FLY ASH BASED GEOPOLYMER AS LIGHTWEIGHT AGGREGATE WITH LOW PROCESSING TEMPERATURE FOR STRUCTURAL INSULATING CONCRETE APPLICATION

by

ALIDA BINTI ABDULLAH
(1340410994)

A thesis submitted in fulfillment of the requirements for the degree of
Doctor of Philosophy

School of Materials Engineering
UNIVERSITI MALAYSIA PERLIS

2019

ACKNOWLEDGMENT

Alhamdulillah, I want to thank Allah for this opportunity to complete PhD study. Million thanks as well for those who are involved direct or indirectly in the process of completing this thesis. Completion of this thesis marks the conclusion of my life as a postgraduate student in School of Materials Engineering at Universiti Malaysia Perlis.

First and foremost, I would like to take this opportunity to express my sincere appreciation to my project supervisor; Prof. Dr. Kamarudin Hussin and my co-supervisor Assoc. Prof Dr. Mohd Mustafa Al Bakri Abdullah for their help, guidance, chance and all sorts of support. Without their guide, the present study would have been impossible. I believe I gain a lot of self-confidence throughout this work and the experience that I have is invaluable. I have enjoyed their mentorship and friendship, and have learned about life as well as research from them. I am grateful for their guidance and encouragement. They have provided me with a solid educational background.

A special thanks to my family especially my husband, Abdul Basit, my daughter Amanda, my mother Che Mek Saman and my Father and mother in law for their endless support that never stops and guides me along the correct path of education with much sacrification and determination. Special thanks also go to my siblings who were supportive of all this work. My family has always stood by me, through all the ups and downs, and has been very patient and encouraging in everything I have ventured to do. I could not make this far without them.

My utmost appreciation and thanks are given to all my geopolymer group friends for all the support throughout my studies. My friends have been my rock to whom I could always turn to comfort, understanding, and motivation. They made me see the silver lining in the clouds when all I could see was an abysmal black hole. Their friendship provided me the endurance to pass through the difficult stages in life.

Other than that, I am also thankful to all technicians and teaching engineers, patient and assistance to guide me how to do the work and using the machine in the laboratory. Special thanks for their great help in supplying materials and technical information. It is impossible for me to do all the lab work without guidance from all of them.

Finally, my appreciation also goes to Centre of Excellence Geopolymer & Green Technology (CEGeoGTech), Faculty of Engineering Technology, School of Materials Engineering and for giving me a space for superb facilities and Universiti Malaysia Perlis for sponsor my study. Lastly, thank you to all individuals who is contributes in this study. Without all of name stated above and named not mention here, it is impossible for me to complete my study.

-Alida Abdullah-

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

PAGE

LIST OF ABBREVIATIONS

ACI	American Concrete Institute
Al_2O_3	Aluminium Oxide
ASTM	American Society for Testing and Materials
AIV	Aggregate Impact Value
BS	British Standard
CaO	Calcium Oxide
EDX	Energy Dispersive X-ray
FA/AA	Fly Ash/Alkali Activator
FTIR	Fourier Transform Infra-Red
H_2O	Water
ITZ	Interfacial Transition Zone
LECA	Lightweight Expanded Clay Aggregate
NaOH	Sodium Hydroxide
Na_2SiO_3	Sodium Silicate
N-A-S-H	Sodium Aluminate Silicate Hydrate
OPC	Ordinary Portland Cement
SiO_2	Silica Dioxide
SEM	Scanning Electron Microscopy
TPS	Transient Plane Source
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

LIST OF SYMBOLS

A	Net weight of the aggregates in the measure (g)
B	Weight of crushed aggregate that passing through sieved (g)
g	Gram
H	Hydrogen
kg	Kilogram
L	Litre
M	Concentration of NaOH (M)
Md	Mass of oven-dried sample (g)
Ms	Mass of surface-dried sample (g)
Mw	Molecular weight (g/mol)
n	Polymerization degree
O	Oxygen
R (t)	Resistance of the TPS sensor at time t
R_0	Resistance of the TPS sensor at time zero
W1	Mass of cube concrete in the air (kg)
W2	Mass of cube concrete in water (kg)
V	Volume (ml)
α	Temperature coefficient of resistivity
$\Delta T(\tau)$	Mean value of the temperature rise in the TPS element
%	Percentage
θ	Theta

Geopolimer Berasaskan Abu Terbang Sebagai Agregat Ringan Dengan Suhu Pemprosesan Rendah Bagi Aplikasi Konkrit Penebat Struktur

ABSTRAK

Agregat ringan dalam konkrit telah digunakan secara meluas pada masa kini kerana ketumpatan rendah dengan sifat mekanik yang hebat. Agregat ringan ini boleh dihasilkan dengan rawatan haba dari sumber semulajadi atau dari produk sampingan perindustrian. Walau bagaimanapun, kaedah pengeluaran semasa biasanya melibatkan tenaga yang tinggi kerana suhu pembakaran yang tinggi digunakan walaupun memberikan sifat mekanikal yang hebat. Oleh itu, terdapat keperluan mencari dan menggantikan kaedah yang lebih kompeten dan cekap melebihi batasan kaedah semasa. Geopolimer menjadi penyelidikan yang menarik kerana meningkatkan sifat konkrit dan mengekalkan persekitaran melalui penggunaan sisa industri seperti abu terbang. Kajian ini memberi tumpuan kepada penghasilan agregat ringan geopolimer abu terbang dengan sifat penebat haba yang baik untuk aplikasi konkrit struktur dengan suhu pembakaran yang minimum dengan menggunakan kaedah pengeopolimeran. Kesan parameter sintesis geopolimer seperti kepekatan NaOH (6 M, 8 M, 10 M, 12 M dan 14 M), nisbah abu terbang/pengaktif alkali (2.0, 2.5, 3.0 dan 3.5), dan suhu pembakaran (400 °C hingga 1200 °C) kepada agregat ringan geopolimer abu terbang yang mempengaruhi sifat-sifat mekanik dan mikrostruktur dikaji secara terperinci. Agregat optimum dari segi kekuatan impak tertinggi dengan kepadatan dan penyerapan air yang rendah kemudian diuji sifat penebat habanya melalui kesan kekonduksian terma, kelesuan haba dan kapasiti haba tertentu agregat. Keputusan menunjukkan agregat geopolimer abu terbang mempunyai kepekatan NaOH optimum 12 M dengan AIV 22.43 % dan nisbah optimum abu terbang/pengaktif alkali 3.0 dengan AIV sebanyak 21.43%. Untuk kesan suhu pembakaran, keputusan mendapati agregat dengan suhu pembakaran 900 °C memberikan nilai AIV terendah (14.77 %) yang menunjukkan kekuatan impak tertinggi dengan kepadatan ringan (1730 kg/m^3) dan penyerapan air terendah (4.50 %). Bagi sifat terma, agregat pada 900°C menunjukkan kekonduksian terma dan kelembapan termaju masing-masing 0.585 W / mK dan 0.358 mm^2/s. Prestasi agregat ringan geopolimer abu terbang dalam konkrit OPC telah diuji sifat-sifat mekanikal dan terma dibandingkan dengan konkrit agregat ringan komersial. Hasil konkrit dengan agregat ringan geopolimer abu terbang menunjukkan sifat yang lebih baik dengan 43.71 MPa kekuatan mampatan pada 28 hari, penyerapan air 8.36 % dan kepadatan 1735 kg/m^3 yang boleh diklasifikasikan sebagai konkrit agregat ringan struktur mengikut ACI 213R. Konkrit dengan agregat ringan geopolimer abu terbang menunjukkan sifat penebat haba yang baik degan kekonduksian terma serendah 0.28 W/mK yang menjadikannya sesuai digunakan sebagai bahan penebat haba yang baik. Kajian ini memperluaskan penemuan sumbangan mikrosfera dalam abu terbang dan kesan kandungan besi (Fe) terhadap proses pengeopolimeran disamping menghasilkan agregat geopolimer ringan dengan sifat terma yang baik dan kekuatan impak yang tinggi pada suhu pemprosesan yang rendah.

Fly Ash Based Geopolymer as Lightweight Aggregate with Low Processing Temperature for Structural Insulating Concrete Application

ABSTRACT

The lightweight aggregate in concrete has been broadly used nowadays due to its low density with great mechanical properties. These lightweight aggregates can be produced by thermal treatment from either naturally resource or from industrial by-product. However, the current production methods usually involving high energy due to high sintering temperature used despite of giving a great mechanical properties. Hence, there is a clear need of searching and replacing for more competent and proficient methods beyond the limitations of the current methods. Geopolymer becomes an attractive research due to its improving concrete properties and preserves the environment by using industrial waste such as fly ash. This research focuses on producing a fly ash geopolymer lightweight aggregate with good thermal insulation properties for structural concrete application with minimal sintering temperature by using geopolymerization methods. The effects of geopolymeric synthesis parameters such as the NaOH concentration (6 M, 8 M, 10 M, 12 M and 14 M), ratio of fly ash/alkali activator (2.0, 2.5, 3.0 and 3.5), and sintering temperature (400 °C to 1200 °C) to the fly ash geopolymer lightweight aggregate on mechanical and microstructure properties were studied. The optimum aggregate properties in term of highest impact strength with low density and water absorption then tested its thermal insulation properties through the effects of thermal conductivity, thermal diffusivity and specific heat capacity of aggregates. The results indicated that the fly ash geopolymer aggregate have an optimum NaOH concentration of 12 M with AIV of 22.43 % and an optimum ratio fly ash/alkali activator of 3.0 with AIV of 21.43 %. For the effect of sintering temperature, the results showed aggregate with sintering temperature of 900 °C gives the lowest AIV value (14.77 %) indicating highest impact strength with lightweight density (1730 kg/m^3) and lowest water absorption (4.50 %). For thermal properties, at the aggregate of 900 °C shows the lowest thermal conductivity and diffusivity of 0.585 W/mK and 0.358 mm^2/s, respectively. The performance of fly ash geopolymer lightweight aggregate in OPC concrete were tested for its mechanical and thermal properties and compared with the concrete of commercial lightweight aggregate. The results of concrete with fly ash geopolymer lightweight aggregate has shown better properties in term of strength with 43.71 MPa of compressive strength at 28 days, water absorption of 8.36 % and density of 1735 kg/m^3 which can be classified as structural lightweight aggregate concrete according to ACI 213R. Concrete with fly ash geopolymer lightweight aggregate presented good thermal insulation properties through thermal conductivity results as low as 0.28 W/mK which makes it suitable for use as a good thermal insulation material. This work expands the findings contribution of microspheres in fly ash and the effect of iron (Fe) content to the geopolymerization process as well as produces a geopolymer lightweight aggregate with good thermal properties and high impact strength at low processing temperature

CHAPTER 1 : INTRODUCTION

1.1 Research Background

Aggregate is the most commonly used material applied as a main material construction in concrete system. Aggregate occupies more than 70 % of the concrete matrix (Viveka & Ranuka, 2016). In 2015, the global demand for construction aggregates exceeded 48.3 billion tons and this value is expected to grow 5.2 % annually (Shivaprasad & Das, 2018). The tremendous growth in the infrastructural sector around the world and the large demand for aggregates in construction industry makes it a useful alternative construction material nowadays.

In order to preserve the natural resource for supplying natural aggregates, the researchers from all over the world have studied the production of artificial aggregate. The constructive development of industrial waste materials to produce artificial aggregates can be a choice for concrete production (Jagadish & Jagadeesan, 2015). This consequently results in large scale consumptions of industrial waste materials in concrete and can reduce the environmental pollution hazard. Furthermore, in Malaysia the production of fly ash is believed to be approaching two million tons annually (Putri, Hashim & Nur, 2016).

The use of lightweight aggregate has many advantages in concrete production where the light in weight of aggregate would be less expensive in transporting and handling equipment. Furthermore it will improve thermal properties by reducing the amount of heat transfer for structural and non-structural building (Iman et al., 2018).

The lightweight aggregate can be classified into two categories which are those occur naturally and ready to be used with mechanical treatment only as well as those produced by thermal treatment from either naturally resource or from industrial by-product. However, the production of lightweight artificial aggregate by thermal treatment methods has some weaknesses despite of giving great mechanical properties. These methods usually involving high energy due to high sintering temperature used, leading to high cost of production. For example, the commercialize Lightweight Expanded Clay Aggregate (LECA) is produced at very high temperatures of approximately 1300 °C (Alaa, 2018).

As an environmental friendly alternative on producing artificial lightweight aggregates is from industrial by-products waste, over the last few years, a lot of researchers conducted numerous studies in the development of new lightweight building materials. The strength and physical properties of artificial sintered aggregates produced from various industrial by products were previously investigated. The fly ash used as the lightweight material was reported to be able to enhance crushing strength with low water absorption due to the occurrence of hydration and pozzolanic reaction during the mixing (Narattha & Chaipanich, 2018). The usage of fly ash is not only because of its by-product materials, but also due to its pozzolanic activity that makes it a good choice and very useable as a fine additive in concrete system in the construction building industry. The usage of fly ash is economical despite its environmental aspects (Rawaz, Jose & Jorgede, 2018; Marcela & Nadezda, 2013) as fly ash constituting about 60 % – 80 % of total combustion residue (Abdallah et al., 2019).

Geopolymers are innovative binders that have been studied in recent years consisting of amorphous aluminosilicates that are synthesized using alkali activation of solid materials such as fly ash (Colangelo et al., 2017), calcined clay (Raphaelle & Martin, 2016; Messina et al., 2017) and blast furnace slag (Ismail et al., 2014). Lightweight geopolymer have been prepared with different lightweight aggregates (Medri et al., 2015; Zhang et al., 2015). The utilization of fly ash in geopolymer provide a concrete with high compressive strength, low shrinkage, good acid resistance and low creep (Norshahrizan et al., 2016). In this research, the fly ash is mixed with alkali activator solution to produce a fly ash geopolymer lightweight aggregate that produced an aggregate with great mechanical properties and lighter in weight.

Based on the reading from previous researches, there were several problems with available aggregate nowadays. The natural aggregate resources now is reducing and increasing of the demands of artificial lightweight aggregate in the construction industry due to the low total cost of the structure. However, there were problems with the production of lightweight aggregate which is the usage of high energy due to high temperature involves to produce a lightweight aggregate, thus will increase the production cost. Another additional issue with the lightweight aggregate is the limited source of lightweight aggregate that offers a good thermal insulation properties to be applied as an insulator aggregate in the structural concrete. Therefore, this study is conducted to produce a lightweight aggregate by using low temperature, nevertheless offer good mechanical properties and thermal properties that can be applied for structural concrete application.

1.2 Problem Statement

The issue is high demand for lightweight aggregate in the market and keep on increasing in the construction industry due to the low total cost of the structure (Payam et al., 2016). With regards to this problem, the production of an artificial lightweight aggregate from natural resources or waste product is one of the better alternatives that can be done. The production of artificial lightweight aggregate could solve the depleting usage of natural resource as an aggregate can produce a lightweight aggregate with better properties. Lightweight structural concrete provides many advantages in construction such as it has low density, low thermal conductivity, low shrinkage and high heat resistance (Watcharapong et al., 2012). At the same time, a recycling option for fly ash to remain in the economic cycle is provided through its use in new sustainable materials (Colangelo et al., 2017). The study will discover the contribution of microspheres in fly ash to the geopolymerization process to produce a lightweight aggregate which has not widely studied before.

Regarding the previous research on the lightweight aggregate, there were too many researchers producing artificial aggregate by many methods. One of the most common methods used was by using the sintering temperature which heated up the aggregate in the furnace. However, the problems with this method is the usage of high energy due to high temperature involves to produce a lightweight aggregate, normally higher than 1000 °C up 1300 °C (Ayati et al., 2019; Manu & Dinakar, 2018; Bamdad et al., 2018; Wei, Weng & Xie, 2018; Ibrahim et al., 2016). Ayati et al. (2019) in the production of lightweight aggregate from waste drill cutting has been used in sintering temperature of 1180 °C. Manu & Dinakar (2018) in the study of the influence of the type of binder on high-performance sintered fly ash lightweight concrete stated that this lightweight aggregate is produced by sintering the mixture of fly ash, clay binder and coke breeze and sintering them at a temperature between 1200 °C – 1300 °C. Bamdad et al. (2018) has produced the lightweight aggregate using clay and sintered at 1050 °C to 1250 °C in the kiln. Meanwhile, Wei, Weng & Xie (2018) studied on the reduction of sintering energy by application of calcium fluoride as flux in lightweight aggregate with the use of sintering temperature in the range of 1000 °C to 1100 °C in order to produce the aggregate. Thus, this research is focussing to produce an artificial lightweight aggregate with minimal and lowest sintering temperature compared to the past research by using geopolymerization process.

Another issue with the lightweight aggregate is the limited source of lightweight aggregate with good thermal insulation properties to be applied as an insulator aggregate in the structural concrete. From the past studies about the structural concrete with improved heat-insulation, the lightweight aggregate concrete has achieved a density of 1700 kg/m^3 and compressive strength of 30 MPa only with the thermal conductivity of 0.58 W/mK (Michael et al., 2014) while only 7.5 MPa with density ranging from 930 kg/m^3 to 1130 kg/m^3 for the study on improving thermal insulation properties for prefabricated wall components made of lightweight aggregate concrete with open structure by Marcin, (2017). Therefore, to obtain the lightweight aggregate with good thermal insulation properties for structural insulating concrete application and with minimal sintering temperature, this study is carried out by producing the lightweight aggregate from fly ash by using geopolymerization method.

1.3 Research Objectives

The aim of this research is to produce a fly ash geopolymer lightweight aggregate for structural insulating concrete application. The aggregates are produced through geopolymerization process. The details of the objectives are:

1. To determine the optimum molarity of sodium hydroxide (NaOH) and optimum ratio of fly ash/alkali activator (FA/AA) as a mix design to produce fly ash geopolymer lightweight aggregate.
2. To determine the effect of different sintering temperature on producing fly ash geopolymer lightweight aggregate based on density value.
3. To investigate the thermal properties of fly ash geopolymer lightweight aggregate as an insulator materials for structural concrete application.

1.4 Scope of Study

The focus of this study is to identify the optimum parameters that influenced the properties of fly ash geopolymer lightweight aggregate as an insulator aggregate for structural concrete application. This research is conducted with four-phase approach. The first phase of the research is to prepare and characterize the raw materials, in this case is fly ash. The characterization includes X-Ray Fluorescence (XRF), Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR).

The second phase involving the preparation of fly ash geopolymer lightweight aggregate with two different parameters which are molarity of sodium hydroxide (NaOH) and ratio of fly ash/alkali activator (FA/AA). This phase includes all the characterization of aggregate including mechanical and physical properties, microstructure and phase analysis. The best mix design has been chosen to be tested for the next phase.

For the third phase, the aggregate produced undergoes various sintering temperature to obtain the temperature where the aggregate starting to change into lightweight aggregate according to BS standard based on the densities recorded. From this phase, the samples from a range of sintering temperature have been chosen to be tested for the next phase based on the density obtained.

The final stage of this study is to test the performance of fly ash geopolymer lightweight aggregate as an insulator material for structural concrete application. At first, the aggregate itself were tested for its thermal insulation properties before applied to an OPC concrete. This concrete were then tested for its thermal insulation and mechanical properties and were compared with commercial lightweight aggregate.

1.5 Thesis Outline

In this research, the thesis is divided into five chapters. Chapter 1 introduces the research background, problem statement, research objectives, scope of study and the thesis outline.

In Chapter 2 of this thesis reviews the past literatures and researches regarding lightweight aggregate, geopolymerization process, factors affecting the properties of geopolymer, properties of lightweight aggregate, and reviews about the application of insulator aggregate for thermal insulation application in concrete field.

Chapter 3 elaborates in details the experimental procedures in producing the fly ash geopolymer lightweight aggregate including the material used, the characterization involved and the testing that has been applied. This chapter also discusses about the mix design, the mixing process, palletizing process and sintering process.

Chapter 4 presenting the test results and discussing on the findings from the experiment conducted. The materials characterization, the effect of NaOH molarity and ratio of fly ash/alkali activator, the effect of sintering temperature to the properties of aggregate are discussed in this chapter. The next chapter presenting the comparison the performance of fly ash geopolymer lightweight aggregate with commercial lightweight aggregate in term of thermal insulation properties for structural concrete application.

Chapter 5 for this thesis is to justify and summarize the findings of this study. Some recommendations for future work are also included in this chapter. The thesis ends with a References List and several Appendices.

CHAPTER 2 : LITERATURE REVIEW

2.1 Introduction

In the production of concrete and mortar, aggregate is the main constituent in term of volume. Nowadays, the requirement for better concrete performance such as high in strength and toughness and light in weight are very demanding due to rapid development of a very tall buildings, larger-sized building and a long span concrete structures. The lightweight concrete has been used for structural purpose for several years (Kayali, Haque & Zhu, 2003; Balendran et al., 2002). From the skyscrapers and huge dams around the world, aggregate is an important part of the concrete structures.

Recently, the research and development in the production of artificial aggregate is increasing as an alternative materials to the natural aggregate such as quartz, basalt, granite, sandstone and limestone. Despite the fact that Ordinary Portland Cement (OPC) is an important component for the artificial aggregate, there are too many environmental problems are associated with the process of the production of OPC. As the population increased, the worldwide consumption of OPC increases and the requirement to new structures is increased (Majid, Weena & Warna, 2014). McLellan et al. (2011) estimated that 44 % to 64 % of greenhouse gas emission caused by OPC can be reduced by replacing it with geopolymer based products. Countable effort had been taken to study on replacing OPC based artificial aggregate with geopolymer source materials.

Awareness needs to be increased towards excessive exploitation of natural aggregate requirement as it is diminishing with population growth and can be replaced with sources from industrial waste known as artificial lightweight aggregate. Lightweight aggregates are more porous compared to natural aggregate (Mahdy, 2016). Generally, concrete produce with more porous aggregate shows low strength and durability. Therefore, several research has been done to the artificial lightweight aggregate to enhance the quality of lightweight aggregate to produce a better properties of concrete. Several past research suggesting to produce artificial lightweight aggregate through thermal treatment which is by sintering technique (Alaa, 2018; Manu & Dinakar, 2018; Tommy et al., 2016). However, the production of lightweight artificial aggregate by sintering technique methods have some weakness despite of giving a great mechanical properties such as the requirement of high energy due to high sintering temperature used, up to 1300 °C (Alaa, 2018).

2.2 Geopolymer

Davidovits in 1970s first introduced geopolymer in France as an alternative cementitious materials. Geopolymer is manufactured by mixing source materials which are rich in silica and alumina with strong alkali solutions. The most commonly sources materials used is fly ash while alkali solutions are sodium hydroxide (NaOH), potassium hydroxide (KOH) and soluble silicates such as sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3). According to Hardjito et al. (2004) geopolymer synthesizing technology is based on the alkali activation of the source material contains mostly silicon (Si) and Aluminium (Al) in their amorphous form.

The dissolved aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) species in source material formed a three-dimensional aluminosilicate network during the geopolymerization process. According to Robina & Ankush (2015), a similar or higher strength produced from this network as compared to the strength from OPC concrete. Provis & Bernal (2014) define the geopolymer as Alkali-acivated materials (AAM) which gives the same meaning for material formed by the reaction between an aluminosilicate precursor and an alkali activator, where the properties of AAM product is comparable to traditional cement binder.

2.3 Geopolymer Constituent

In the geopolymerization process, there are two main components for the production of geopolymer. The first component is source materials and the second component is alkali activator. The sources materials for geopolymer are normally from an aluminosilicate materials that have geological origins such as clay, fly ash, ground granulated blast slag (GGBS) and kaolin (Davidovits, 2005). Whereas for alkali activator solution, it is normally from (sodium hydroxide solution and sodium silicate solution) (Wongsa et al., 2016).

2.3.1 Source Material (Fly Ash)

The sources materials in the geopolymerization process commonly consist of silicon (Si) and almininum (Al) minerals. There are many types of aluminosilicate precursors than can be considered to be used as geopolymer sources materials including natural raw materials and industrial by products. Fundamentally, any silica and alumina containing mineral can be used as precursor for geopolymer synthesis (Nath & Sanjay, 2019).

As for the concern towards producing a lightweight artificial aggregate for the usage in the lightweight concrete, more research need to be discover in order to find the suitable materials that can fulfil the requirement to achieve a lightweight properties with better mechanical and thermal properties. Geopolymer aggregate should have a source of materials consist high content of silicon (Si) and aluminum (Al). In the construction industry, the production of artificial lightweight aggregate by using fly ash has large potential for utilization and attract a better consideration over the world (Gomathi & Sivakumar, 2012).

Fly ash is a by-product materials of coal burning industry or power generation plant and is typically spherical shape and finer than the particle of Portland cement dust. Fly ash is defined by the finely divided residue that results from the combustion of ground or powdered coal and that is transported by flue gasses from the combustion zone to the particle removal system by American Concrete Institute, ACI Committee 232 (2004). American Society for Testing and Materials, ASTM C 618 (2012) stated that fly ash is classified into three types namely class F fly ash, class C fly ash and class N fly ash. Table 2.1 presented the chemical composition requirement for fly ash class N, class F and class C.

Table 2.1 Chemical composition for classification of fly ash class N, class F and class C (ASTM standard C 618, 2012)

Composition	**Class N**	**Class F**	**Class C**
Silicon oxide + aluminum oxide +iron oxide (min %)	70.0	70.0	50.0
Sulfur trioxide (max %)	4.0	5.0	5.0
Moisture content (max %)	3.0	3.0	3.0
Loss On Ignition (max %)	10.0	6.0	6.0

The class N fly ash is from the raw or calcined natural pozzolan while Class F and Class C fly ash are from the combustion process in power station where Class F fly ash is the product bituminous coal or anthracite burning and Class C fly ash is from the product of burning sub bituminous coal or lignite. Class F and class C fly ashes are regularly used as cement partial replacement materials due to its pozzolanic characteristics.

The difference between class F and class C fly ashes is the content of Calcium (Ca). The fly ash is classified as Class F fly ash if the Ca content less than 10 %, whereas Ca content in class C fly ash is higher than 10 % (Temuujin et al., 2019). Fly ash chemical composition is mainly of silicon oxides, aluminum, iron and calcium where there are also magnesium, potassium, titanium, and sulfur in lesser quantities (Belz & Caramuscio, 2004).

According to Ahmaruzzaman (2010) fly ash generally used to enhance the mechanical and durability properties in the construction industry. The fly ash generally able to be a good replacement for the use of cement as a binder in concrete because of its appearance which is almost similar to cement particle. There are abundant of fly ash produced around the world and dumped in landfills. Before the geopolymer was introduced, fly ash is considered as the waste material and not being recycled or reused. By utilizing fly ash in geopolymeric application especially in concrete production, it can produce significant environmental benefits. Fly ash used in geopolymer concrete or as a binder or aggregate will improve concrete durability, reduced energy use, conservation of natural resources and economical effect (Kayali, 2008).

On the other hand, Fenghon et al. (2018) in the studies for mechanical and thermal properties of fly ash based geopolymers had chosen fly ash Class F as the source materials due to its large quantity of SiO_2 and Al_2O_3 to synthesize the geopolymers. The results presented that the geopolymer can achieve a compressive strength up to 100 MPa. The use of class F fly ash in concrete contributed to an excellent mechanical properties. A research reported that by replacing cement with fly ash for testing up to 275 days proven that it is highly effective in inhibiting alkali-silica reaction (Ahmaruzzaman, 2010).

2.3.2 Alkali Activator Solution

In order to synthesize silica and alumina content in the source materials during the geopolymerization process, a strong alkali medium solution is needed. Alkali activation can be described as a chemical reaction process where a powdery or solid aluminosilicate materials such as fly ash is mixed with alkali activator solution to produce a paste at a reasonable short period of time. The chemical reaction that comprises of a significant change for some types of structures either fully or partially amorphous to cement and solid framework (Fernandez-Jimenez & Palomo, 2003).

Normally from the previous research, alkali activator solution used may consist o the combination of NaOH or KOH with Na_2SiO_3 or K_2SiO_3 (Mustafa et al., 2012). This is because these materials are usually cheap in price and easily available in the market. The common used of NaOH, KOH, Na_2SiO_3 and K_2SiO_3 are discovered by many previous researchers such as (Davidovits, 2015; Provis & Bernal, 2014).

The most frequently used as activator in the geopolymer mixture is NaOH because it is most widely available with the cheapest price. The silicate monomers that are present in the NaOH solution can be stabilize by the smaller size of Na^+ in the solution hence promoting an increase in the mineral dissolution rates as reported by Liew et al., (2016). However, if it is necessary to use the optimum amount of NaOH to produce a large amount of hydroxide to produce a geopolymer product considering of the nature of concentrated NaOH is highly corrosive. This is the reason Provis & Deventer (2009) suggested the combination with silicate activation.

Ghasan et al. (2017) stated that the use of Na_2SiO_3 in geopolymerization resulted in additional silicate in the system and this has led to an increase in the compressive strength. However, when only Na_2SiO_3 was used as an alkali activator, it was noted that the geopolymer exhibited a lower mechanical properties. This statement is supported by finding from Gorhan & Kurklu (2014) in which reported that the compressive strength of the geopolymer materials is higher when NaOH is used together with Na_2SiO_3 compared to using NaOH itself. Many researchers agreed that the most common alkali activator used to produce geopolymer is the combination of NaOH or KOH based and Na_2SiO_3 or K_2SiO_3 (Hardjito et al., 2004; Davidovits, 1999; Palomo, Grutzeck & Blanco, 1999).

Rattanasak & Chindaprasirt, (2009) reported that during the synthesis of geopolymer, the concentration of NaOH can be affected the dissolution of Si and Al where higher concentration of NaOH lead to better compressive strength by increasing dissolution rate of silica and aluminum (Xu & van Deventer, 2000). A study carried out by Mustafa et al. (2011) has concluded that geopolymer using 12 M of NaOH concentration gives the highest compressive strength compared to the geopolymer using NaOH concentration of 14 M and 16 M.

In the study by Herwani et al. (2018) for fly ash based geopolymer concrete has indicated that the increase of NaOH leads to improve the compressive strength where the optimal concentration of NaOH is depicted at 12 M. The study reported that geopolymer with 12 M of NaOH has achieved an optimum compressive strength compared to geopolymer with 10 M and 14 M of NaOH concentration. This result in agreement with finding from Palomo, Grutzeck & Blanco (1999) which stated that a 12 M NaOH molarity produced better outcomes than 18 M concentration.

A contradict result was reported by the study of Rattanasak & Chindaprasirt (2009) which determined that when the concentration of NaOH at 10 M is used, the strength of geopolymer mortar can achieve up to 70 MPa. Livi (2017) also found the different results in the study of NaOH concentration effect and curing regime geopolymer where the highest strength was obtained with the 16 M NaOH solution. In this study, a lower amount of NaOH solution shows no significant differences between the strength results. Other than that, Bakkali, Ammari & Frar (2016) had found that by preparing the sample with 14 M of NaOH molarity in the study by using Morrocon fly ash (ASTM class F) can achieve 30 MPa of compressive strength. However, even though the excessive of alkali NaOH concentration may lead to increase the dissolution of Si and Al of precursor materials, it may also reduce the mechanical strength due to quick formation of alumina-silicates gel at early stages and lead to precipitation as reported by Lee & Van Deventer (2002).

2.4 Geopolymerization Process

Geopolymerization process can be describe as a geosynthesis in which reaction that chemically integrates minerals that involves naturally occurring silico-aluminates (Khale & Chaudhary, 2007). Any pozzolanic source containing of silica and alumina, that is readily dissolved in the alkali solution, acts as a source of geopolymer precursor species thus lend itself to geopolymerization (Xu &Van Deventer, 2000). Davidovits (2005) reported that the geopolymerization process induce empirical formula as shown in Equation 2.1.

$$M_n[-(SiO_2)_z-AlO2]_n.wH_2O \quad (2.1)$$

Where:

M is cation (K, Na, Ca)

n is polycondensation degree and z is 1, 2, 3, or >3.

This frameworks of geopolymerization process are described as polysialate, where sialate is the silicon-oxo-aluminate building unit. Sialate composed of SiO_4 and AlO_4 tetrahedras linked by sharing all oxygen atom (Davidovits, 2005). The presence of positive ions (Na^+, K^+, Ca^{2+}) is to balance the negative charge of Al in 4-fold coordination. Formation of chains and rings which cross-linked to each other is through the Si-O-Al bridge (Davidovits, 2005).

Generally, the mechanism of geopolymerization can be divided into three main stages: (1) Dissolution of oxide minerals from the source materials (usually silica and alumina) under highly alkaline condition; (2) transportation/orientation of dissolved oxide minerals, followed by coagulation/gelation; (3) polycondensation to form 3D network of silico-aluminates structures. Based on the types of resultant chemical bonding, three types of structures can be derived from the 3D aluminosilicate network: poly(sialate) (–Si–O–Al–O–), poly(sialate-siloxo) (Si–O–Al–O–Si–O) and poly(sialate-disiloxo) (Si–O–Al–O–Si–O–Si–O–) (Part, Ramli & Cheah, 2015).

Figure 2.1 shows the geopolymerization process where the chemical reaction of Si-Al mineral in alkali condition. The geopolymer structure consist of cross-linked, SiO_4 and AlO_4^- tetrahedral species which the negative charge on Al^{3+} is balanced by the positive charges of the alkali ions (Na^+, K^+) from alkaline activator to form aluminosilicate structure. The polycondensation process occurred upon heating to form the geopolymer structures. Geopolymers with the structure of poly(sialate-siloxo) and poly(sialate-disiloxo) are more stable and stronger than poly(sialate) structures (Duxson, Lukey & Van Deventer, 2007).

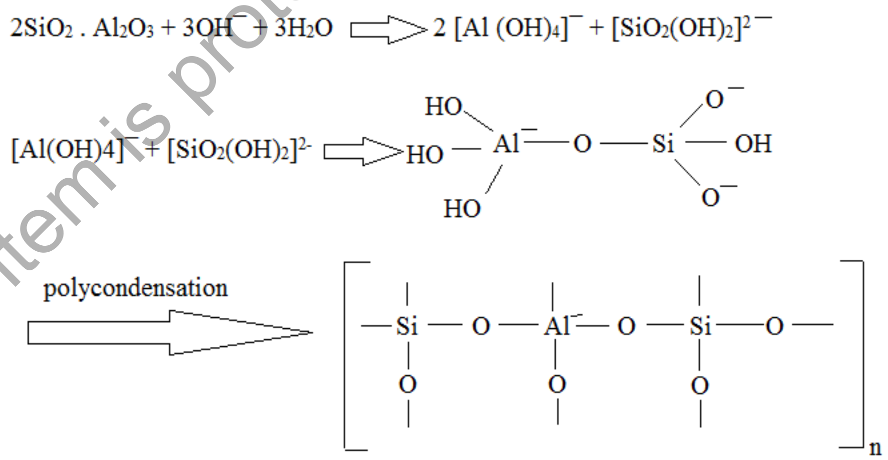

Figure 2.1 Geopolymerization reaction (Duxson, Lukey & Van Deventer, 2007).

Figure 2.2 shows the reaction mechanism of geopolymerization process which involves a number of processes including dissolution, reorientation, and solidification.

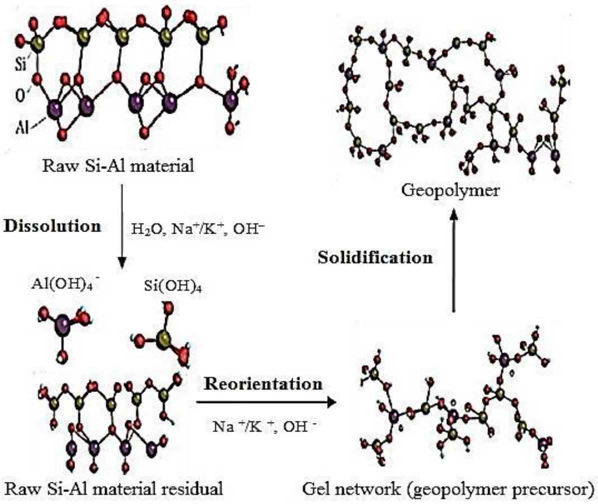

Figure 2.2 Reaction mechanism of geopolymerization (Duxson, Lukey & Van Deventer, 2007).

The dissolution process is the first stage in the geopolymerization process where the process occur as raw materials of Si-Al is in contact with alkali solution (Na^+ or K^+) and causes the breaking of the aluminosilicate bond. The alkali dissolution of solid aluminate precursor will generate the aluminate and silicate tetrahedral monomers (Satpathy, Patel & Nayak, 2019). The dissolution process releases both silicon (Si) and aluminum (Al) species which will react to produce the sialate chain. These Si and Al content in the source materials plays an important role to the performance of geopolymer as in this dissolution stage, the negative charge in the aluminosilicate chain is balanced by alkali cations such as sodium, potassium or calcium (Zhuang et al., 2016).

The second stage of geopolymerization process is the reorientation stage where the monomers of Si and Al creating the oligomers. This will lead to the dissolution of more precursor materials so that the solution is saturated with a complex mixture of silicate (Si^{4+}), aluminate (Al^{3+}), and aluminosilicates species and then polymerize into an amorphous gel (Satpathy, Patel & Nayak, 2019). The formation from oligomers to the amorphous phase has formed many networks by condensation to gel formation, filtration of reactive Al and Si species from the raw materials is happening at Al^{+3} and Si^{+4} dissolving on the surface of source Si-Al materials are removed. Thus, the alkali cations is two fold of the Si^{4+} and Al^{3+} cations in geopolymer gels that are tetrahedrally coordinated as $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ and are linked by oxygen bonds (Wei, Weng & Xie, 2018).

The factors affecting reorientation are time and the intensity of stirring where the dissolved Si and Al species can maximally remove from the surface of materials by a longer leaching period with more intense stirring. The barrier between the gel phase and the Si-Al particle surface, hence will be broken and allowed to accelerate to the reorientation of Si and Al. The solidification stage involves the formation of continuous gel (Wei, Weng & Xie, 2018). In this stage, as the connectivity of the gel network increases, the gelation system continues to rearrange. This will produce three-dimensional aluminosilicate network in amorphous or semi-crystalline form which is attributed to the geopolymer (Duxson, Lukey & Van Deventer, 2007).

2.4.1 Application of Geopolymer

The geopolymer technology provides a new good and green solution to the utilization of various source materials, avoiding its negative impact on environment and ecology. The alumina and silica in natural or industrial based source materials can be activated with alkali to form geopolymer. The founder of geopolymer, Davidovits (1999) has proposed the geopolymer potential application according on the molar ratio of Si to Al as showed in Table 2.2.

Table 2.2 Applications of geopolymer based on Si: Al ratio (Davidovits, 1999)

Si:Al	**Applications**
1:1	Bricks, ceramics and fire protection
2:1	Low CO_2 cements and concrete, radioactive and toxic waste encapsulation
3:1	Foundry equipment, fibre glass composites and heat resistant composites
>3:1	Sealants for industry
20:1<Si: Al<35:1	Fire resistance and heat resistance fibre composites

Generally, the application of geopolymer technology nowadays is because of the awareness to produce and discover new materials that can solve environment issues. Hence, the usage of geopolymer technology is an alternative way to prevent the environment by reducing the emission of CO_2. The previous researchers had also discovered the properties of geopolymer product such as follow (Guo et al., 2010):

- High early strength
- Low thermal conductivity
- Low alkali-aggregate expansion
- Low permeability and low shrinkage
- Resistance to acid and chemical attack
- Cost saving

Therefore, by referring to the wide application of geopolymer, it can be an alternative for the researchers to discover a new technology in the production of certain products with the required properties needed.

2.5 Characterization of Fly Ash Geopolymer Aggregate

With the aim to determine the final properties of the geopolymer matrix, the characterization of fly ash used during the synthesis of geopolymer need to be characterized. It is an important stage towards determining the suitability to be used as geopolymer materials.

2.5.1 Chemical Composition Properties

In general, the components of fly ash are predominantly composed of SiO_2, Al_2O_3, Fe_2O_3 and CaO, which exists in the form of amorphous and crystalline oxides or various minerals. The chemical composition of fly ash can be affected by many factors which are mainly contributed by the sources of the coal (geological origin) being burned such as anthracite, bituminous, sub-bituminous, and lignite.

Some of the chemical composition of fly ash by several sources from previous researches is presented at Table 2.3 which shows that the main constituent in fly ash is dominated by SiO_2 and Al_2O_3. The geopolymerization requires a precursor that contains a significant amount of Si and Al held in the amorphous phase (Nath & Sanjay, 2019; Fenghon, 2018; Ahmaruzzaman, 2010; Davidovits, 1993). Hence, from the chemical composition properties of fly ash, it shows that fly ash has a huge potential as the source materials for geopolymer.

Numerous previous researches have concluded that the geopolymer depends primarily on the ratio of Si/Al (Davidovits, 1999; Duxson, Lukey & Van Deventer, 2007). It has been observed that the percentage of alumina-silicates oxides has been predominantly influenced the strength of geopolymer. However, the lesser amount of oxides such as Fe_2O_3 and CaO also influenced the strength build up to the properties of the geopolymer materials (Reddy, Dinakar & Rao, 2016). Lemougna et al. (2013) concluded that a high content of iron in source material can be used for alkali activation where the presence of Fe_2O_3 gives a good effect. During the geopolymerization process, Fe^{3+} ions will be substituting the Al^{3+} ions in the solution.

Table 2.3 Chemical composition of fly ash from previous research.

Fly Ash	**Main mineral oxides (%)**				
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**Location**
Gunasekara et al. (2019)	52.67	29.60	11.27	0.64	Collie power plant, Australia
Alehyen, Achouri & Taibi (2017)	52.5	30.2	2.94	0.822	Jorf Lasfar Plant, Morrocan.
Fauzi et al., (2016)	55.23	25.95	10.17	1.32	Electric generating plant in Paka, Terengganu, Malaysia.
Huidong et al. (2016)	48.27	21.59	14.09	5.72	Luohuang Power Plant, Chongqing, Southwestern China
Khairul Nizar et al. (2014)	52.11	23.59	7.39	2.61	Sultan Abdul Aziz Power Station, Kapar, Selangor.

A study by Reddy, Dinakar & Rao (2016) has found out that the strength of concretes has been improved with the addition of Fe_2O_3 nanoparticles up to 4.0 % to act as foreign nucleation site and nanofillers recovering the pore structure of the specimens and accelerating the C-S-H gel formation. This is an agreement with Lemoughna et al. (2013). Meanwhile, Khoshakhlagh et al. (2012) stated that the high iron content in volcanic ashes (up to 12 wt% to 14 wt%) was not contributed for the strength development of geopolymer, but it was concentrated to the crystalline phases. The production of geopolymer with a high amount of iron (>30 wt%) donates to the low mechanical properties at an earlier stage of geopolymerization. Geopolymers with 100 % of iron content cannot achieve the complete solidification even after a year of curing as reported by Wagh & Douse (1991).

Chindaprasirt et al. (2012) stated that as the CaO content in the source materials is increase, the compressive strength of geopolymer concretes also increased. This is an agreement with Wongpa et al. (2010). However, according to Duxson & Provis (2008) it was found that the increasing of CaO content in geopolymer would hugely affect the setting times of geopolymer concrete. This statement also supported by Oh et al. (2010) by reporting that faster setting time can be obtained if the geopolymer is made with fly ash with high CaO content compared to geopolymer made with fly ash class F which has much lower CaO content.

2.5.2 Morphology Properties

The microstructures of the fly ash normally consisted mostly of glassy, hollow, and spherical particles with various sizes. Fly ash represents commonly spherical particles with less than 100 micron in size with properties depending on its chemical composition (Temuujin et al. 2019). Figure 2.3 shows the microstructure image of fly ash obtained by utilizing Scanning Electron Microscope (SEM) for original fly ash particle and the SEM image of fly ash particle after activated at 85 °C for 5h with 8 M of NaOH solution.