THE EFFECT OF LIMESTONE AGGREGATE ON THE PROPERTIES OF FLY ASH BASED GEOPOLYMER CONCRETE

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ABSTRACT

The uses of Portland cement give disadvantages to the nature which is by releasing carbon dioxide gas to the air. This situation can cause global warming at the same time contribute to the green house effect. Besides, the production of Portland cement causes depletion of raw material. In order to solve this problem, the fly ash based geopolymer concrete was produced. This research is focus on the effect of limestone aggregate on the properties of fly ash based geopolymer concrete. The research was done to obtain the optimum proportion of limestone aggregate in fly ash based geopolymer concrete, to determine the effect of limestone aggregate on the characteristic of fresh fly ash based geopolymer concrete and to determine the compressive strength of fly ash based geopolymer concrete with limestone aggregate inclusion. The effect of limestone aggregate as a granite aggregate replacement in geopolymer concrete were investigated 60 numbers of cube dimension 100mm x 100mm x 100mm with two difference condition which is $60^{o}c$ oven and ambient curing for compression test, and 20 numbers of small cube dimension 50mm x 40mm x 80mm for porosity test were prepared. There are five difference mix design which is 0%, 25%, 50%, 75%, and 100%. The specimens were tested at the age of 1, 7, and 28 day for compressive strength while for porosity test was at day 28. The slump test for sample 0%, 25%, 50%, 75%, and 100% were 190mm, 205mm, 190mm, 196mm, and 190mm are respectively and all mix sample obtain was collapse slump. Concrete setting time for sample 0%, 25%, 50%, 75%, and 100% was 45 minute, 36 minute, 35 minute, 33 minute, and 25 minute are respectively. The optimum proportion of limestone aggregate in fly ash base geopolymer concrete is 25% for both $60^{o}c$ oven and ambient curing. The compressive strength at day 28 of sample 0%, 25%, 50%, 75%, and 100% for ambient curing was 19.3Mpa, 26.1Mpa, 23.07Mpa, 22.03Mpa, and 17.33Mpa respectively while for 60oc oven curing was 32.02Mpa, 32.77Mpa, 30.94Mpa, 24.46Mpa, and 21.69Mpa respectively.

ABSTRAK

Penggunaan simen Portland membawa banyak keburukan kepada persekitaran di mana gas karbon dioksida di bebaskan ke uadara. Keadaan ini boleh menyebabkan pemanasan global dan pada masa yang sama menyebabkan kesan rumah hijau. Selain daripada itu, penghasilan simen Portland menyebabkan kehabisan bahan mentah. Bagi menyelesaikan masalah ini, konkrit geopolimer berasaskan abu terbang dihasilkan. Kajian ini lebih diberi tumpuan kepada kesan agregat batu kapur terhadap sifat konkrit geopolimer berasaskan abu terbang. Kajian ini dilakukan untuk mendapatkan kadar yang optimum agregat batu kapur di dalam konkrit geopolimer berasaskan abu terbang, untuk menentukan kesan agregat batu kapur terhadap ciri-ciri konkrit geopolimer basah, dan untuk menentukan kekuatan mampatan konkrit geopolimer berasaskan abu terbang yang mengandungi agregat batu kapur. Kesan agregat batu kapur sebagai pengganti agregat granit di dalam konkrit geopolimer di siasat sebanyak 60 kiub yang berukuran 100mm x 100mm x 100mm dengan dua keadaan yang berbeza iaitu pengawetan di dalam ketuhar 60^{o}c dan pengawetan ambien untuk ujian mampatan manakala 20 kiub kecil berukuran 50mm x 40mm x 80mm untuk ujian keliangan telah disediakan. Terdapat lima perbezaan reka bentuk campuran iaitu 0%, 25%, 50%, 75%, dan 100%. Spesimen diuji pada hari ke 1, 7, dan 28 untuk kekuatan mampatan manakala untuk ujian keliangan pada hari ke 28. Ujian keruntuhan bagi sampel 0%, 25%, 50%, 75%, dan 100% adalah 190mm, 205mm, 190mm, 196mm, dan 190mm dan semua sampel campuran yang terhasil adalah keruntuhan sebenar. Masa tetapan konkrit bagi sampel 0%, 25%, 50%, 75%, dan 100% adalah 45 minit, 36 minit, 35 minit, 33 minit, dan 25 minit. Nisbah optimum agregat batu kapur di dalam konkrit geopolimer berasaskan abu terbang adalah 25% untuk pengawetan di dalam ketuhar 60^{o}c dan juga pengawetan ambien. Kekuatan mampatan pada hari yang ke 28 bagi sampel 0%, 25%, 50%, 75%, dan 100% untuk pengawetan ambien adalah 19.3Mpa, 26.1Mpa, 23.07Mpa, 22.03Mpa, dan 17.33Mpa manakala bagi pengawetan ketuhar 60^{o}c adalah 32.02Mpa, 32.77Mpa, 30.94Mpa, 24.46Mpa, dan 21.69Mpa.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

BS	=	British Standard
ASTM	=	American Society for Testing and Materials
MPa	=	Mega Pascal
^{o}C	=	Celsius
g	=	Gram
Kg/m^3	=	Kilogram per meter
mm	=	Millimeter
OPC	=	Ordinary Portland Cement
NaOH	=	Sodium Hydroxide
Na_2SiO_3	=	Sodium Silicate
CO_2	=	Carbon dioxide
CaO	=	Lime
Si	=	Silicon
Al	=	Aluminium
KOH	=	Potassium hydroxide
M	=	Molarity
MS	=	Malaysian standard

CHAPTER 1

INTRODUCTION

1.1 Background of study

In construction, concrete is the most important thing or material that has been used since a long time ago. The main component in concrete is Portland cement. In Malaysia, the demand of Portland cement for the construction industry is increase rapidly. This indirectly cause the producing of Portland cement is increasing. Unfortunately, there are a lot of disadvantage in Portland cement. The production of Portland cement can cause global warming which is can contribute to green house effect. This is happen because of the carbon dioxide (CO_2) gas that is emitting from the process of production of cement. The production of one ton of cement release about one ton of CO_2 gas into the air (Roy, 1999). The production of cement is increase from about 1.5 billion ton in1995 to 2.2 billion ton in 2010. (Malhotra, 1999). Furthermore, Portland cement is environmentally expensive.

This problem has become a major concern. In order to overcome this problem, there is other alternative way that can be done. Instead of using Portland cement, the effective solution for this problem is by using geopolymer concrete. Geopolymer is a new binder that is used in concrete to replace the cement role in concrete construction. In 1999, Davidovits said that geopolymer is the new material for coating and adhesive, new cement for concrete and it is a new binder that is use for fiber composite. Fly ash based geopolymer concrete consist of alkaline solution and raw material. In this study, the alkaline solution that is use is sodium hydroxide and sodium silicate while the raw material is fly ash, fine aggregate, and coarse aggregate which consist of granite and limestone. There are a lot of advantages by using fly ash based geopolymer concrete which is eco friendly, can reduce cost and also reduce the CO_2 gas. Geopolymer is a reaction process of alkaline solution with silicon and aluminium in fly ash which is produces an aluminosilicate based binder. The process of geopolymer is called geopolymerization.

In this project, it is a study of the effect of limestone aggregate on the properties of fly ash based geopolymer concrete. Limestone is one of the aggregate to be use in geopolymer concrete. It is a sedimentary rock that has flaky and elongated shape. Furthermore, limestone consists of calcium carbonate with the percentage of 38 to 42 percent of lime (CaO).

1.2 Problem statement

In Malaysia, the study of geopolymer concrete is in new version and not develops well. In this research, the material that is use is limestone aggregate in order to know the effect of geopolymer concrete. This is because, fly ash based geopolymer binder is very responsive to the presence of calcium in the system. The limestone aggregate is use because of it high percentage value of calcium. Study the effect of high calcium in limestone aggregate to the fly ash based geopolymer concrete performance is essential.

1.3 Objective of study

In this study there are three main objectives which are as follows:

i. To obtain the optimum proportion of limestone aggregate in fly ash based geopolymer concrete.

ii. To determine the effect of limestone aggregate on the characteristic of fresh fly ash based geopolymer concrete.

iii. To determine the compressive strength of fly ash based geopolymer concrete with limestone aggregate inclusion.

1.4 Scope of study

This study is basically are focus on the effect of limestone on the properties of fly ash based geopolymer concrete. The mix proportion percentage between limestone aggregate and granite aggregate is 0%, 25%, 50%, 75%, and also 100%. There are two types of aggregate that is use which is limestone and granite aggregate. The limestone aggregate is replaced with granite aggregate with the percentage of 0%, 25%, 50%, 75%, and 100%. The limestone aggregate is obtained from Bukit Sagu, Kuantan. The fine aggregate that is use is sand. Class F fly ash is obtained from Manjung power station, Perak.

This research is done in order to observe the effect of limestone aggregate on the characteristic of fresh fly ash based geopolymer concrete. This is done by doing the setting time test. The workability test that was done is slump test. Other than that, to obtain the optimum proportion of limestone aggregate in fly ash based geopolymer concrete. This can be known by which percentage of mix proportion that contributes to highest value of stress. Furthermore, this research is done to determine the compressive strength of fly ash based geopolymer concrete with limestone aggregate inclusion. The geopolymer concrete is exposing with two different types of condition which is ambient curing and oven curing. The oven curing is set to 60^{o}c.

The early stage is a mixture of geopolymer concrete is done without any limestone aggregate or also known as control subject. Each mix proportion which is consisting of two cube of geopolymer concrete for two different curing is prepared for testing. The compression testing is done on day 1, 7, and 28 while for porosity test is done at day 28. The specimen size for compression test is 100mm x 100mm x 100mm. The specimen size for porosity test is 50mm x 40mm x 80mm. The concrete strength data of the geopolymer concrete cube can be obtained from the compressive test.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Nowadays, the amount of CO_2 gas is increasing and the production of one ton of cement can produce about one ton of CO_2 gas to the air (Roy, 1999). In order to overcome this problem, the use of cement can be replaced with geopolymer. The studies conducted in this literature review are the properties of fly ash based geopolymer concrete. Fly ash based geopolymer concrete consist of alkaline solution and raw material. In this study, the alkaline solution that is use is sodium hydroxide and sodium silicate while the raw material is fly ash, fine aggregate, and coarse aggregate which consist of granite and limestone.

2.2 Geopolymer.

Geopolymer is a new binder that is use in concrete which is replacing the cement. It is the new material for coating and adhesive, new cement for concrete and it is a new binder that is used for fiber composite. (Davidovits, 1999). In the construction industry, geopolymer materials indicate an inventive technology that is generating significant interest. Davidovits stated that there are hundreds of papers and patents were published dealing with geopolymer science and technology which is from the first industrial research efforts at the Cordi-Gĕopolymĕre private research laboratory, Saint-Quentin, France. In geopolymer, there are nine different groups and the most prospective use is aluminosilicate materials that may be used to completely replace Ordinary Portland Cement (OPC) in concrete construction (Davidovits, 1999).

Geopolymers are inorganic polymeric materials that have a chemical composition same to zeolites but prossesing an amorphous structure (H.W.Nugteren, 2008) . It can be produced by reacting solid alumino silicates with an alkali hydroxide or silicate solution. Geopolymer is the reaction.process of alkaline solution with silicon and aluminium (Duxson, 2006).

In polymerization process, it involves a significantly quick chemical reaction under alkaline condition on Si-Al minerals, which result in a three dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. Si-O-Al-O is also known as poly(sialate). Geopolymers are also referred to as alkali-activated alumino-slilicate binders and it is containing four classes of inorganic polymers that, depending on the ratio of silica to alumina (silica/alumina) which is based on the following four different monomeric units which is polysialate, polysialatesiloxo, and polysialatedisiloxo and sialate link. Davidovits said that sialate is a shorten form for alkali silicon-oxo-aluminate and sialate molecular structure consist of four element units which is classified base on the Si:Al atomic ratio: (Davidovits, 1999)

Si:Al = 1, sialate,
Si:Al = 2, sialate-siloxo
Si:Al = 3, sialate-disiloxo
Si:Al > 3, sialate link

(a) Si:Al = 1, sialate, poly(sialate)

(-Si-O-Al-O-) is the chain that is the consequence of the polycondensation of the monomer ortho-sialate.

(b) Si:Al = 2, sialate-siloxo, poly(sialate-siloxo)

(-Si-O-Al-O-Si-O-) is a consequence of orthosialate with ortho-silicic acid Si(OH)4. A linear (-Si-O-Si-O-Al-O-), mono-siloxo-sialate and 3 cycles is a three type that consist in isomorphs.

(c) Si:Al = 3, sialate-disiloxo, poly(sialate-disiloxo)

(-Si-O-Al-O-Si-O-Si-O) is a consequence of orthosialate with two ortho-silicic Si(OH)4. There are six type of isomorphs which is 2 linear, 2 branched and 2 cylces.

(d) Si:Al > 3, sialate link, poly(sialate-multisiloxo)

It designates the bridge Si-O-Al between two poly(siloxonate), poly(silanol) or poly(sialate) chains.

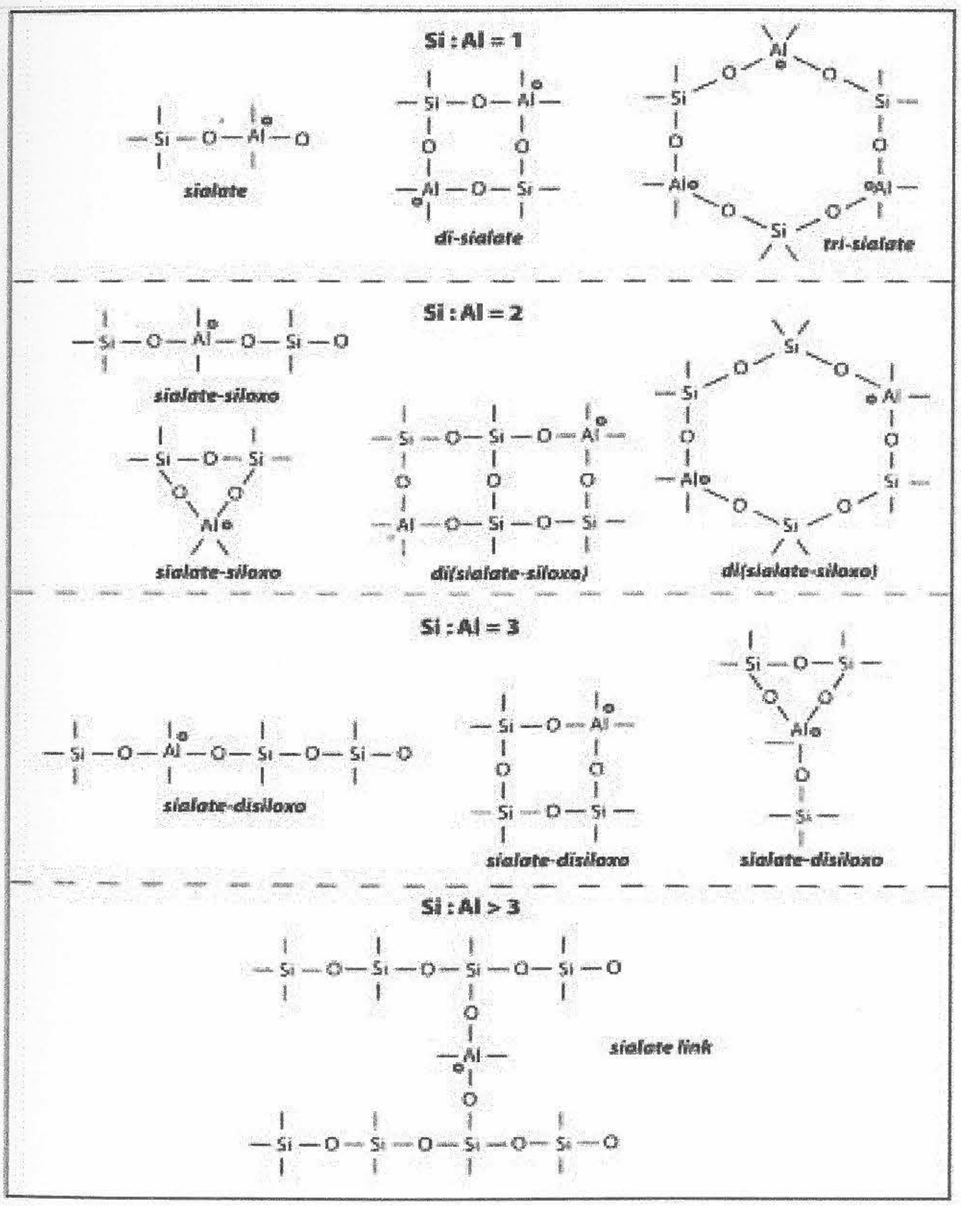

Figure 2.1 Sialate molecular structures (Davidovits, 1999)

In this research, the alkaline solution that is use is sodium hydroxide and sodium silicate while the silicon and aluminium element is in the fly ash. In fly ash based geopolymer concrete, the source material that consists of alumina and silica make by alkaline solution to produce aluminosilicate gel (Mohd Mustafa Al Bakri, 2010). The reaction of this can form a binder which is aluminosilicate gel. This gel binds with the fine aggregate, coarse aggregate and other un-reacted materials in mixture to form the geopolymer concrete (Wallah, 2009). This gel at the same time can replace Ordinary Portland Cement (OPC). The process of this is call geopolymerization. The concept of geopolymerization can be refer to figure below.

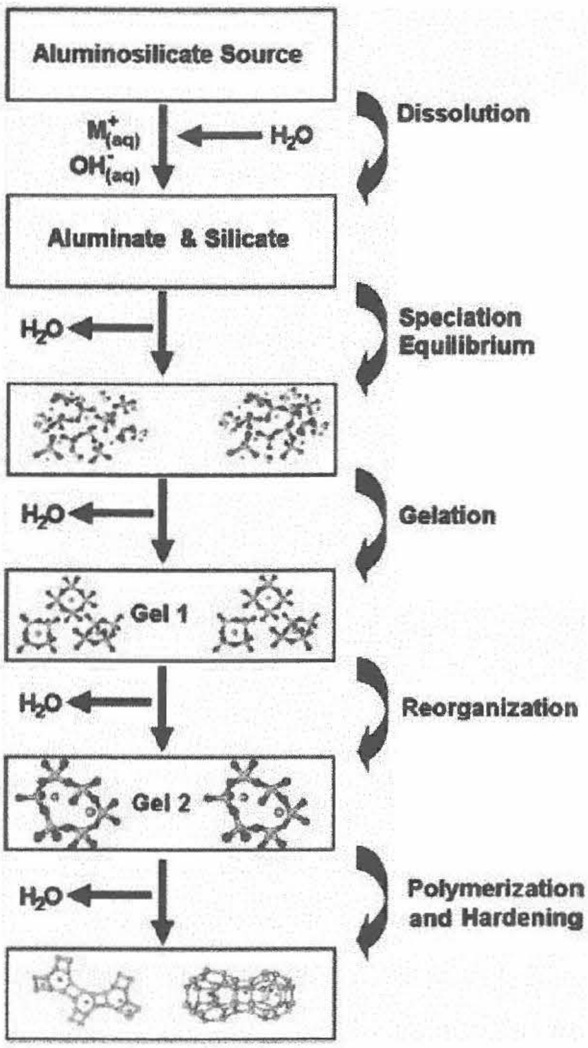

Figure 2.2 Conceptual models for geopolymerization (Duxson, 2006)

For alumina-silicate geopolymers based, the source material should be rich in silicon (Si) and aluminium (Al). On the other hand, consequence materials such as fly ash, slag and many more can be used as source materials. There are many factors that affecting in choice of the source material for geopolymers production which is type of application, cost, and availability.

In 1999, Davidovits said that the physical characteristic of fly ash is similar to that of ordinary Portland cement (OPC) and they have been considered as an improvement on cement in term of fire, heat and acidity resistance, compressive strength, and as a medium for the process of hazardous or low level radioactive waste.

For this research, the geopolymer is made with fly ash. The function of calcium in this process is very important. The presence of calcium in fly ash can result in flash setting and therefore must be carefully controlled. Furthermore, the temperature during curing play very important role, and depending upon the source materials and activating solution, heat often must be applied to smooth the progress of polymerization, although some systems have been developed that are designed to be cured at room temperature (Davidovits, 1999).

2.2.1 Fly ash.

Geopolymer concrete did not use Ordinary Portland Cement (OPC), but it use fly ash in concrete. Geopolymer are made from calcined source material and one of the materials is fly ash. Fly ash is a fine grey powder that is produced from power generation in coal fired power station. Fly ash is considered as a waste material. On the other hand, the waste material which is fly ash can be made as a substitute material for ordinary Portland cement (OPC) to produced concrete. The use of fly ash is automatically can bring benefit because of the price which is cheaper than Ordinary Portland Cement (OPC).

Besides, by using fly ash based geopolymer concrete, it can reduce approximately 80% of CO_2 to the atmosphere that is cause by Ordinary Portland Cement (K.Vijai, 2010). Davidovits state that the binders can be produced by a polymeric reaction of alkaline liquids with the silicon and the aluminium in source of fly ash. Fly ash which has silica and alumina is use as one of the source material for geopolymer binder. In this research, the fly ash that is use is class F fly ash. The class F fly ash has low calcium and this low calcium fly ash will slow down the hardening process. Low calcium fly ash based geopolymer concrete has high compressive strength, low shrinkage, low creep and acid resistance (Ladeiro G, 2007).

One ton of low-calcium fly ash which is class F fly ash can be utilized to produce about 2.5 cubic meter of high quality geopolymer concrete, and the total cost of chemicals needed to produce this concrete is cheaper than the total cost of one ton of ordinary Portland cement (OPC) (K.Vijai, 2010). Furthermore, we know that fly ash is considered as a waste material, the low calcium fly ash-based geopolymer concrete is, therefore, cheaper than the Portland cement concrete (OPC). These advantages of fly ash indirectly can be economically.

2.2.2 Alkaline solution

There are so many type of alkaline solution that can be use as an alkaline activator of alkali activated cements and concrete which is usually caustic alkalis and alkaline salt. (Shi, 2006) stated that it can be classified six group according to their chemical composition. The six groups are:

1) caustic alkalis
2) non silicate weak acid salt
3) aluminates
4) aluminosilicates
5) non silicate strong acid salts

The alkaline solution is one of the important materials in geopolymer. In geopolymerization, the most common materials that are used in fly ash base geopolymer concrete as an alkaline solution is sodium silicate or potassium hydroxide and sodium hydroxide (NaOH) or potassium hydroxide (KOH). But for this research, the alkaline solution that is use is the combination of the sodium hydroxide (NaOH) and sodium silicate. The sodium solution is choosing rather than potassium because it is cheaper. NaOH is the most economical chemical and it is widely available and also used. The molarity of the sodium hydroxide is 8M. The concentration of sodium hydroxide between 10 and 20M can give small effect on the strength (Chindaprasirt P, 2007). The sodium hydroxide can be get in pellets form.

2.3 Aggregate.

In geopolymer concrete, the aggregate is one of the raw materials. For this research, the aggregate that is use is fine aggregate, and coarse aggregate which consist of granite and limestone.

2.3.1 Granite.

One of the coarse aggregate in geopolymer concrete is granite. In construction, the use of granite is the most important thing in concrete. The good grade granite is use. The granite will sieve for size of 20mm, 14mm, 10mm, and

5mm. There are so many type of particle shape aggregate. The particle shape can be referring to table 1.1 below.

Table 2.1: Particle shape classification of aggregates according to (BS 8U: Part 1: 1975)

Classification	Description	Examples
Rounded	Fully water-worn or completely shaped by attraction	River or seashore gravel; desert, seashore and windblown sand
Irregular	Naturally irregular, or partly shaped by attrition and having rounded edges	Other gravels; land or dug flint
Flaky	Material of which the thickness is small relative to the other two dimensions	Laminated rock
Angular	Possessing well-defined edges formed at the intersection of roughly planar faces	Crushed rocks of all types; talus; crushed slag
Elongated	Material, usually angular, in which the other two dimensions	-
Flaky and elongated	Material having the length considerably larger than the width, and the width considerably larger than the thickness	-

2.3.2 Limestone.

Limestone is sedimentary rock that consist calcium carbonate and the other common mineral in limestone is dolomite [CaMg (CO_3):]. The common impurities in limestone include chert (microcrystalline, cryptocrystalline quartz or amorphous silica, SiO_2), clay, organic matter and iron oxides. These rocks formed at the bottom of lakes and seas with the build up of shells, bones and other calcium rich goods. Over thousands and millions of years, layer after layer is built up adding weight. The heat and pressure causes chemical reaction at the bottom and the sediments turn into solid stone and this stone is also known as limestone. The stone that contain calcium carbonate more than 95% is known as high calcium limestone. There are a lot of limestone types in limestone group. For example, a good polish recrystallised limestone is usually use for building stone and decorative. Most people consider limestone's that take a polish is marbles. In this research, limestone is used together with granite. The limestone aggregate will be sieved similar as granite which is 20mm, 14mm, 10mm, and 5mm size.

Table 2.2: Classification of natural aggregates according to rock type (BS 812: Part 1:1975) (Neville, 1996)

Basalt Group	**Flint Group**	**Gabbro Group**
-Andesite -Basalt -Basic porphyrites -Diabase -Dolerites of all kinds including theralite and teschenite -Epidiorite -Lamprophyre -Quartz-dolerite -Spilite	-Chert -Flint	-Basic diorite -Basic gneiss -Gabbro -Hornblende-rock -Norite -Peridotite -Picrite -Serpentinite
Limestone Group	**Porphyry Group**	**Quartzite Group**
-Dolomite -Limestone -Marble	-Aplite -Dacite -Felsite -Granophyre -Keratophyre -Microgranite -Trachyte -Quartz-porphyrite -Rhyolite -Porphyry	-Ganister -Quartzitic sandstones quartzite Re-crystallized
Granite Group	**Gritstone Group (including fragmental volcanic rocks)**	**Hornfels Group**
-Gneiss -Granite -Granodiorite -Granulite -Pegnatite -Quartz-diorite -Syenite	-Arkose -Greywacke -Grit -Tuff -Sandstone	-Contact-altered rocks of all kinds except marble
Schist Group		

-Phyllite -Schist -Slate I -All severely sheared rocks		

2.3.2.1 Chemical properties of limestone

In limestone, there are calcareous rocks principally of calcic minerals with minor amounts of alumina, ferric & alkaline oxides. The chemical of the properties limestone can be refer to table below.

Table 2.3: Chemical properties of limestone aggregate

Oxide	Percentage
Lime (CaO)	38-42%
Silica (SiO_2)	15-18%
Alumina (Al_2O_3)	3-5%
MgO	0.5 to 3%
FeO + Fe_2O_3	1-1.5%
Alkalies	1-1.5%
Loss On Ignition (LOI)	30-32%

2.2.3 Sand.

Sand is a fine aggregate that is commercially used in concrete. In geopolymer concrete, the raw material which is the combination of coarse aggregate and sand is mix with alkaline solution and fly ash. The sand will be sieved for size less than 5mm. The sand that is use in this research is natural Malaysian sand.

CHAPTER 3

METHODOLOGY

3.1 Introduction

For this research, fly ash based geopolymer concrete with lime stone aggregates will be use. Geopolymer concrete consist of fly ash, alkaline solution, fine aggregates and coarse aggregate.

3.2 Material for concrete

In this study, the material that will use in the process of geopolymer concrete is fly ash, alkaline solution, fine aggregates and coarse aggregate. This material will be mix and the process will be done at UMP heavy structure laboratory.

3.2.1 Fly Ash

Fly ash is a fine grey powder that is produced from power generation in coal fired power station. Fly ash contains amount of silicon dioxide (SiO_2) and calcium oxide (CaO). There are two type of fly ash which is class F and class C fly ash. For this research, fly ash ASTM standard class F will be use. The source of fly ash material will obtain from Manjung power station, Perak, Malaysia. In this research, the use of fly ash is to replace OPC.

Figure 3.1: Class F fly ash

3.2.2 Alkaline solution

The process that involve in geopolymer is geopolymerization. In geopolymerization, alkaline solution is one of the most important material and the common material use as alkaline solution in producing fly ash based geopolymer is a combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) or potassium hydroxide (KOH). For this research, the sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) will be use as an alkaline liquid. The molarity (M) of the sodium hydroxide is 8 Mol.