportions between main aluminosilicates material with the additive from SCBA is discussed as in the Chapter 3 earlier. In this experiment the concentration of the precursor solution is set at 14M and the operating temperatures are set for both room temperature 25^{o}C and at 60^{o}C. Figure 19 shows the result for this experiment where the graph of Vicat Needle penetration's depth vs. time is plotted to represent the effect of SCBA in solidification of geopolymer for 14M concentration of NaOH solution. . For this experiment, in ratio of Fly Ash:SCBA for 100:0 ratio, the result is kept constant as in subsection 4.1.1 for both operating temperature of 25^{o}C and 60^{o}C as it is considered as the constant set for geopolymer mould without any additives added.

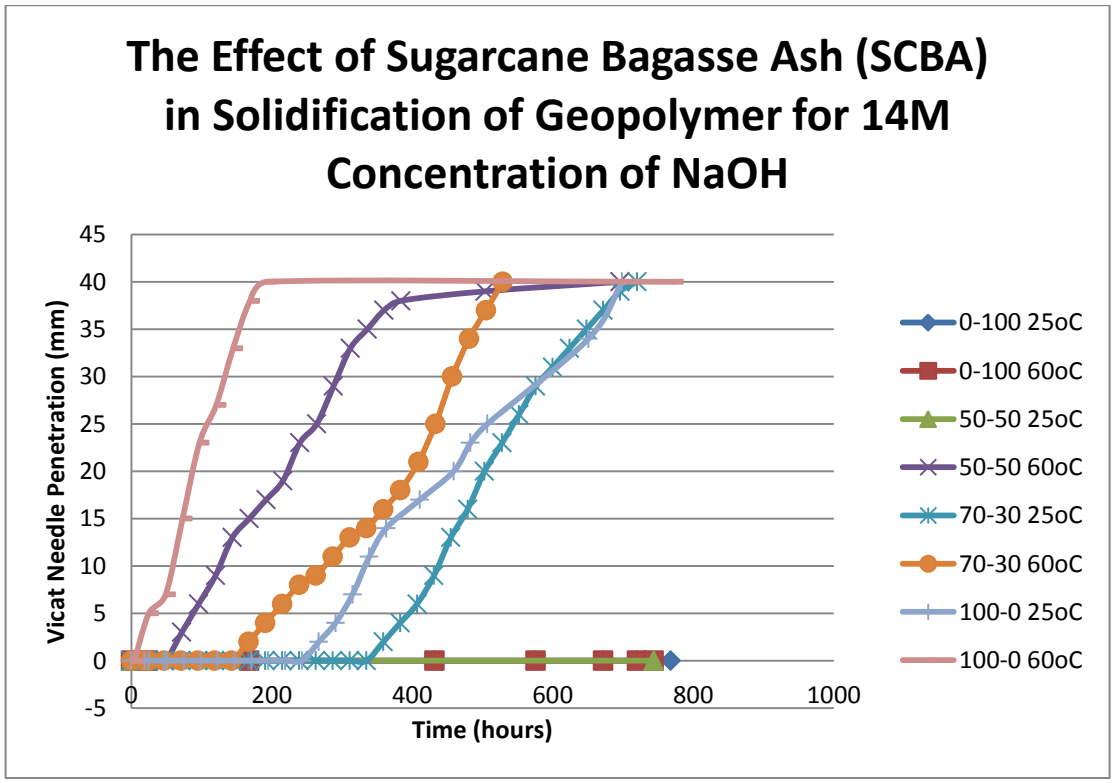


Figure 19. The effect of sugarcane bagasse ash (SCBA) in solidification of geopolymer for 14M concentration of NaOH

The overall trend for the S-curve as in Figure 19 shows that the increasing amount of additive added into the geopolymer mould resulting in increasing time taken needed for the geopolymer to completely solidify (De Silva & Sagoe-Crenstil, 2009). Figuratively, the fastest solidification time recorded is for ratio of Fly Ash:SCBA of 70:30 at working temperature of 60^{o}C. The time recorded for the geopolymer to completely solidify is 529 hours. Similar as in sub-section 4.1.1 and 4.1.2, this is due to the alteration of the aluminosilicate material used for the geopolymerization process. The presence of SCBA, which contain a high composition of silica rather than alumina (Ganesan et al., 2007), hindered the setting time for the solidification of geopolymer. The alteration of the initial recipe of the aluminosilicate mixture for the geopolymerization decelerated the transformation of amorphous to crystalline structure in the geopolymer itself, especially when the composition of the silica is high (De Silva & Sagoe-Crenstil, 2009). Since SCBA is known for its high silica traits, this additive basically slow down the setting time required for the geopolymer to solidify. Figure 20 shows the geopolymer mould for ratio of 70:30 at operating temperature of 60^{o}C.

Figure 20. Geopolymer mould for ratio of 70:30 at working temperature of 60^{o}C

As in sigmoidal curve in Figure 19, for the ratio of Fly Ash:SCBA (50:50) and working temperature of 60^{o}C, an observation can be assumed that the geopolymer undergoes two stage of crystallization process. This assumption made based on the presence of one early maximum peak at point (360, 37). Basically the crystal growth on that particular ratio is presumed undergoes first crystal nucleation at the first peak of the maximum point of the graph. This crystal later promotes the secondary nucleation of crystal and larger crystals are produced in this secondary nucleation phase. The secondary

crystallization stopped at the maximum point of penetration, when there is no penetration can be made on the geopolymer mould.

Conversely, from this S-curve, the kinetics of the reaction cannot be assumed directly from the graph itself. This series of data need to be analyzed by using Avrami's Kinetic Theory and translated from sigmoidal curve into a linear graph. From this graph, the gradient of the graph represent the Avrami's exponent that will give the hypothetical view on how the crystal growth during the geopolymerization. The intercept of the vertical axis of the linear graph will indicate the growth value of the graphs thus represent the actual kinetics for the reaction. This will be covered further in subsection 4.2 where the data will be analyzed by using Avrami's Kinetic Theory.

4.2 Analyzing Data by Using Avrami's Kinetic Theory

From the experimental works, the setting time of the geopolymer to solidify will be recorded and be further analyzed by using the Avrami's Kinetic Theory. During this stage, the S-curve plotted earlier will be linearizing by taking log-log graph. The Avrami's Kinetic Theory is used to extract the kinetic of crystallization of geopolymer. The linearizing of the sigmoidal graph from the three experiments really affected by the significance different of data, thus average data from the Vicat Needle's penetration plays an imperative part in acquire a more precise result. The data deviation might lead to the deviation of the actual values of Avrami's exponent (m) and growth rate (K). From the linear graph, the gradient of the graph is define as the values of Avrami's exponent (m) and the intercept of the graph at the vertical axis represent the growth rate of the geopolymer crystals. By referring the Avrami's parameter table as in Chapter 2, the solidification of the crystal mechanism for the geopolymer can be known.

Figure 20 shows the Avrami's plot for the effect of palm oil fuel ash in solidification of geopolymer while Figure 21 shows the Avrami's plot for the effect of rice husk ash in solidification of geopolymer and Figure 22 shows the effect of sugarcane bagasse ash in solidification of geopolymer. From these Avrami's plot, the gradient of the graph represent the value of Avrami's exponent (*m*) and the y-intercept of the linear graph indicates the growth rate constant (*K*) are extracted and tabulated as in Table 9, 10 and 11 respectively.

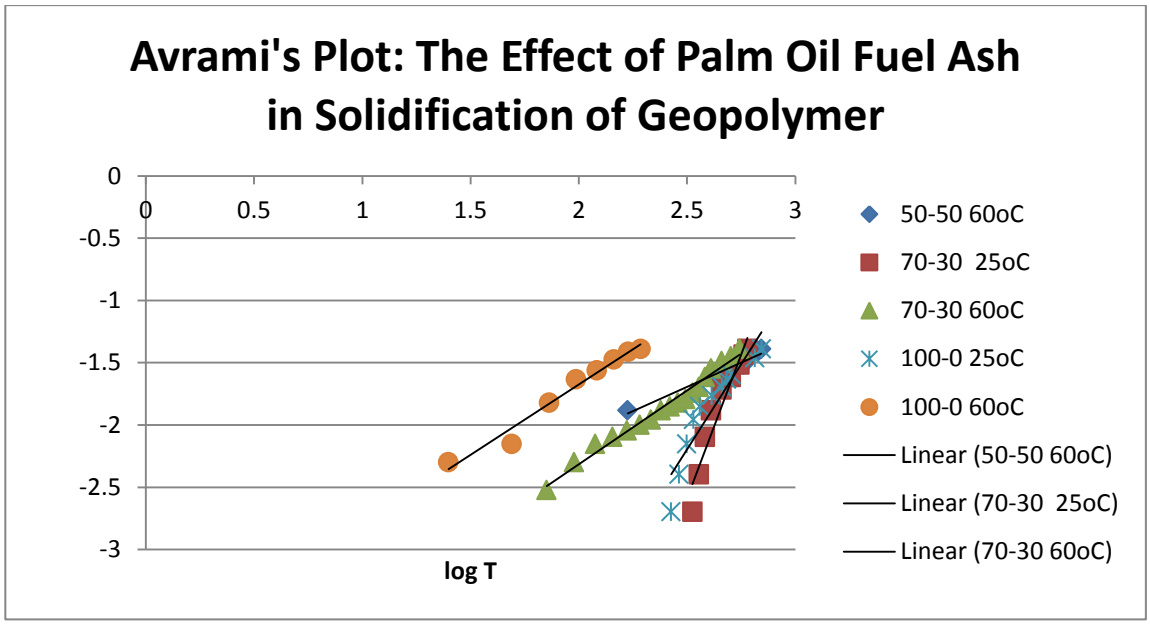


Figure 21. Avrami's plot for Experiment 1

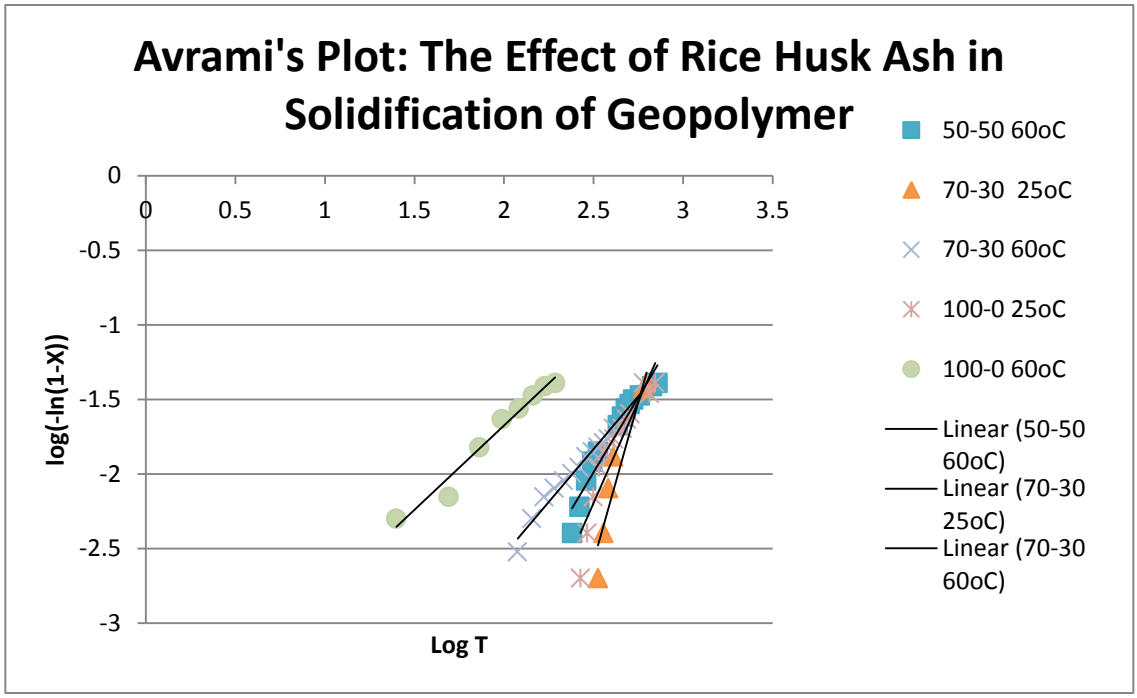


Figure 22. Avrami's plot for Experiment 2

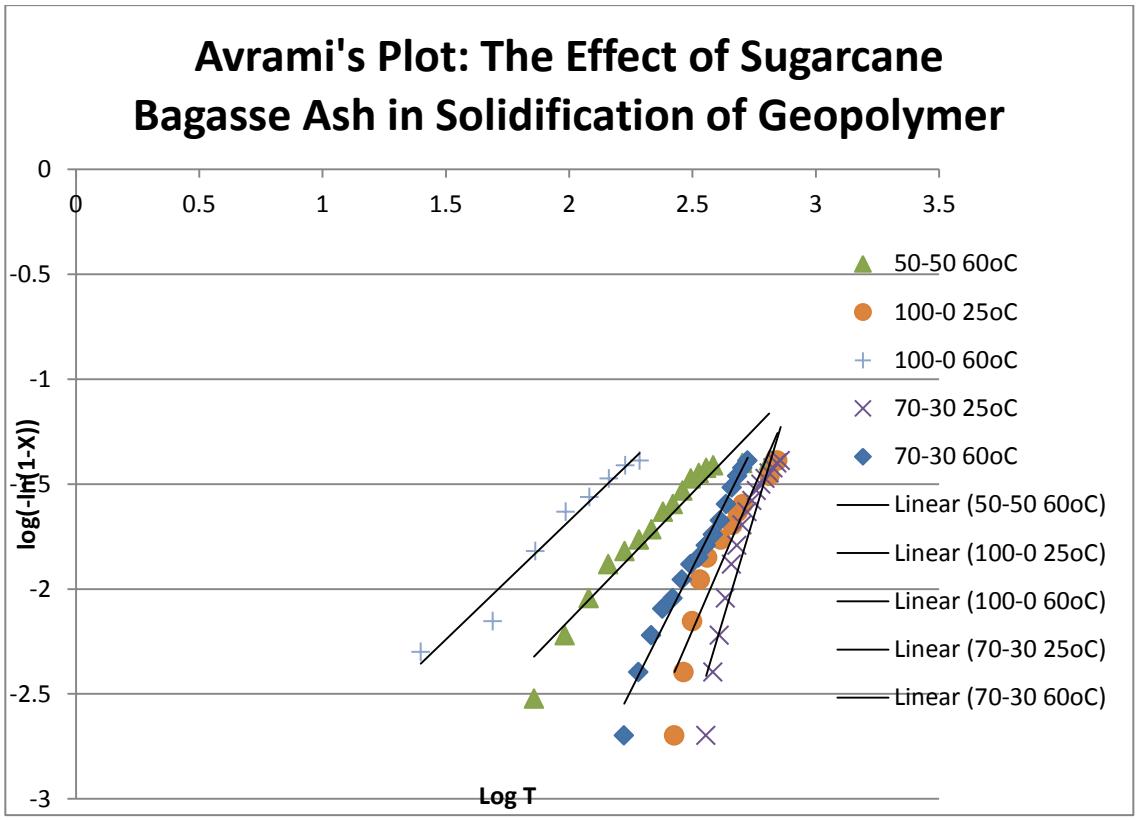


Figure 23. Avrami's plot for Experiment 3

From these Avrami's plots, the data for Avrami's exponent (*m)* and growth rate (*K*) are extracted and tabulated as in Table 9, 10 and 11 respectively.

Table 9. Avrami's exponent for Experiment 1

Ratio Fly Ash:POFA	Temperature	Avrami Exponent, m	Growth value, K
50:50	60°C	0.7781	2.29562×10^{-4}
70:30	25°C	4.6334	6.66807×10^{-15}
70:30	60°C	1.1834	2.08497×10^{-5}
100:0	25°C	2.7259	9.77687×10^{-10}
100:0	60°C	1.1295	1.16332×10^{-4}

Table 10. Avrami's exponent for Experiment 2

Ratio Fly Ash:RHA	Temperature	Avrami Exponent, m	Growth value, K
50:50	60^{o}C	2.0132	$9.48855x10^{-8}$
70:30	25^{o}C	4.2812	$5.1168x10^{-14}$
70:30	60^{o}C	1.14142	$4.2776x10^{-6}$
100:0	25^{o}C	2.7259	$9.77687x10^{-10}$
100:0	60^{o}C	1.1295	$1.16333x10^{-4}$

Table 11. Avrami's exponent for Experiment 3

Ratio Fly Ash:SCBA	Temperature	Avrami Exponent, m	Growth value, K
50:50	60^{o}C	1.2136	$2.65155x10^{-5}$
70:30	25^{o}C	3.9283	$3.53183x10^{-13}$
70-30	60^{o}C	2.34	$1.78855x10^{-8}$
100:0	25^{o}C	2.7259	$9.77687x10^{-10}$
100:0	60^{o}C	1.1295	$1.16333x10^{-4}$

Based on the data extracted from the Avrami's plot, the overall trend shows that the value of Avrami's exponents are varies in all type of additives used in this experiments. The value of *m* is stretching from 0.7781 up to 4.6334 where both of the value, the largest and the smallest *m* values are calculated from experiment 1 which used POFA as an additive at the ratio of 70:30 at 25^{o}C and ratio 50:50 at 60^{o}C in the geopolymer solidification respectively. These Avrami's exponent will indicates on the crystal growth mechanism in that particular geopolymer mould. In addition, there are some of the linear Avrami's plots as in experiment 3 that show the two values of the *m* values in a single graph. Significantly, it can be found at the ratio of Fly Ash:SCBA of 50:50 at 60^{o}C, 100:0 at 25^{o}C, 70:30 at 25^{o}C and at 60^{o}C respectively. This might be due to the secondary crystallization in the geopolymer samples.

As discussed earlier in Chapter 2, the Avrami's exponent (*m*) represent to crystal growth mechanism either it is sporadic or instantaneous nucleation. (Ismail et al., 2008) describe the growth mechanism by classifying the Avrami's exponent values accordingly. For *m*=1, it is presumed that the nuclei growth instantaneously, while for *m*=3 and *m*=4 denotes to spherulitic growth from whichever sporadic or instantaneous nucleation. The growth form of the crystal for two- or three- dimensional forms can also be predicted based on the Avrami's exponent *m*, ranging from values of 2 to 3. Additionally, for *m* value larger than 4, (Toro-Vazquez, Briceño-Montelongo, Dibildox-Alvarado, Charó-Alonso, & Reyes-Hernández, 2000) claimed that heterogeneous nucleation is occurred in the crystal growth process and designate the result of sporadic nucleation on the growth of the new crystal. Referring back to the Avrami's exponent results earlier, there are two ratios that display the Avrami's exponent value more than 4. The results that show the *m* values larger than 4 are for ratio of Fly Ash:POFA (70:30 at temperature of 25^{o}C) and ratio of Fly Ash:RHA (70:30 at temperature of 25^{o}C) where the *m* values are 4.6334 and 4.2812 respectively. Based on the claimed made earlier by (Toro-Vazquez et al., 2000), these geopolymers in that particular ratios might undergoes heterogeneous nucleation and perhaps sporadic nucleation is occurred during the formation of the new crystal. From the tabulated data as in Table 9, 10 and 11 respectively, the calculated Avrami's exponents are varies and not fixed to only one formation of crystal growth. This might due to the effect of the setting time required for the geopolymer to solidify. As an overall, the increase in setting time in solidification of the geopolymer to solidify completely, the higher the increment of the Avrami's exponent, *m* values and led to the formation of three-dimensional crystal structure during the geopolymerization process.

On top of that, the *K* value or the growth rate is vital in predicting the rate of the geopolymerization process. Theoretically, the values of the Avrami's exponent (*m*) are inversely proportional to the growth rate (*K*) value, as the values of *m* increase, the values of *K* decrease (Pauzi, 2013). For experiment 1, 2 and 3, basically shows the same trending where the increase on the Avrami's exponent (*m)* values, the growth value (*K)* values will be decrease. This results are consistent to the theory that by increasing the amount of additives, which all of them basically silica-rich additives, the slower the time taken for the geopolymer to solidify completely. This is due to the increasing percentage

of the silica in the main aluminosilicate material hindered the setting time, similar idea proposed by (Autef, Joussein, Gasgnier, & Rossignol, 2012; De Silva & Sagoe-Crenstil, 2009). The anticipated value of growth is increases as the value of the additives are decreases in each geopolymer samples. In addition, by adjusting the operating temperature of the geopolymer which is 25^{o}C and 60^{o}C, the effect of the adjustment is significant. Low operating temperature gives a lower growth value (*K*) as the Avrami's exponent (*m*) is increases. Meanwhile at 60^{o}C, the time taken for the geopolymer to solidify is shorter and thus the growth value (*K*) is higher and the resulting Avrami's exponent (*m*) is low. This parameter changes adhered to the idea proposed by (Muñiz-Villarreal et al., 2011) who claimed that at temperature of 60^{o}C, the geopolymerization rate is optimum. However, the variation of the temperature is not the main objective in these experiments. The most important part for this project is to study the effect of the additives in geopolymer's kinetic formation. Indeed, these three agricultural-based additives are high in silica thus hindered the setting time requires for the geopolymer to completely solidify. Since the main parameters such as alkali activator used and working temperature is kept at minimum based, the result are predicted to be much slower.

CHAPTER 5
CONCLUSION AND FUTURE WORK

5.1 Conclusion

As discussed earlier in the Chapter 4, the additives such as POFA, RHA and SCBA give significant effect on the geopolymerization rate. The solidification of the geopolymer is really affected by the composition changes in the initial aluminosilicate material. In summarizing the result, it can be concluded that:

- Using of POFA as an additive hindered the setting time for the solidification of geopolymer since the high content of silica slower down the solidification rate of geopolymerization.
- RHA-based additive affected the solidification time by increasing the time taken required for the geopolymer to solidify completely as RHA is rich in silica composition.
- The introduction of SCBA as an additive in geopolymerization promotes the setting time to increase as the SCBA is rich in silica.

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Based on Avrami's Kinetic Theory:

- Based on the calculated data, as the growth rate (*K*) increases, the Avrami's exponent (*m*) decreases.
- As an overall, the range values for the Avrami's exponent are varied from 0.7781 to 4.6334. This can be assumed that the crystal growth form is not fixed and very dependable on the Avrami's exponent respectively.
- In the usage of SCBA as an additive in the geopolymerization process, there are numerous samples that indicates the secondary crystallization as there are more than one Avrami's exponent spotted on the graph in Figure 23. . Significantly, it can be found at the ratio of Fly Ash:SCBA of 50:50 at 60^{o}C, 100:0 at 25^{o}C, 70:30 at 25^{o}C and at 60^{o}C respectively.
- For Avrami's exponent *m* larger than 4, it is presumed that the geopolymer undergoes the heterogeneous nucleation and the growth form is assumed sporadically.
- Among all additives used, the fastest kinetic formation is noticed in the usage of POFA at ratio of 50:50 with operating temperature is 60^{o}C where the Avrami's exponent m=0.7881 and the growth value K=2.29562x10^{-4}.
- Among all additives used, the slowest kinetic formation is noticed in the usage of POFA at ratio of 70:30 with operating temperature is 25^{o}C where the Avrami's exponent m=4.6334 and the growth value K=6.66807x10^{-15}.

5.2 Recommendations

As a way forward, there are few future works that can be suggested in order to expand and improve this project.

- The sizing of the additive mixture can be manipulated in order to see the effect of additive particle sizes in geopolymer kinetic formation. A finer size of additive increase the reactivity of the additive.
- Introducing another modulus alkaline solution to speed up the geopolymerization rate. For example, sodium silicate.
- Instead of using three additives that have a major composition of silica, perhaps in future the usage of additives that have a major composition of alumina can be utilized since the high amount of alumina in raw material of aluminosilicates cause the setting time to decrease.
- In minimizing the error during the process of data extraction especially from the Vicat Needle, the average data should be taken and thus resulting in a more accurate result of Avrami's plot.

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