Study on the Effect of Rice Husk Ash, Fly Ash and Palm Frond Ash in Geopolymer Cement

by

Shathiskumar A/L Sockalingam

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Petroleum Engineering)

MAY 2013

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Study on the Effect of Rice Husk Ash, Fly Ash and Palm Frond Ash in Geopolymer Cement

by

Shathiskumar A/L Sockalingam

A project dissertation submitted to the
Petroleum Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(PETROLEUM ENGINEERING)

Approved by,

____

(Raja Rajeswary Suppiah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

May 2013

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

____

SHATHISKUMAR A/L SOCKALINGAM

ABSTRACT

The research or the study of the effect of rice husk ash, fly ash and palm frond ash on geopolymer cement has been carried out and completed. The objective of the research is to determine the suitability of the produced geopolymer cement to be used in oil well cementing applications. Meanwhile, the effect of the curing period of cement and also the composition it is made of on the compressive strength of the geopolymer cement were also studied. The compressive strength testing was carried out on produced geopolymer cements since compressive strength is one of the main factors that determine the appropriateness of a cement to be used in cementing applications. The evolution of geopolymer cements is due to the environmental pollution caused by carbon dioxide release by industries particularly cementing and aggregate industries which could lead to global warming. Geopolymer cements also are good substitute for Ordinary Portland Cement (OPC) since OPC is known for its corrosion potential with carbon dioxide. Thus, the production and usage of geopolymer cement could curb all these problems. The scope of the research is limited to the three aforementioned raw materials to be used in compressive testing study in determining its suitability to be used in real life applications. Thus, the whole research is laboratory based.

The methodology of the research can be divided into five major sections, which are, gathering relevant data and information, calculation of cement slurry proportions, geopolymer cement production, compressive strength testing of geopolymer cement and finally analysis of the results. The last two sections are very vital in justifying the results obtained from the research. Based on the results of the research, the curing period and composition of the cement significantly influence the compressive strength of the geopolymer cement. With the inclusion of aggregates and plasticizers, which were not used in this research, the geopolymer cement composed of rice husk ash, fly ash and palm frond ash has a high potential to be used in oil well cementing and might be an alternative for class G cement used currently, where further study is necessary in justifying it.

ACKNOWLEDGEMENTS

I would like to acknowledge my deepest gratitude to GOD firstly, for he has given me the guidance, strength and confidence in completing my Final Year Project while overcoming all the barriers that were faced throughout the period. I would also like to greet my family for giving me great support from the beginning of my journey until the end.

My sincerest appreciation goes to my Final Year Project Supervisor, Miss Raja Rajeswary Suppiah for giving me an opportunity to conduct Final Year Project under her supervision. Her patience in guiding me and her determination in making me to learn as much as I can throughout the project is highly appreciated. She has always been there to guide and resolve my questions and problems. Her support for my project is very much appreciated.

Following that, I would like to express my greatest gratitude to Mr. Muhammad Aslam B Md Yusof, Final Year Project Coordinator, for his continuous support and direction for my project. I also like to thank Mr. Jukhairi Bin Selamat, Technologist for his willingness to teach and supervise my activities in the laboratory. To all my friends, thank you all for your support and motivation. I truly appreciate the knowledge and experience shared that made my project a success. Hope we continue the friendship and cooperation in the future.

Thank you very much.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

MIRHA	Microwave Incinerated Rice Husk Ash
FA	Fly Ash
POFA	Palm Oil Frond Ash
RHA	Rice Husk Ash
PFA	Pulverized Fuel Ash
OPC	Ordinary Portland Cement
PC	Portland Cement
FTIR	Fourier Transform Infra-Red
IPCC	Intergovernmental Panel on Climate Change
ASTM	American Society for Testing and Materials
US	United States
CO^2	Carbon Dioxide
MPa	Mega Pascal
°C	Degree Celcius
pH	Power of Hydrogen
KOH	Pottasium Hydroxide
NaOH	Sodium Hydroxide
psi	Pounds per Square Inch

CHAPTER 1

INTRODUCTION

1.1 Background of Study

How geopolymers should be considered? Are they a new binder, a new material or new cement? Geopolymers are all of these. They are the new cement for concrete, new materials for adhesives and coatings and new binders for fiber composites (Davidovits J. , July 2011). Geosynthesis, a reaction that chemically integrates minerals that involves naturally occurring silico-aluminates is called geopolymerization (Hermann E, 1999). Davidovits coined the term geopolymer in 1978 to represent a broad range of materials characterized by chains or networks of inorganic molecules (Institute, 2010). The classes of greatest potential application for cementing purposes are comprised of aluminosilicate materials that maybe used to completely replace Portland cement in cementing applications, out of the nine different classes of geopolymers (Davidovits, 2008). Industrial byproducts such as fly ash or slag or thermally activated natural materials such as kaolinite clay provide a source of silicon and aluminium which dissolve in an alkaline activating solution and subsequently polymerizes into molecular chains and networks to create the hardened binder upon which the geopolymers depends on. As such, it is referred as alkali-activated cements or inorganic polymer cements (Dam, March 2010).

Any pozzolanic compound, silicate based materials that react with calcium hydroxide generated by hydrating cement to form additional cementitious materials (Girard, 2011) or source of silica and alumina that is readily dissolved in the alkaline solution acts as a source of geopolymer predecessor species and thus lends itself to geopolymerization (Xu H, 2000). An innovating technology that is generating considerable interest in the cementing applications is the production of geopolymer materials, especially in the ongoing prominence on sustainability. Geopolymer systems provide the binding agents by depending on industrial byproducts or minimally processed natural materials, in contrast to Portland cement. (Dam, March 2010).

1.2 Objective and Scope of Study

The ultimate objective of the project or research is to study the effect of rice husk ash, fly ash and palm frond ash in geopolymer cement by examining the compressive strength to determine its suitability in cementing applications. This is done by studying the effect of curing period and also the composition of raw materials in the compressive strength of the produced cement. Compressive stress or strength is termed as the maximum stress a material can sustain under crush loading (Instron, 2013). Crush loading refers to the pressing action between opposing bodies as to break or fail (Farlex, 2013). In a simpler manner, compressive strength could be indicated as the resistance of a material towards the forces that attempt to squeeze or compress the material together (ToolingU, 2012). The most important of all the properties of cement is the compressive strength of the hardened cement. Therefore, it has been always a common practice to test cement for its compressive strength in the laboratory before the cement is used in important works or cementing applications (Paul, 2011).

The scope of the project is intended to be focused on the use of rice husk ash, fly ash and palm frond ash in geopolymer cements to study the effect of these organic byproducts on the compressive strength of the hardened cement. The project or research will be laboratory based, where the cement produced from the composition or mixture of all the three materials will be tested to investigate its compressive strength of the hardened cement in the laboratory, while directly indicating its suitability to be used in cementing jobs. Individually, rice husk ash is an agricultural byproduct from rice milling which accounts for about one-fifth of the annual gross rice production of the world (Feng, 2004). On the other hand, the derivative from smoldering pounded coal in electric power plant is called fly ash (Kim D. Basham, 2007) or even commercially known as pulverized fuel ash (PFA) (The Concrete Society, 2006). Palm frond ash is the product from burning oil palm frond which is the most abundant yet untapped biomass waste in our country, Malaysia (Fiseha Mekonnen Guangul, 2011). These three materials will be discussed further in **Chapter 2**.

1.3 Problem Statement

Undesirable pollutants are being generated and released into the environment at an increasing and alarming rate due to the advancement in industrialization. (Divya Khale, 2007). One of the major environmental challenges all around the world is the threat of climate change. One of the major green house gases, carbon dioxide (CO_2) accounts for 82% of the total (Amir H. Mahmoudkhani, 2008). The excessive usage of fossil fuels including coal has rapidly increased greenhouse gas emissions in the globe. In conjunction with that, it has been estimated that there will be a significant increase in the global temperature in the next 50 to 100 years. The Intergovernmental Panel on Climate Change (IPCC) estimates that the global carbon dioxide emissions will reach approximately 77 Gigatonnes per year by 2100 and the average atmospheric carbon dioxide concentration will reach approximately 750 parts per million by volume (Nasvi, 2012).

It has been clear now that in the selection of any process for a task, utmost consideration should be given to minimize environmental pollution while keeping in pace with rapid industrialization. Recently, the quantity and diversity of hazardous solid waste generation and its impact on human health have been given prior attention. Mounting concern on environmental consequences of waste disposal has triggered investigation of new utilization avenues (Woolard CD, 2000). To overcome all the problems mentioned, geopolymers emerged as a potential solution by using byproducts and wastes to manufacture precast structure and non-structural elements, concrete pavements, concrete products and immobilization of toxic waste that are resistant to heat and aggressive environment (Davidovits, 1991). Geopolymers contribution in cementing applications has played a very major role in oil and gas industries. Geopolymer cements made of wastes and organic byproducts are being used vastly in the industries. Besides, geopolymer cement is increasingly replacing the application of Ordinary Portland Cement (OPC), a powdery cementitious building material made from finely pulverized alumina, iron oxide, lime, magnesia and silica (Business Dictionary, 2013) since OPC is known for its corrosion potential with carbon dioxide (Tiemeyer, 2013).

1.4 Relevancy of The Project

The research or project conducted is very much relevant to current industrial practices since the use of geopolymer cements is being seen as a good alternative to commonly used cements, particularly Ordinary Portland Cement. The robustness and versatility which enables the products to be engineered from a range of cement, fly ash or aluminosilicate component ratios so that it delivers specific properties for a given application at lowered cost is the key attribute of geopolymer cements. Geopolymer cements offer superior properties especially for low density slurries from 1200 to 1500 kg/m^3 (Amir H. Mahmoudkhani, 2008) for oil and gas well cementing. Geopolymer cements can be economically advantageous but also technically beneficial to cementing applications, typically improving strength and durability (Institute A. C., 2001). Moreover, it has the potential to considerably curb carbon dioxide emissions. Comparing geopolymer cements with Ordinary Portland Cements, geopolymer cements have more advantages too such as better resistance to corrosion and fire, up to 2400˚F, a rapid strength gain, lower shrinkage and high compressive and tensile strengths (Salton, 2009).

1.5 Feasibility of The Project Within The Scope And Time Frame

The project is very feasible to be conducted in the laboratory of Universiti Teknologi Petronas within the specified time frame. As mentioned in the title of the project, the three materials being investigated to be incorporated as geopolymer cements are rice husk ash, fly ash and palm frond ash. All this three materials are already available in the laboratory to progress on the project. Moreover, compressive strength testing equipment is also readily available in the laboratory to aid in the project by testing the compressive strength of the geopolymer cement that will be produced. In this academic calendar, 14 weeks have been allocated to complete the project. However, only one academic semester of 14 weeks has been allocated for the project, therefore, execution of the laboratory experiments will begin immediately after the data gathering process, when sufficient information has been obtained to proceed with the project. The laboratory experiments and report writing phase will be conducted simultaneously.

CHAPTER 2

LITERATURE REVIEW

2.1 What are Geopolymers?

Due to its revolutionary approach in the production of alternative cement binder, geopolmer has progressively enticed many concrete and cementing communities around the world. In 1957, Glukhovsky started the early research on this material which was named as “soil cement”, derived from the low basic calcium or calcium-free aluminosilicate (clays) and alkali metal solution used in the cement production (Andri Kusbiantoro, 2012). However, the first industrial research on geopolymer was introduced by Davidovits for the development of new binder material using inorganic materials in 1972. Geopolymer term was taken referring to its source material which is a geological origin or by product material that is rich in silicon and aluminum. Its reaction product with alkaline solution possessed an amorphous to semi-crystalline three-dimensional silico-aluminate on the material properties (Davidovits, 2008).

Geopolymer cement, basically it is termed as an innovative material and a real material to conventional Portland cement, the major components of which are tri- and di-calcium silicates (G.C.Bye, 1999) for use in transportation infrastructure, construction and offshore applications. To significantly reduce its carbon footprint, it relies on minimally processed natural materials or industrial by products (Davidovits J. , January 2013) . A TechBrief titled Geopolymer Concrete released by the US Department of Transportation Federal Highway Administration on March 2010 states that the production of versatile, cost-effective geopolymer cements that can be mixed and hardened essentially like Portland cement represents a game changing advancement, revolutionizing the construction of transportation infrastructure and the building industry (TechBrief: Geopolymer Concrete, 2010).

Geopolymer cements belong to the category of inorganic polymer, has been summarized by numerous publications on geopolymers. On this matter, according to Joseph Davidovits, he has developed the notion of geopolymer to better explain this chemical processes and the resultant material properties. A major shift in perspective was much needed to move away from the classical crystalline hydration chemistry of conventional cement chemistry. However, this shift has not been well accepted by practitioners in the field of alkali activated cements who still tend to explain such reaction chemistry in Portland cement terminology (The Geopolymerization Process).

Commonly the term geopolymer is used to describe the amorphous to crystalline reaction products from synthesis of alkali aluminosilicates. However, geopolymeric gels and composites are also referred to as low-temperature aluminosilicate glass (Rahier, 1996), alkali-activated cement (Palomo A, 2003), geocement (PV, 1994), alkali bonded ceramic (Mallicoat, 2005), inorganic polymer concrete (Sofi, 2006) and hydroceramic (Bao, 2005). Despite this variety of nomenclature, these terms describe materials synthesized utilizing same chemistry, which can be described as a complex system of coupled alkali mediated dissolution and precipitation reactions in an aqueous reaction substrate (Phair, 2003).

The alkali compound from the elements of the first group of the periodic table acts as an activator, so called alkali activated cementitious material or alkali activated aluminocilicate binders (Xiong CJ, 2004). The inorganic polymeric materials are synthesized in a manner similar to thermosetting organic polymers and can be considered as an amorphous equivalent of geological feldspars. Thus, these materials are termed as geopolymers (Hos JP, 2002). Although various macroscopic characteristics of geopolymers prepared from different aluminosilicate sources may appear similar, their microstructure and physical, mechanical, chemical and thermal properties vary to a large extent depending predominantly on the raw material from which they are derived. **Figure 1** and **Figure 2** illustrates the microstructures of geopolymers synthesized from metakaolin and fly ash.

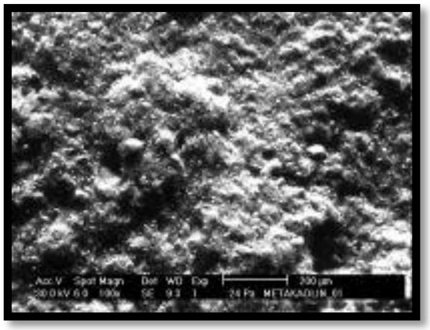


Figure 1: Microstructure of geopolymer synthesized from metakaoline.
(Technology, 2009)

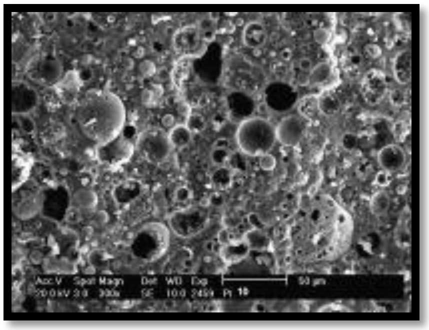


Figure 2: Microstructure of geopolymer synthesized from fly ash.
(Technology, 2009)

The carbon dioxide savings and potential energy through the use of geopolymers can be considerable since Portland cement is responsible for upward of 90 percent of the carbon dioxide and 85 percent of the energy attributed to a typically ready mixed cement (Marceau, 2007). Although the common perception of looking at geopolymer technology as new, the technology has carved along the ancient roots and has been postulated as the building materials in the Giza pyramids construction as well as in other ancient construction (Davidovits, 1984). Besides, since the mid-20th century, alkali-activated slag cement, a type of geopolymer has been in use (Barsoum, 2006).

Although the mechanism of polymerization is yet to be fully understood, a critical feature is that water is present only to facilitate workability and does not become a part of the resulting geopolymer structure. In other words, water is not involved in the chemical reaction and instead is expelled during curing and subsequent drying. This is in contrast to the hydration reactions that occur when Portland cement is mixed with water, which produce the primary hydration products calcium silicate hydrate and calcium hydroxide. This different has a significant impact in the mechanical and chemical properties of the resulting geopolymer concrete, and also renders it more resistant to heat, water ingress, alkali-aggregate reactivity and other types of chemical attack (Davidovits, 2008).

2.2 Materials to be Incorporated in Geopolymer Cement

In this project, three materials are incorporated in the production of the geopolymer cement, namely, rice husk ash, fly ash and palm frond ash. These three materials will be discussed further in this section.

a) Rice Husk Ash (RHA)

A byproduct of rice milling is called husk. This surrounds the paddy grain. About 78% of weight is received as rice, broken rice and bran during milling of paddy. Husk accounts for the remaining 22% of the weight of paddy. In the rice mills, husk is used as fuel to generate steam for the parboiling process. 75% of the husk is organic volatile matter, while the rest 25% of the weight is converted into ash during the firing process, known as rice husk ash (Corotis, 2007). Huge quantities of agro residues that are being produced in many developing countries cause extensive pollution to the environment and being used inefficiently. Either the strength or the durability of the cement has been identified to be improved by partially replacing OPC with RHA through current researches (Sensale, 2006). By replacing 10% of the cement by RHA, compressive strength can be increased up to 30% (Corotis, 2007). **Figure 3** and **Figure 4** shows the image of rice husk and rice husk ash respectively.

Figure 3: Rice husk (Viet Cargo)

Figure 4: Rice husk ash (Qrbiz, 2012)

Silica is one of the major component contained in the RHA produced from the burning process of paddy husk, a pozzolanic material. Over the years, it has been identified that the common characteristics shown by pozzolanic material in cement strength development is lower on early days but higher on lately days (Bouzoubaa, 2001). Other studies also show that the addition of RHA increases the water demand of the cement, a problem that can be counteracted by incorporating superplasticizers (D.D. Bui, 2001). The ash produced by burning method contains about 95% of pure silica and it is in an active form which behaves very much like cement if properly prepared (Hwang, 1996).

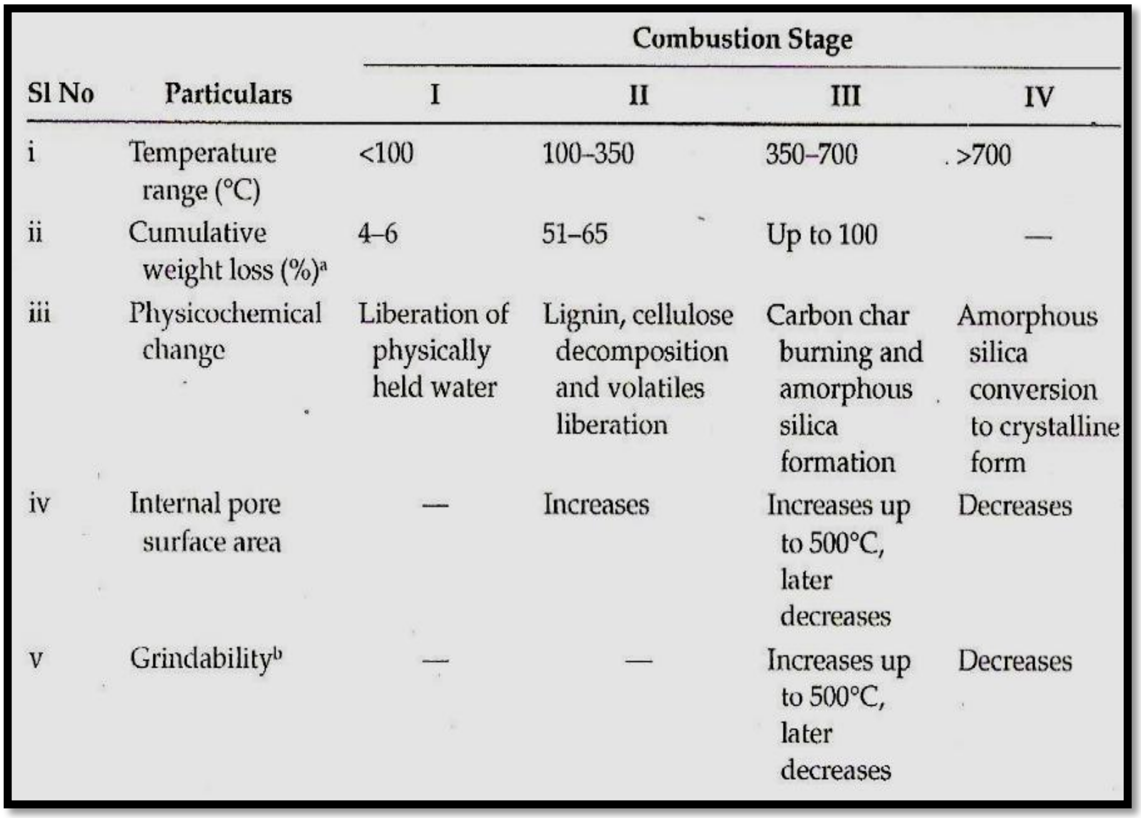
Because the husk is hard to handle, normally people just burn it and bury it under paddy fields as organic manure. By controlling the burning temperature, rice husk ash can be a green material and re-utilized in cementing applications. Therefore, burning procedure to obtain rice husk ash that is highly reactive needs to be established so that it can be used as cement replacement and the optimum replacement percentage of Ordinary Portland Cement by rice husk ash that improves the quality of cement need to be identified (Kamal, 2008).

Burning rice husk at higher temperature increases the silicon dioxide content but it is not suggested to burn rice husk above 800 ̊C longer than one hour because it tend to cause a sintering effect and is indicated by a dramatic reduction in the specific surface area. In order to produce Microwave Incinerated Rice Husk Ash (MIRHA) with high reactive silica content, controlled combustion of rice husk is required. **Figure 5** shows the image of a microwave incinerator (Hwang, 1996).

Figure 5: Microwave incinerator (Vishie, 2009)

Rice Husk is difficult to burn due to its typical silica-wood composite morphological structure, high mineral content, large bulk volume and a pronounced tendency to cake and agglomerate during combustion. The important physical and mineralogical characteristics of rice husk ash such as the content of amorphous silica, surface area, grindability and carbon content depend upon the temperature, environment and the duration of combustion. Along with the other changes, the combustion in air is marked by the weight loss due to the removal of organic matter (Kumar, 1993). It is exothermic and the fuel calorific value ranges between 13.8 and 15 × 10^6 J/kg. **Table 1** summarizes the characteristic changes that occur during the combustion of rice husk. As shown in the table, the combustion process is divided into four stages marked by the temperature range, weight loss and corresponding physicochemical and other changes (D.Bapat, 2012).

Table 1: Combustion of rice husk (D.Bapat, 2012)



Sl No	Particulars	Combustion Stage			
		I	II	III	IV
i	Temperature range (°C)	<100	100–350	350–700	>700
ii	Cumulative weight loss (%)[a]	4–6	51–65	Up to 100	—
iii	Physicochemical change	Liberation of physically held water	Lignin, cellulose decomposition and volatiles liberation	Carbon char burning and amorphous silica formation	Amorphous silica conversion to crystalline form
iv	Internal pore surface area	—	Increases	Increases up to 500°C, later decreases	Decreases
v	Grindability[b]	—	—	Increases up to 500°C, later decreases	Decreases

b) Fly Ash (FA)

Coal is a complex, heterogeneous material, in widespread use as an energy source throughout the world. It is the end product of a series of biological and physicochemical processes which have resulted in the wide variety of minable materials currently utilized in industry. When pulverized coal is burnt to generate electrical power, extremely large quantities of fly ash and bottom ash are produced (Wesche, 1991). Fly ash must be distinguished from the coarser ash that collects at the bottom of the furnace. The most uniform and highest quality ash is likely to be that produced by efficient, base load power stations. Fine grade fly ash has acquired considerable importance in the cementing applications (Taylor, 1997). **Figure 6** and **Figure 7** illustrates the image of coal and the resulting fly ash respectively.

Figure 6: Coal (Clean Coal, 2013)

Figure 7: Fly ash (Pauler, 2009)

The chemical composition depends on the mineral composition of the coal gangue, the inorganic part of the coal. Silica usually varied from 40% to 60% and alumina from 20% to 30%. The iron content varies quite widely. Alkalis are present in an appreciable amount and potassium prevails over sodium (Hewlette, 1998). When calcium oxide is more than 20%, then it can be categorized as cementitious material. When calcium oxide varies between 10% and 20%, it is categorized as cementitious and pozzolanic material. A pozzolanic material requires calcium hydroxide in order to form strength-imparting products. Usually the calcium oxide content in this material is not enough to react with all the quantity of the pozzolanic compounds and exhibit pozzolanic activity. It is used with Portland Cement (PC), which yields calcium hydroxide on hydration. For geopolymerization, high alkaline solutions are used to induce the silicon and aluminium atom in the source material to dissolve and form geopolymeric paste (Divya Khale, 2007).

The physical characteristics of fly ash such as shape, specific gravity, size and fineness affect its performance in the concrete in terms of volume, rheology and water demand at a given slump, porosity and reactivity. The shape and surface characteristics of fly ash particles affect the water requirement of concrete at the desired slump. The spherical particles reduce inter-particle friction in the concrete mix, improve its flow properties and reduce water requirement. This phenomenon is commonly observed when fly ash replaces cement in concrete. Fly ash from bituminous coal is darker in color, usually gray and that from lignite or subbituminous coal is lighter in color. In ash without carbon or low carbon content, the color is likely due to the presence of iron compounds. The particle size and fineness of fly ash is considered as one of the most important properties. Particle size may refer to a size of a single or an average of many particles lying in the narrow range and the size distribution refers to a range of the size of particles in a powder sample, often expressed as the mass of particles having a particular average particle size. Particles with identical specific surface areas may actually exhibit different size distributions. The particle size distribution is an important parameter determining the cementitious activity (D.Bapat, 2012).

ASTM C618 classifies fly ash based on the source of mineral coal as illustrated in **Table 2.** It defines two classes of fly ash suitable to be used in concrete, which are Class F and Class C. While the two classes have identical physical characteristics, they are distinguished by their chemical compositions. The class F fly ash, which normally results from the burning of anthracite or bituminous coal, is the more readily available of the two. The sum of silica, alumina and iron oxide in Class F must constitute at least 7% of the total mass. It also has low (typically less than 10%) calcium oxide content. Even though its crystalline mineral constituents are not reactive, Class F fly ash has pozzolanic properties. The Class C fly ash normally results from the burning of lignite or subbituminous coal and the sum of silica, alumina and iron oxide must constitute at least 50% of the total mass. The Class C fly ash has high calcium oxide content (10% - 30%) and almost all of its mineral constituents are reactive, giving it both pozzolanic as well as cementitious properties. **Table 3** lists and **Table 4** compares some national standards on fly ash for use in cement and concrete (D.Bapat, 2012).

Table 2: Classification of fly ash as per ASTM C618 (D.Bapat, 2012)

Class	Description
N	Raw or calcined natural pozzolan, for example, some diatomaceous earths; opaline cherts and shales; tuff and volcanic ashes or pumices.
F	Fly ash with pozzolanic properties normally produced from anthracite or bituminous coal.
C	Fly ash with pozzolanic and cementitious properties normally produced from lignite or subbituminous coal. May have lime content more than 10%.

Table 3: Some national standards on fly ash (D.Bapat, 2012)

SI No	Standards Organization	Standard Number	Standard Title
i	Bureau of Indian Standards	IS 3812	Specification for FA for use as pozzolan and admixture.
		IS 6491	Methods of sampling fly ash.
		IS 10153	Guidelines for utilization and disposal of FA.
ii	British Standards Institution	BS 3892-1	Specification of FA for use with Portland Cement (PC).
		BS EN 450	FA for concrete.
iii	American Society for Testing and Materials	ASTM C311	Test methods for sampling and testing FA or natural pozzolan for use in PC concrete.
		ASTM C618	Specification for coal FA and raw or calcined natural pozzolan for use in concrete.

Table 4: Comparison of some national standards on fly ash (D.Bapat, 2012)

SI No	Particulars	ASTM C618 Type F	BS 3892 Part 1	IS 3812
i	Particle density (kg/m^3,min)	Not specified	2000	Not specified
ii	Blaine fineness (m^2/kg)	Not specified	Not specified	320
iii	Retention on 45µm (325 mesh) sieve (%,max)	34.0	12.0	34.0
iv	Loss of ignition (%,max)	6.0	7.0	5.0
v	Water requirement (% of PC,max)	105	95	Not specified

c) Palm Oil Frond Ash (POFA)

The palm oil industry is one of the most important agro industries in Malaysia, Indonesia and Thailand. It produces a large quantity of solid waste, besides the crude palm oil. On average, processing of 1 ton fresh palm fruit bunches in oil mill produces 0.21 ton palm oil and residues consisting of 0.06 to 0.07 ton kernels, 0.06 to 0.07 ton shells, 0.14 to 0.15 ton fibers, 0.23 ton empty fruit bunches and 0.65 ton effluent. These are being illustrated by **Figure 8**, **Figure 9** and **Figure 10**. The solid palm oil residue is mostly burned as fuel in power plants and generates ash, about 5% of its mass. With the increase in palm oil production, the quantity of POFA continues to increase. However, its utilization remains minimal and most of it is disposed of in landfills, causing environmental hazard.

Figure 8: Fresh oil palm fruit bunch (Berkhout, 2013)

Figure 9: Empty fruit bunch (Singh, 2012)

Figure 10: Empty fruit bunch fibre (Diggbuyer, 2011)

POFA is characterized by a spongy and porous structure. The particles have an angular and irregular form and a typical specific gravity of 2.33. Although it is not a natural pozzolan, when ground finely, it can be classified as a natural pozzolan, based on the chemical composition according to ASTM C618. The pozzolanic reactivity improves with the size reduction. Initially, POFA was used as a substitute for cement to make structural grade concrete. It is observed that finely ground POFA, as a mineral admixture, enhances the strength and durability characteristics of concrete, for cement replacement on the order of 20% to 30%.

2.3 Mechanical Property of Geopolymer Under Study

The most prominent property that will be discussed here is the **unconfined compressive strength** of the produced geopolymer cement. Source materials with a high reactivity are required to produce a geopolymer with a high compressive strength (Xu, 2002). A higher strength geopolymer is associated with a more desirable microstructure (Van Deventer, 2002). Some of the important factors affecting unconfined compressive strength will be discussed in this section.

a) Curing Temperature

Curing temperature is an important factor in the setting of the cement. Pozzolanic reactions are accelerated by temperature increase (Hardjito, 2003). **Table 5** illustrates the factors affecting the strength of geopolymers on other binders. Increase in the curing temperature in the range of 30 ° C to 90 ° C increased the compressive strength. Curing at 70 ° C improved the strength compared to curing at 30 ° C for the same period of time. Curing at higher temperature for more than a couple of hours possibly affects the development of the compressive strength (Wiles, 1988). This phenomena is illustrated in **Figure 11** and **Figure 12**.

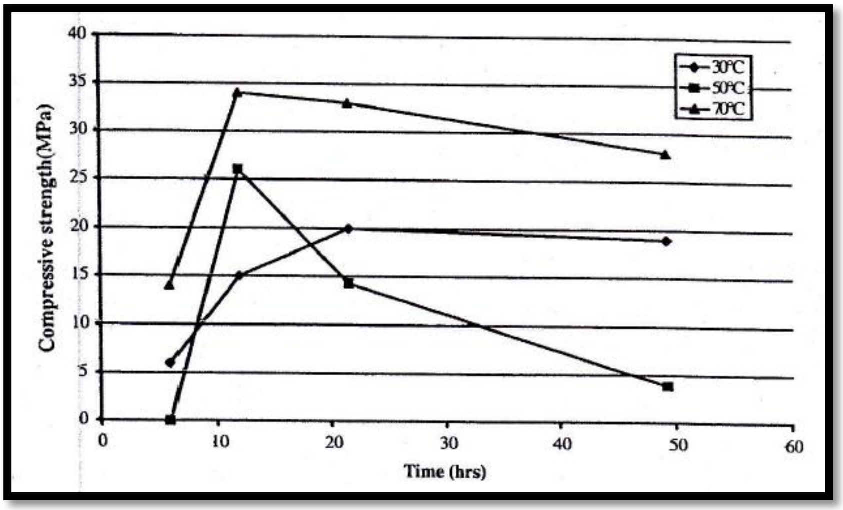


Figure 11: Variation of compressive strength with time at different curing temperature (Divya Khale, 2007)

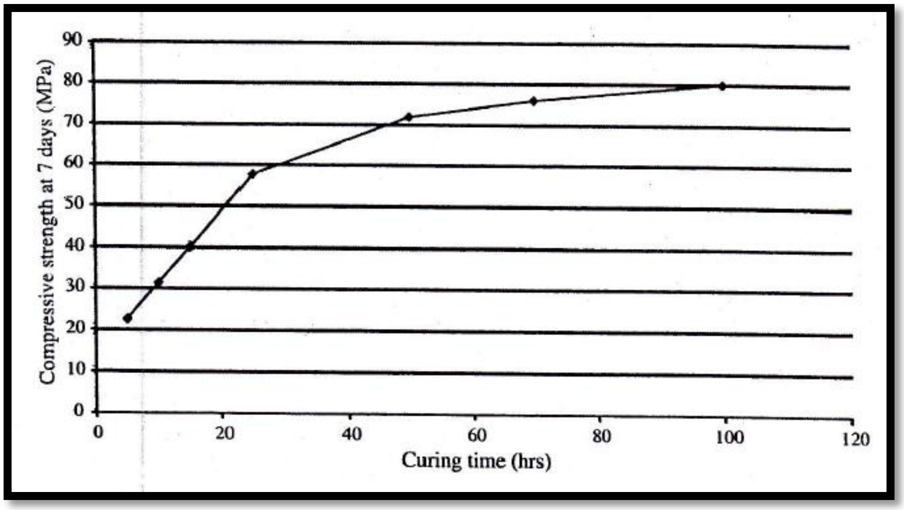
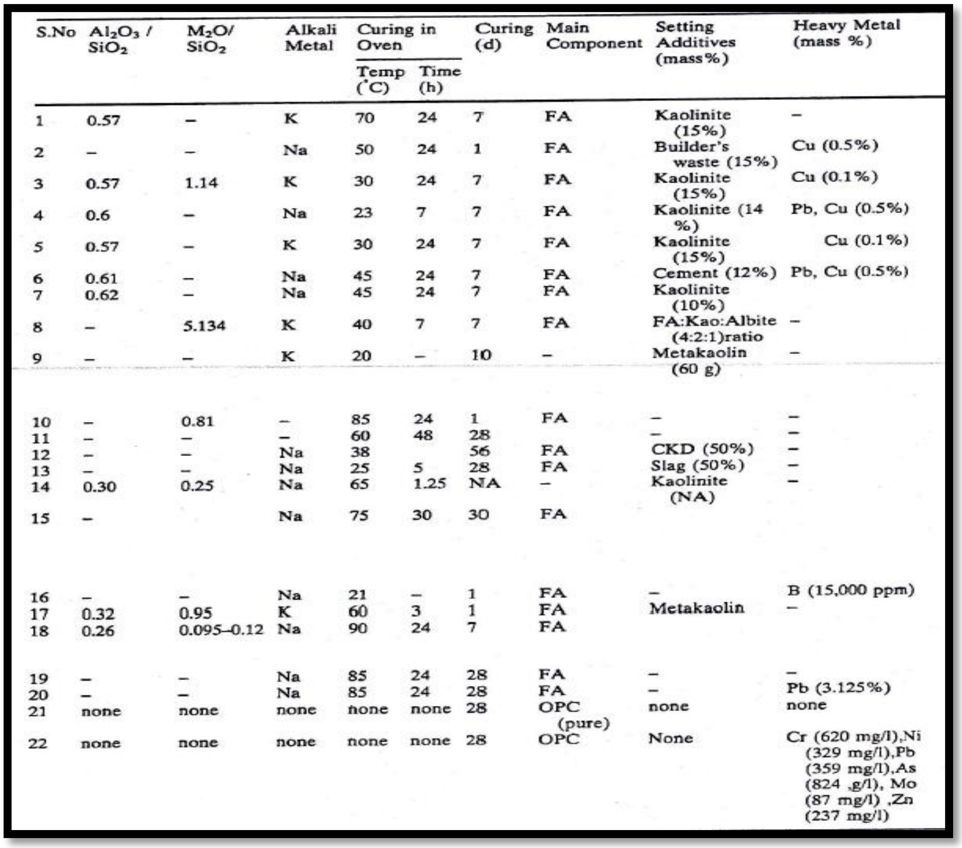


Figure 12: Effect of curing temperature on compressive strength (Divya Khale, 2007)

Table 5: Factors affecting on the strength of geopolymers and other binders (Divya Khale, 2007)



S.No	Al_2O_3 / SiO_2	M_2O/ SiO_2	Alkali Metal	Curing in Oven		Curing (d)	Main Component	Setting Additives (mass%)	Heavy Metal (mass %)
				Temp (°C)	Time (h)				
1	0.57	–	K	70	24	7	FA	Kaolinite (15%)	–
2	–	–	Na	50	24	1	FA	Builder's waste (15%)	Cu (0.5%)
3	0.57	1.14	K	30	24	7	FA	Kaolinite (15%)	Cu (0.1%)
4	0.6	–	Na	23	7	7	FA	Kaolinite (14 %)	Pb, Cu (0.5%)
5	0.57	–	K	30	24	7	FA	Kaolinite (15%)	Cu (0.1%)
6	0.61	–	Na	45	24	7	FA	Cement (12%)	Pb, Cu (0.5%)
7	0.62	–	Na	45	24	7	FA	Kaolinite (10%)	
8	–	5.134	K	40	7	7	FA	FA:Kao:Albite (4:2:1)ratio	–
9	–	–	K	20	–	10	–	Metakaolin (60 g)	–
10	–	0.81	–	85	24	1	FA	–	–
11	–	–	–	60	48	28		–	–
12	–	–	Na	38		56	FA	CKD (50%)	–
13	–	–	Na	25	5	28	FA	Slag (50%)	–
14	0.30	0.25	Na	65	1.25	NA	–	Kaolinite (NA)	–
15	–		Na	75	30	30	FA		
16	–	–	Na	21	–	1	FA	–	B (15,000 ppm)
17	0.32	0.95	K	60	3	1	FA	Metakaolin	–
18	0.26	0.095–0.12	Na	90	24	7	FA		
19	–	–	Na	85	24	28	FA	–	–
20	–	–	Na	85	24	28	FA	–	Pb (3.125%)
21	none	none	none	none	none	28	OPC (pure)	none	none
22	none	none	none	none	none	28	OPC	None	Cr (620 mg/l),Ni (329 mg/l),Pb (359 mg/l),As (824 ,g/l), Mo (87 mg/l) ,Zn (237 mg/l)

b) Curing Time

Geopolymers develop compressive strength of 45MPa in just 24 hours (Palomo, 2003). On a study, it has been shown that the compressive strength for one day was higher when the curing was carried out at 65˚C and at rest of the age, paste cured at 25˚C developed higher compressive strength than those treated at 65˚C. The dissolution of reactive species is favoured by the increase in temperature. Prolonged curing at elevated temperature breaks the granular structure of geopolymer mixture, thus the compressive strength decrease on curing at higher temperature for longer period of time. This will lead to contraction of gel without transforming to a more semi-crystalline form, resulting in dehydration and excessive shrinkage. However, the crystalline part of geopolymer does not get affected by longer curing time, indicating that the change responsible for the difference in the strength originates within the amorphous phase of the structure (Vaan Jaarsveld, 2002).

c) pH

pH is the most significant factor controlling the compressive strength. As the pH of the activating solution increases, the setting time of cement decreases. At higher pH value, the geopolymeric mix attain a more fluid gel composition, which is less viscous and more workable compared to mix at lower pH value, where it remains viscous and behaves like cement. (Divya Khale, 2007). Strength at pH 14 was 50 times larger than those at pH 12, where it is less than 10 MPa at pH 12 and 50 MPa at pH 14 of geopolymeric matrix utilizing cement as setting additive. Higher solubility of monomers was expected by KOH than NaOH because of higher alkalinity. With increase in pH, soluble aluminium increases and reacts with calcium available for reaction (Duxson, 2005). Lower monomer concentration is a result of the lower pH value of the solution. **Figure 13** illustrates an example of pH value of a single alkaline solution, varying in concentration and kind of alkali ions. From the figure, it is clear that pH range 13 to 14 is most suitable for the formation of the geopolymers with better mechanical strength (Divya Khale, 2007).

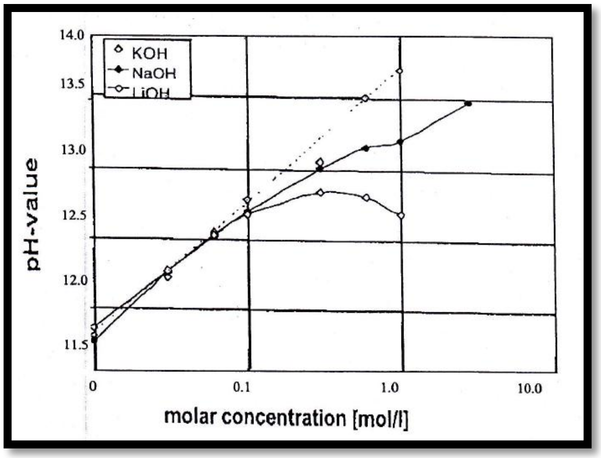


Figure 13: Influence of the concentration and kind of alkaline solution on the pH-value (Divya Khale, 2007)

d) Liquid/Solid Ratio

As the ratio of water to geopolymer solid by mass increases, the compressive strength decreases. This trend is analogous to water to cement ratio in the compressive strength in OPC. The minimum water to cement ratio is approximately 0.4 by weight for OPC, whereas the fresh geopolymeric material is readily workable even at low liquid/solid ratio as shown in **Figure 14** (Conner, 1990)**.**

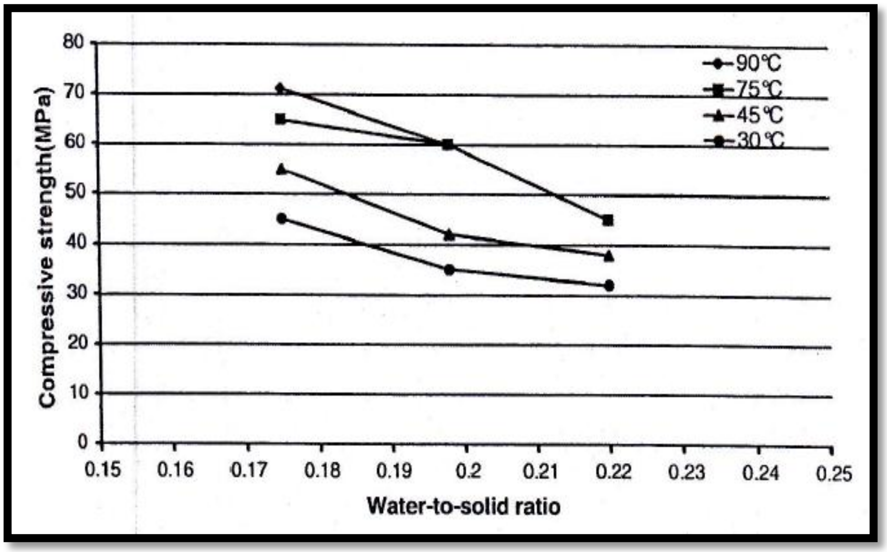


Figure 14: Effect of water to solid ratio on compressive strength at different curing temperature. (Divya Khale, 2007)

2.4 Experiments and Tests Based on Previous Studies on Geopolymer Cements

In this section, some of the previous experiments and tests conducted on geopolymer cements will be discussed. Whitfield reported on the mechanism of compressive strength, based on pressurized curing, whereby the compressive strength of cement increases due to the infiltration of water into the cement particles when the cement paste is cured by pressurizing (Whitfiled, 1953). Yoshimoto suggested that the cause of this fluctuation in the compressive strength of cement under high pressure is due to the variations in the curing mechanism of the hydration pressure in the gel part and in the internal pore pressure in the specimens. These findings are of great significance to learning about compressive strength characteristics of geopolymer cements (Yoshimoto, 1976).

Tamano illustrated the compressive strength characteristic of cements by studying the case of a buried pile construction in which the compressive strength of a sample specimen obtained by core boring was found to increase with the depth of the sample which was composed of the same material as that taken from the underground pile (Tamano, 2004). In addition, Consoli reported that progressive consolidation leads to an increase in compressive strength (Consoli, 2000). However, it is necessary to accurately grasp the mechanism behind the difference in compressive strength between the sample collected from core boring in its original state in situ along the depth direction of the underground and the specimen at room temperature under atmospheric conditions. From this perspective, a series of experiments pertaining to the relation among the compressive strength, the testing method and the curing of the geopolymer cements should be carried out (Masanobu Kanaoka, 2008).

Originally, it was felt that the set cement required a compressive strength at least equal to that of the producing formation. In 1957, Craft published a study of west Texas and east New Mexico producing formations. He found that compressive strengths ranged from 8251 psi to 22500 psi. However, most set cements will only exhibit an ultimate compressive strength in the range of 5000 to 9000 psi. Since primary cementing jobs had been reasonably successful, the comparative compressive strength theory was dispelled. However, it was still felt that the more was better (David Mack, 2012).

In a research conducted by Andri Kusbiantoro, the effect of microwave incinerated rice husk ash on the compressive and bond strength of fly ash based geopolymer concrete has been studied. The MIRHA was obtained from the incineration process in Microwave Incinerator at 800˚C and then was grounded in ball mill for 2000 cycles. MIRHA was introduced into the mixture to replace certain portions of fly ash content as the source material. Activation of these source materials were completed through the inclusion of sodium hydroxide and sodium silicate solution. One kg of 8M sodium hydroxide solution was prepared by diluting 297 gram of sodium hydroxide pellets with 703 gram of water. To prevent the excess heat from sodium hydroxide dissolution, these solutions were prepared one hour before the mixing process (Andri Kusbiantoro, 2012).

To observe the effect of temperature on the geopolymer concrete properties, three curing regimes were conducted in the researches which were ambient, external exposure and oven curing. In ambient curing, the concrete specimens were placed at the shaded area with maximum temperature of 36˚C. These specimens were constantly protected from direct sunlight and rainfall until the testing days. Meanwhile concrete specimens in external exposure curing were placed in a plastic chamber placed at a non-protected area, exposed to direct sunlight yet protected from rainfall. The maximum temperature in the external exposure method reached 56˚C. All these specimens were kept in their respective curing regime until the testing day (Andri Kusbiantoro, 2012).

For comparison purpose, strength of hardened specimens was also measured based on the oven curing exposure. Freshly cast specimens were given 1 hour delay time before they were placed into the oven. The specimens were placed in electrical oven with temperature 65˚C for 24 hours. After 24 hours, all the specimens in the respective curing conditions were de-moulded and placed back at their initial position, except for the oven curing specimens where they were re-placed at the ambient condition. Geopolymer concrete specimens were then tested on their compressive strength and bonding capacity after 3, 7 and 28 curing days. Pull out test was conducted to determine the bonding capacity of geopolymer concrete through direct tension force (Andri Kusbiantoro, 2012). **Figure 15**, **Figure 16** and **Figure 17** shows the results of the experiments.

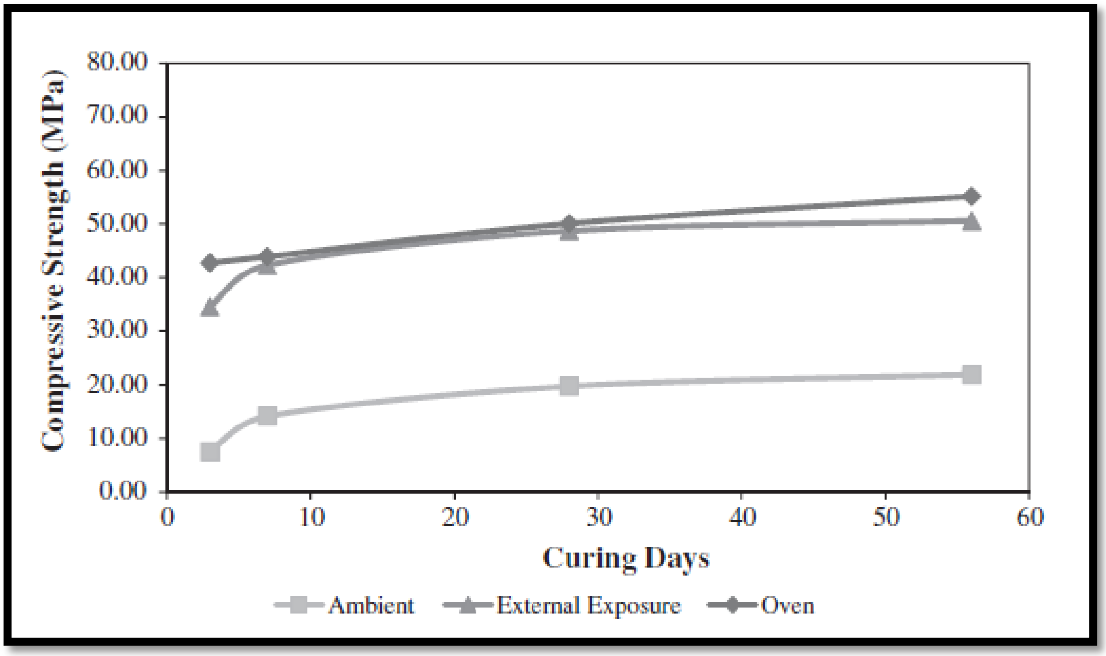


Figure 15: Compressive strength of fly ash based geopolymer concrete with 0% MIRHA (Andri Kusbiantoro, 2012).

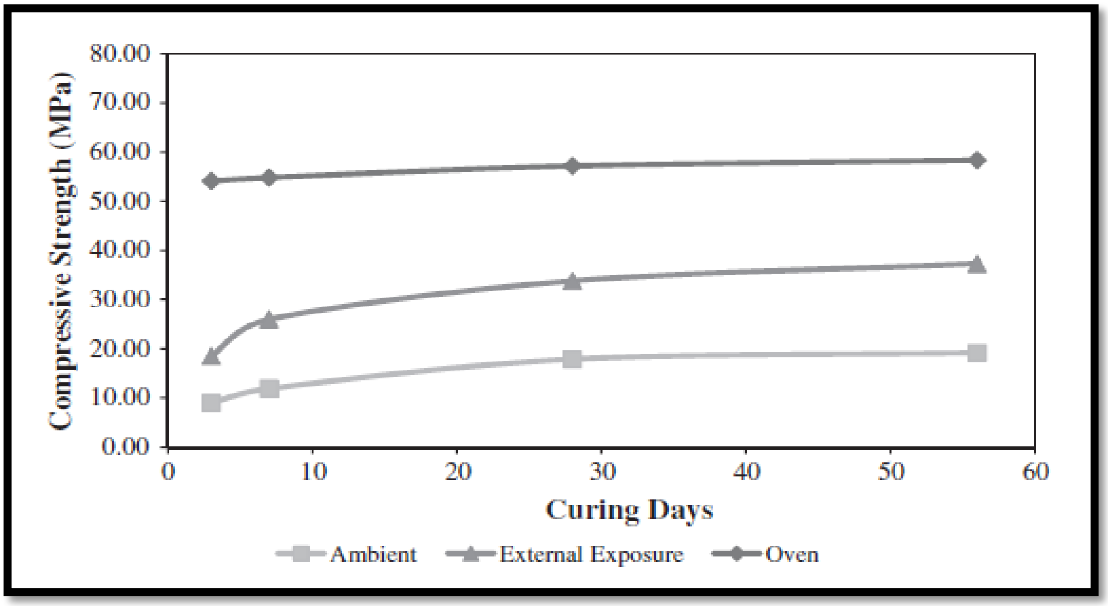


Figure 16: Compressive strength of fly ash based geopolymer concrete with 3% MIRHA (Andri Kusbiantoro, 2012).

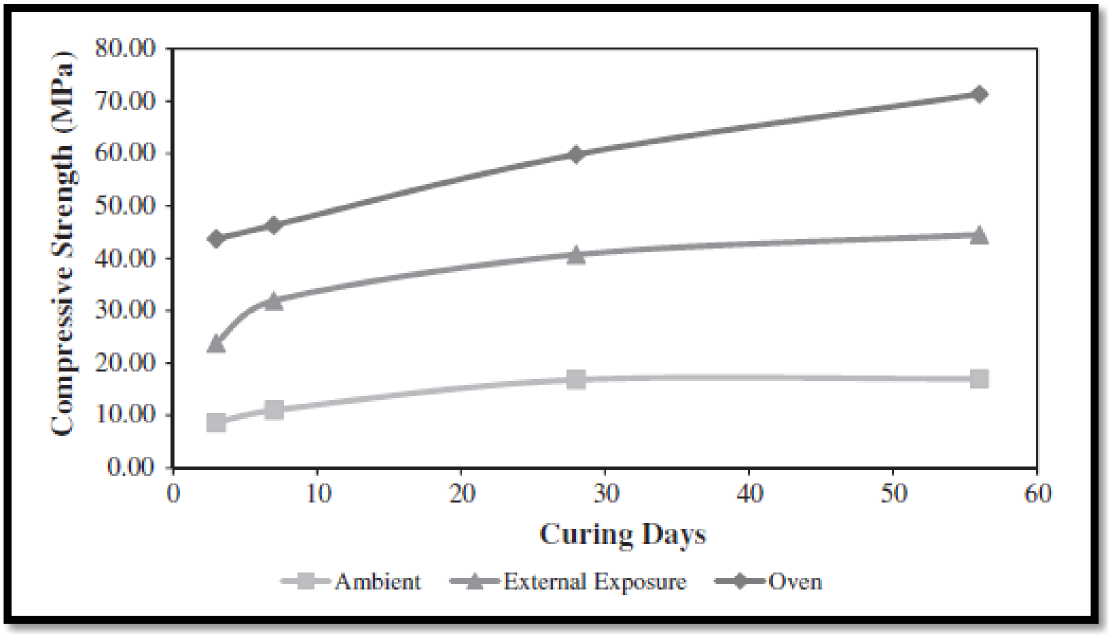


Figure 17: Compressive strength of fly ash based geopolymer concrete with 7% MIRHA (Andri Kusbiantoro, 2012).

Compressive strength development of hardened geopolymer concrete is the basic indicator to the performance of alternative source material, since it provides a fundamental description on the quality of geopolymerization products. It is obviously presented in those figures how the contribution of MIRHA to the fly ash based geopolymer concrete strength development is limited to certain stage. The increment of temperature from ambient and external exposure curing presents a consistent strength development trend. The excessive amount of water in the ambient-cured specimens has hindered the polycondensation process and resulted in a lower compressive strength than external exposure curing. It is a notorious fact that hydroxide activity is significantly affected by the excessive water content in the geopolymer concrete system (Andri Kusbiantoro, 2012).

The temperature during curing is very important and depending upon the source materials and activating solution, heat often must be applied to facilitate polymerization, although some systems have been developed that are designed to be cured at room temperature (Davidovits J. , July 2011). **Figure 18**, for example, shows the compressive strength of two geopolymer mixtures, illustrating the importance of curing temperature on 7 days strength development.

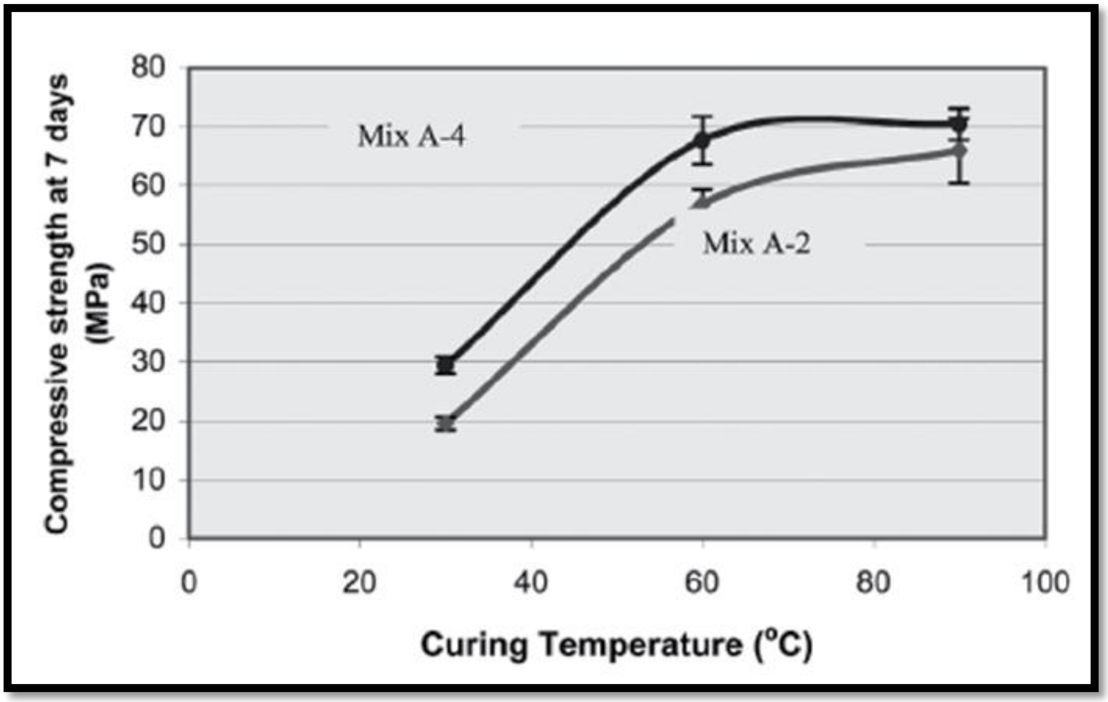


Figure 18: Effect of curing temperature on 7 days compressive strength for two geopolymer concretes (TechBrief: Geopolymer Concrete, 2010).

In another study by Kamal, the influence of burning temperatures and percentage inclusion of MIRHA on normal strength concrete was investigated. Burning the MIRHA with higher temperatures increases the silicon dioxide content but it not suggested to burn rice husk above 800˚C longer than one hour because it tends to cause a sintering effect and is indicated by a dramatic reduction in the specific surface (Kamal, 2008). **Figure 19** and **Figure 20** shows the results of the experiments. From the result, compressive strength developments of MIRHA concrete are significantly higher compared to control concrete. All MIRHA concrete samples, 20%, 15%, 10% and 5% additions of MIRHA had slightly different of strength development at early days but after 28 days the result show 10% MIRHA achieved 3.4% higher than 5% MIRHA concrete and 6.8% higher than 15% MIRHA and 15.3% compared to 20% MIRHA. Since the Portland cement content was reduced by replacement of MIRHA, the lower hydration process was the reason of lower strength of 20%, 15% and 5% MIRHA concrete at early days. Pozzolanic reaction in 10% MIRHA concrete showed more rapid development in producing C-S-H gel as indicated by the increment percentage of compressive strength, which indicate that 10% is the optimum level of replacement.

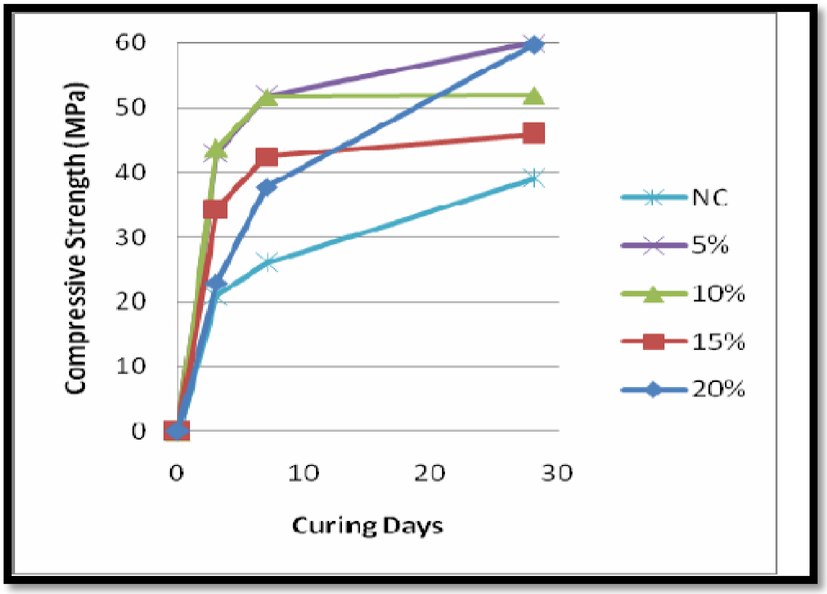


Figure 19: Compressive strength development of concrete sample with MIRHA at 800˚ C (Kamal, 2008)

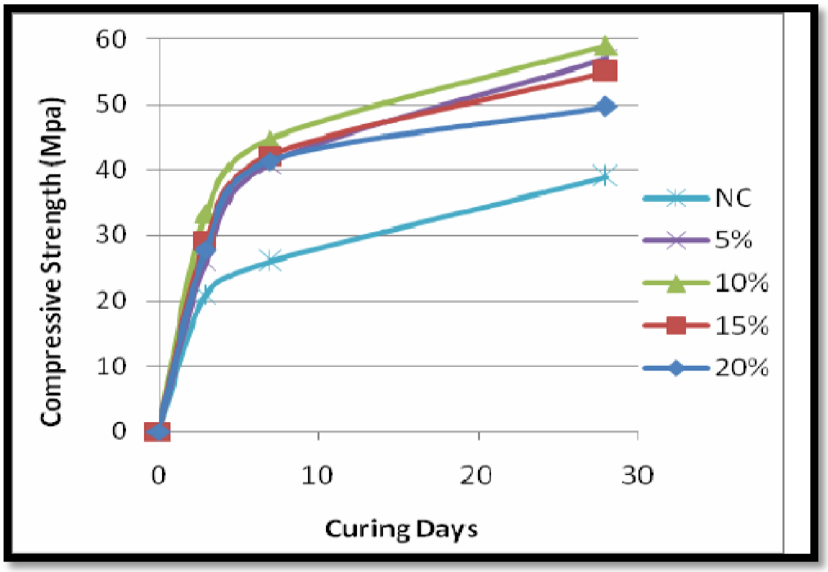
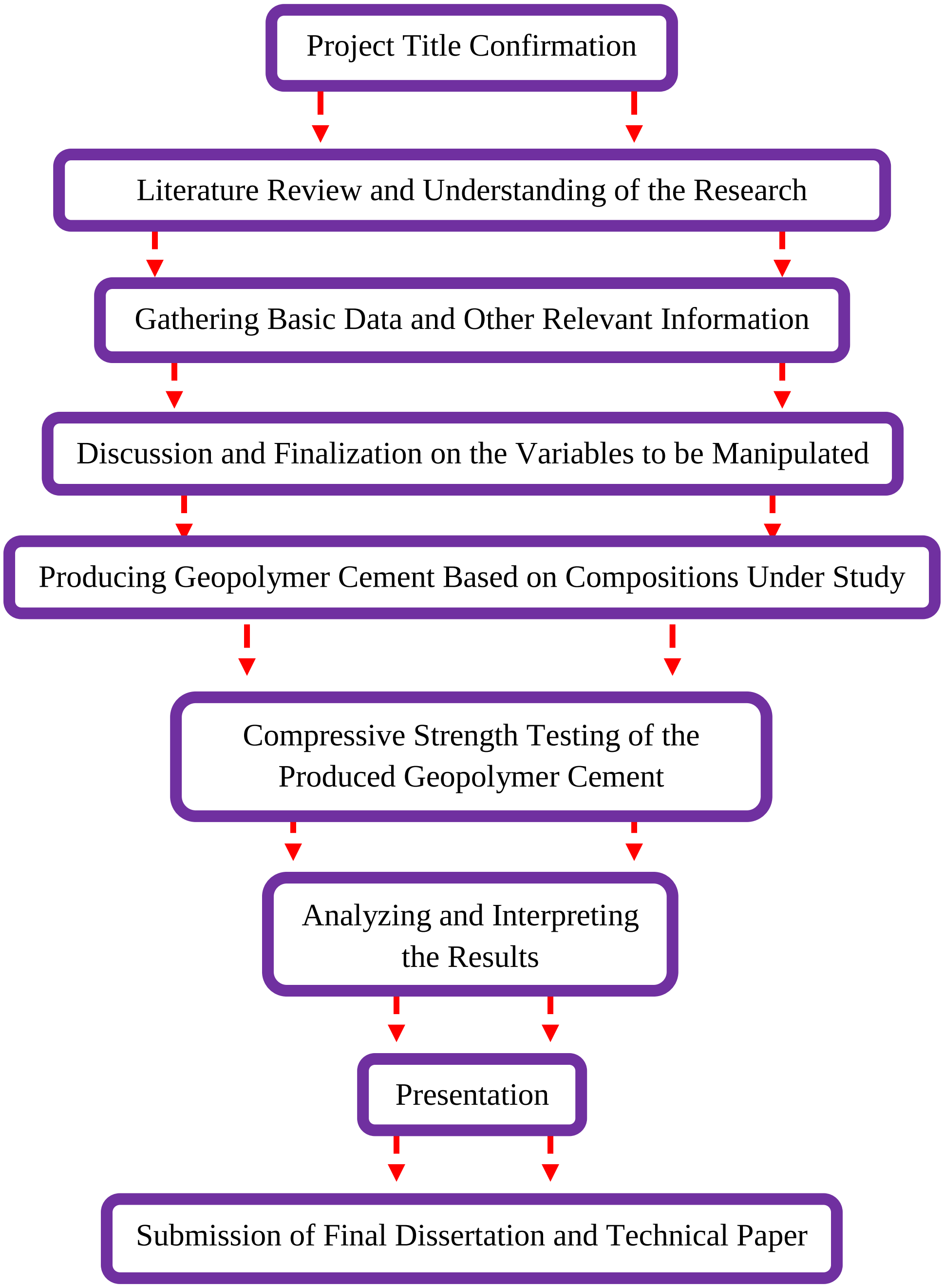


Figure 20: Compressive strength development of concrete sample with MIRHA at 700˚ C (Kamal, 2008)

CHAPTER 3

METHODOLOGY

3.1 Research Methodology



3.2 Project Activities

a) Geopolymer Cement Production Procedure

1) Grease was applied to the cement moulds (50mmx50mmx50mm) to prevent the cement slurry from leaking out of the moulds during the experiments.
2) The ashes were prepared according to preferred compositions :

Table 6: Compositions of the ashes

	Rice Husk Ash (%)	Fly Ash (%)	Palm Frond Ash (%)	Total (%)
Composition 1	33.33	33.34	33.33	100
Composition 2	20	60	20	100

3) 0.4 parts of chemicals (Sodium Hydroxide and Sodium Silicate) were prepared to the mass of the ashes.
4) 2.5 parts of sodium silicate solution to the mass of sodium hydroxide solution were prepared.
5) Sodium silicate solution and sodium hydroxide solution were mixed together using a constant speed mixer for 1 minute.
6) The ashes were added into the mixer and run for 1 minute.
7) Water (10% of the weight of ashes) was added to increase the workability of the cement slurry and run the mixer for another 1 minute.
8) Step 7) was repeated for an interval of 3 times.
9) The cement slurry was filled up into the cement mould and the cement was cured at 60˚C for 24 hours in an oven.
10) After 24 hours, the cement cubes were cured at room temperature for 7 days and 14 days.

11) A total of 3 cubes were produced using the same procedure for one composition for 7 days and 14 days curing respectively.

b) Compressive Strength Testing Procedure

1) Measure the dimensions of the surface in which the load is to be applied. Let it be 'L' and 'W' respectively. Since it is standardized mould of 50 mm X 50 mm, the cross-section area is constant at 2500 mm^2.
2) Place the cube in compressive strength tester and apply load uniformly.
3) Note the load at which the cube fails. Let it be '$\boldsymbol{F_i}$'.
4) Calculate the compressive strength of the cube.
5) Repeat the same procedure with the remaining 2 cubes.
6) 3 cubes should be tested and its average should be taken as its final compressive strength.
7) The calculation of compressive strength is done by using the following formula.

$$\boldsymbol{\sigma_i = \frac{F_i}{A_i}}$$

Where;

σ_i = the compressive strength, N/mm^2

F_i = the maximum load, N

A_i = the cross-section area at which load is applied, mm^2

8) In this project, an advanced compressive strength tester is used, thus, load was applied on the cube and complete data regarding the compressive strength of the cube was produced. The reading was recorded and steps 5) and 6) were repeated.

3.3 Key Milestones

SEMESTER MAY 2013 (WEEK 1-WEEK 14)

1	Confirming project title.
2-3	Doing literature review and understanding the research.
4	Gathering basic data and other relevant information needed to progress with the research.
5-7	Producing geopolymer cement based on compositions under study and also subsequent compressive strength testing.
8-9	Submitting progress report. Project work continues with necessary modifications for desired results.
10-11	Presenting in Pre-SEDEX. Submission of draft report of the research.
12-13	Submission of Dissertation soft bound and Technical Paper hard bound. Presenting for Oral Presentation.
14	Final Dissertation submission.

3.4 Gantt Chart

	SEMESTER MAY 2013 (WEEK 1 – WEEK 14)													
ACTIVITIES	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Title Confirmation	🟥													
Preliminary Research Work ➢ Literature Review ➢ Rheology ➢ Basics of Rheology		🟥	🟥											
Gathering Basic Data and Information				🟥										
Geopolymer Cement Production					🟥	🟥								
Compressive Strength Testing						🟥	🟥	🟥						
Analyzing and Interpreting Results							🟥	🟥						
Submission of Progress Report								🟥						
Modifications or Adjustments to Project Work to Obtain a More Desirable Result									🟥	🟥				
Pre-SEDEX										🟥				
Submission of Draft Report											🟥			
Submission of Dissertation												🟥		
Submission of Technical Paper												🟥		
Oral Presentation													🟥	
Submission of Project Dissertation														🟥

3.5 Materials and Equipments

Tools are necessary elements required in completing a project. The selection of tools depends solely on the nature of the project as well as the expected outcome of the project. Therefore, in this research, materials and equipments utilized for the success of the project are explained below.

3.5.1 Materials

a) Microwave Incinerated Rice Husk Ash (MIRHA)

b) Fly Ash (FA)

c) Palm Frond Ash (POFA)

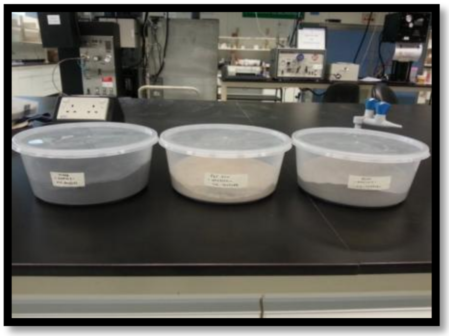


Figure 21: MIRHA, FA and POFA used in the research, respectively.

Figure 22: Sample of MIRHA, FA and POFA for presentation purposes.

d) Sodium Hydroxide Solution

e) Sodium Silicate Solution

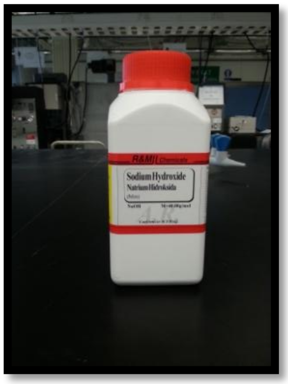


Figure 23: Bottle of sodium hydroxide pellets.

Figure 24: Prepared 12M sodium hydroxide solution.

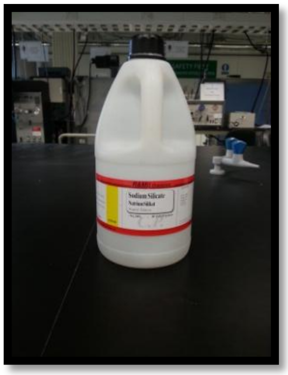


Figure 25: Sodium silicate solution.

3.5.2 Equipments

a) Microwave Incinerator

Figure 26: Microwave Incinerator

Details :	Microwave incinerator is a configured machine to incinerate waste material. Microwave incinerator which is available at Universiti Teknologi Petronas will be used to burn down rice husk to produce ash at a temperature of 800˚C for 24 hours

b) Grinding Machine

Figure 27: Grinding Machine

Details :	Grinding machine is a machine tool used for grinding. Grinding machine which is available in Universiti Teknologi Petronas will be used to grind the rice hush ask for 2000 revolutions of the grinder.

c) Sieve Shaker Set

Figure 28: Sieve Shaker Set

Details :	The sieve shaker set is a vibrating shaker that is used to carry out sieve tests in conjunction with sieve for particle sizing of various material samples. All the three raw materials, rice husk ash, fly ash and palm frond ash will be sieved before being used to ensure only small sized particles will be used in for the research purposes.

d) Weighing Scale

Figure 29: Weighing Scale

Details :	Weighing scale is a tool used to measure the mass of materials. It plays a major role in this research in determining the correct proportions of materials for cement mixing procedures

e) Constant Speed Mixer

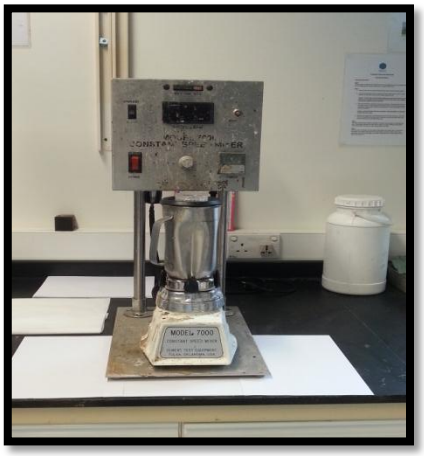


Figure 30: Constant Speed Mixer

Details :	Constant Speed Mixer is used to prepare cement slurry with specific properties and also to mix cement slurries at specific speeds and timer. It plays a paramount role in this research.

f) Compressive Strength Tester

Figure 31: Compressive Strength Tester

Details :	Automated compressive strength tester is designed to determine the compressive strength of well cement. The most common means of determining the compressive strength of cement involves applying a force to the sample at constant rate until the sample fails. The maximum loading at which the cement fails is defined as the cement's compressive strength.

g) Roller Oven

Figure 32: Roller Oven

Details :	Roller oven will be used to cure the cement slurry in the mould for a period of 1 day at a temperature of 60℃. Later, the produced cement cubes will be cured at ambient temperature for the required period.

h) Cement Moulds

Figure 33: Cement Moulds

Details :	Cement moulds as shown in the figure will be used to produce the geopolymer cement cubes for compressive testing purposes. It is of dimension 50mm x 50mm x 50mm.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Findings

4.1.1 Cement Slurry Proportion Calculations

The calculations made are based on the amount of materials needed to produce 3 cement cubes. According to researches done by post graduate students on geopolymer cements in Universiti Teknologi Petronas, a total of 600 gram of raw materials or ash is required to produce 3 cement cubes of 50mm x 50mm x 50mm.

a) **Composition 1**

Table 7: Mass and proportions of ashes used in Composition 1.

	Rice Husk Ash	Fly Ash	Palm Frond Ash	Total
Mass (gram)	200	200	200	600
Percentage (%)	33.33	33.34	33.33	100

Table 8: Mass and remarks of solutions used in Composition 1

	Chemical Solutions	Sodium Hydroxide	Sodium Silicate	Water
Mass (gram)	240	68.57	171.43	60
Remarks	0.4 parts of the total mass of ashes.	0.285 parts of the mass of chemical solutions.	0.715 parts of the mass of chemical solutions.	0.1 parts of the total mass of ashes.

b) Composition 2

Table 9: Mass and proportions of ashes used in Composition 2

	Rice Husk Ash	Fly Ash	Palm Frond Ash	Total
Mass (gram)	120	360	120	600
Percentage (%)	20	60	20	100

Table 10: Mass and remarks of solutions used in Composition 2

	Chemical Solutions	Sodium Hydroxide	Sodium Silicate	Water
Mass (gram)	240	68.57	171.43	60
Remarks	0.4 parts of the total mass of ashes.	0.285 parts of the mass of chemical solutions.	0.715 parts of the mass of chemical solutions.	0.1 parts of the total mass of ashes.

4.1.2 Cement Cubes Production

Following the calculations made on the proportions of raw materials and solutions, the cement slurry for both the different compositions were made and poured into the cement moulds. A total of 12 cement cubes were made, where 6 cubes is for one particular composition. Under one composition, 2 different curing time was studied which were 7 days curing and also 14 days curing. Three cubes were used for one curing period to obtain the average value of compressive strength for reliable results. Figures below shows the cement slurries in the mould, the produced cement cubes and also sample of ashes used for Fourier Transform Infrared Analysis (FTIR) which will be discussed later.

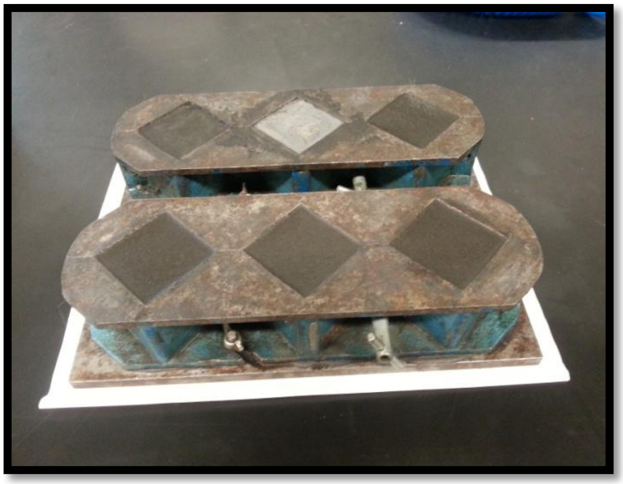


Figure 34: Cement slurry of Composition 1 in the moulds.

Figure 35: Cement slurry of Composition 2 in the moulds.

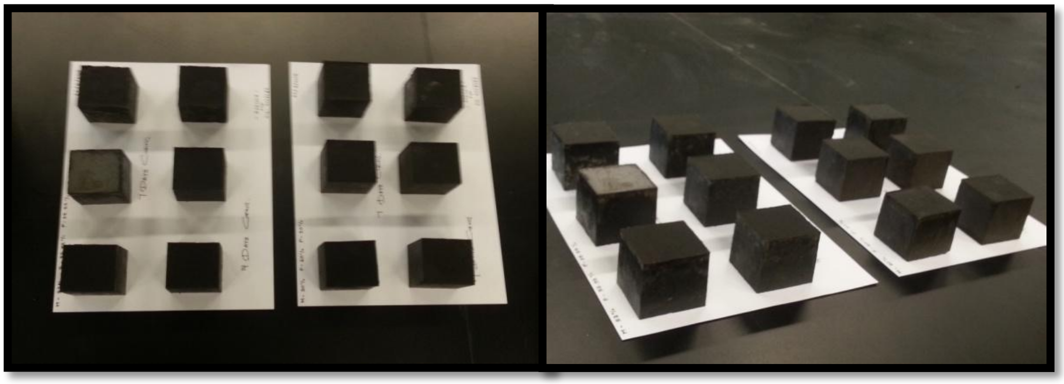


Figure 36: Produced cement cubes for 7 days and 14 days curing respectively.

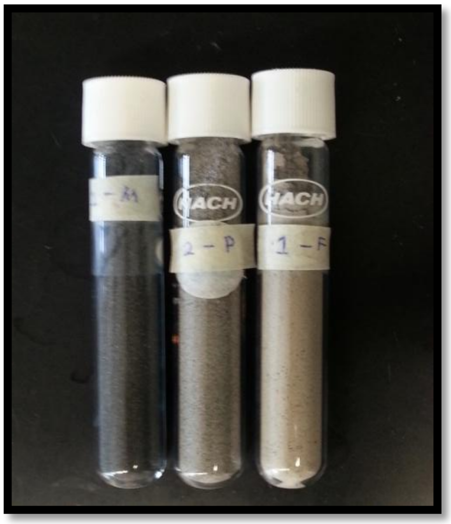


Figure 37: Samples of MIRHA, FA and POFA for FTIR.

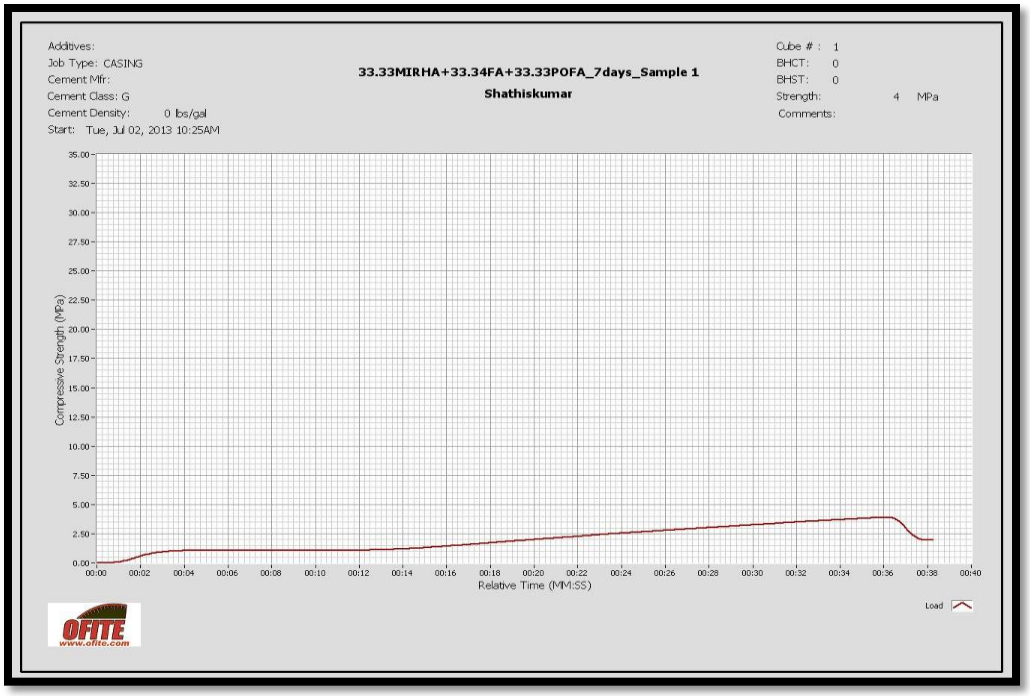
4.2 Results

4.2.1 Compressive Strength Testing Results

After the respective curing periods, the compressive strength of the cement cubes was tested using the advanced compressive strength tester. 3 samples were used for one composition under one curing period where the average value has been taken as the reliable compressive strength. This case is unlikely in cubes produced for Composition 1 under 7 days curing where only 2 cubes were used to produce the average value. The following figures shows the results obtained from the advanced compressive strength tester and the condition of the cement cubes after the testing procedure. Detailed readings of the tester can be found in **Appendix 1- 11**.

a) 7 days curing

i) Composition 1



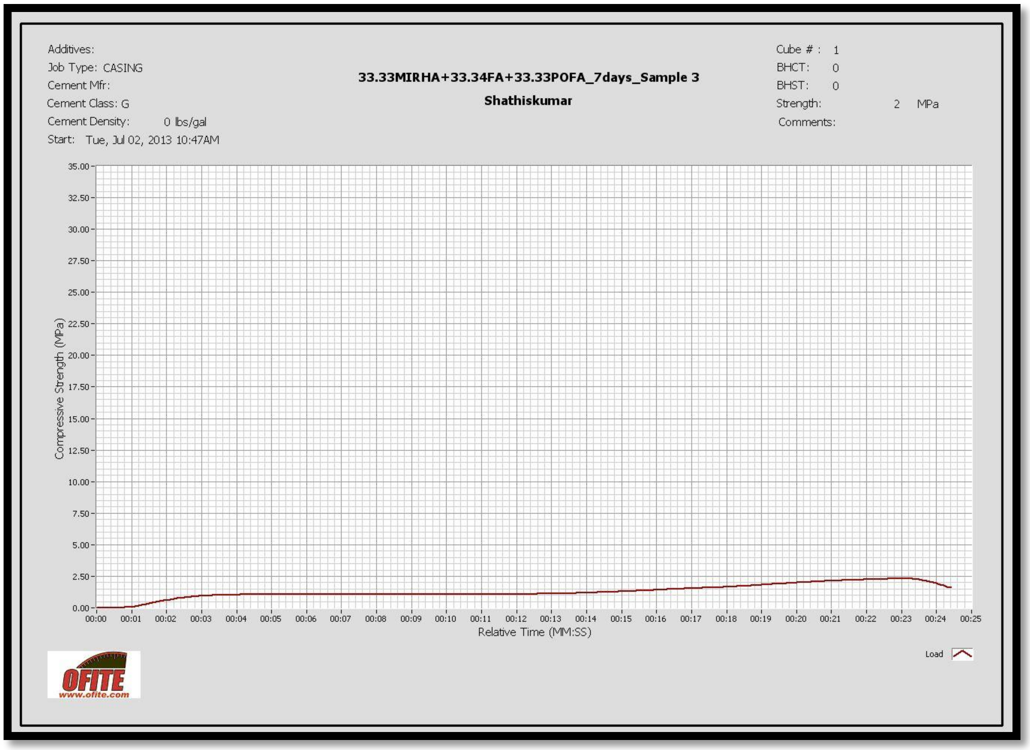
Additives:
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Tue, Jul 02, 2013 10:25AM

33.33MIRHA+33.34FA+33.33POFA_7days_Sample 1
Shathiskumar

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 38: Compressive strength result of sample 1 of 7 days curing of Composition 1.

Figure 38 shows a peak value of 3.87 MPa of compressive strength for sample 1 of 7 days curing of Composition 1.



Additives:
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Tue, Jul 02, 2013 10:47AM

33.33MIRHA+33.34FA+33.33POFA_7days_Sample 3

Shathiskumar

Cube # : 1
BHCT: 0
BHST: 0
Strength: 2 MPa
Comments:

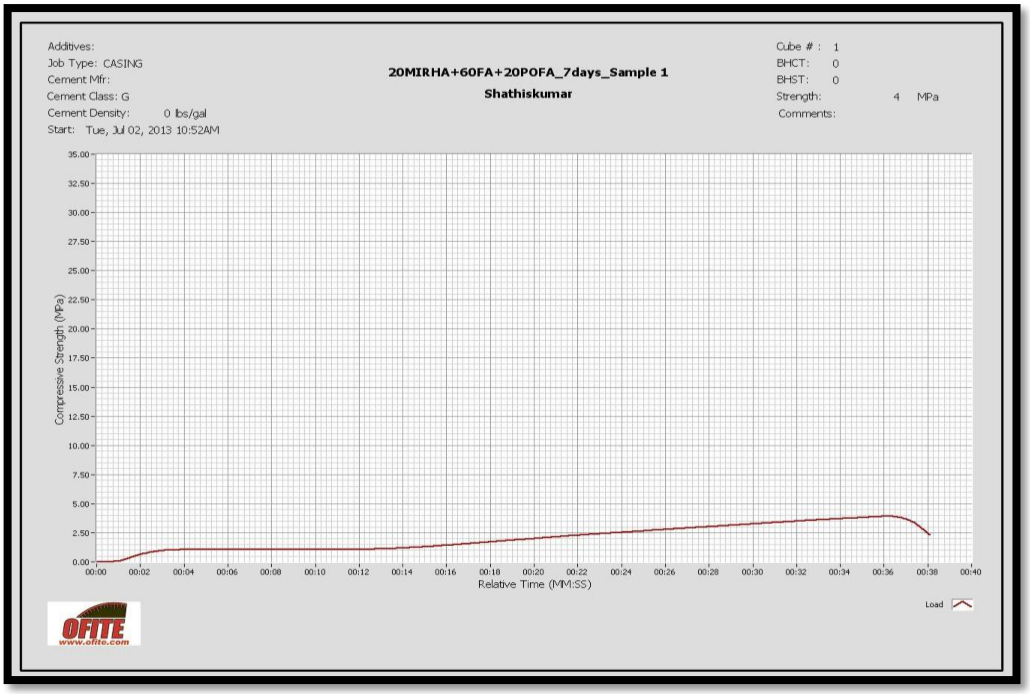
Figure 39: Compressive strength result of sample 2 of 7 days curing of Composition 1.

Figure 39 shows a peak value of 2.32 MPa of compressive strength for sample 2 of 7 days curing of Composition 1. The compressive strength value obtained for sample 2 is lower if compared to sample 1.

Figure 40: Crushed cement cubes of 7 days curing of Composition 1.

Figure 40 shows the condition of the cement cubes after compressive strength testing of cubes of 7 days curing of Composition 1.

ii) Composition 2



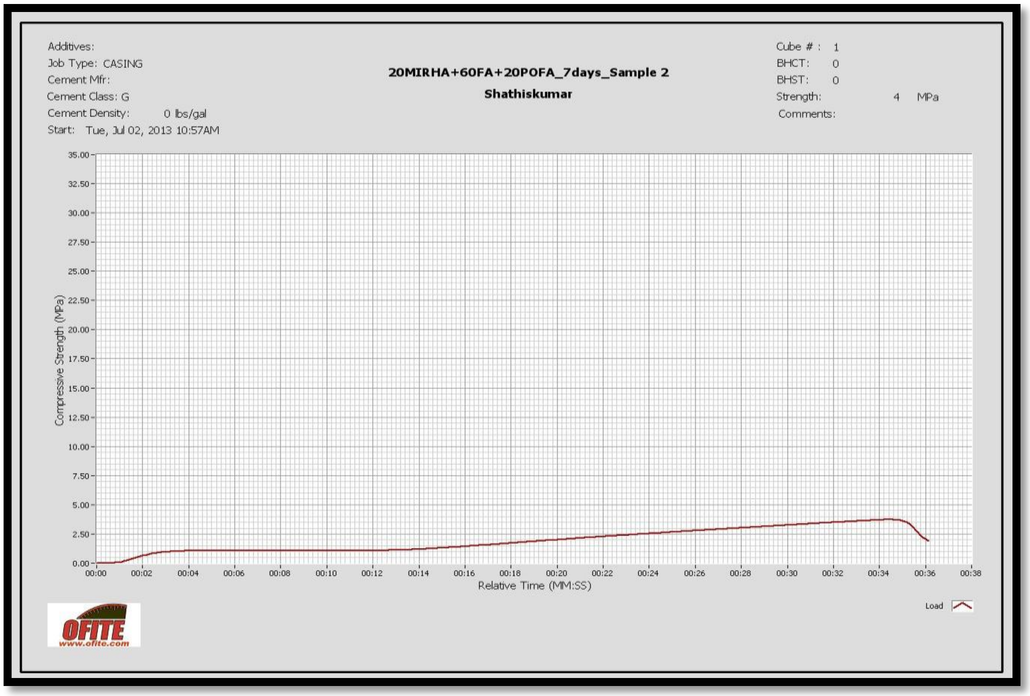
Additives:
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Tue, Jul 02, 2013 10:52AM

20MIRHA+60FA+20POFA_7days_Sample 1
Shathiskumar

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 41: Compressive strength result of sample 1 of 7 days curing of Composition 2.

Figure 41 shows a peak value of 3.63 MPa of compressive strength for sample 1 of 7 days curing of Composition 2.



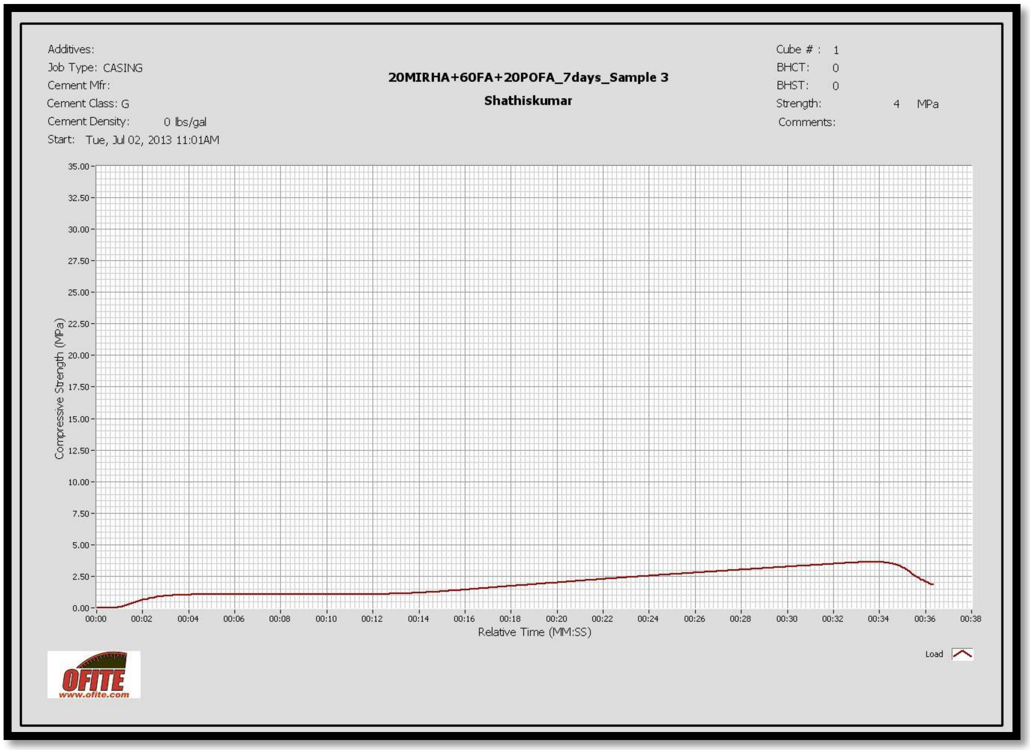
Additives:
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Tue, Jul 02, 2013 10:57AM

20MIRHA+60FA+20POFA_7days_Sample 2
Shathiskumar

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 42: Compressive strength result of sample 2 of 7 days curing of Composition 2.

Figure 42 shows a peak value of 3.73 MPa of compressive strength for sample 2 of 7 days curing of Composition 2. The compressive strength value obtained for sample 2 is higher if compared to sample 1.



Additives:
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Tue, Jul 02, 2013 11:01AM

20MIRHA+60FA+20POFA_7days_Sample 3
Shathiskumar

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 43: Compressive strength result of sample 3 of 7 days curing of Composition 2.

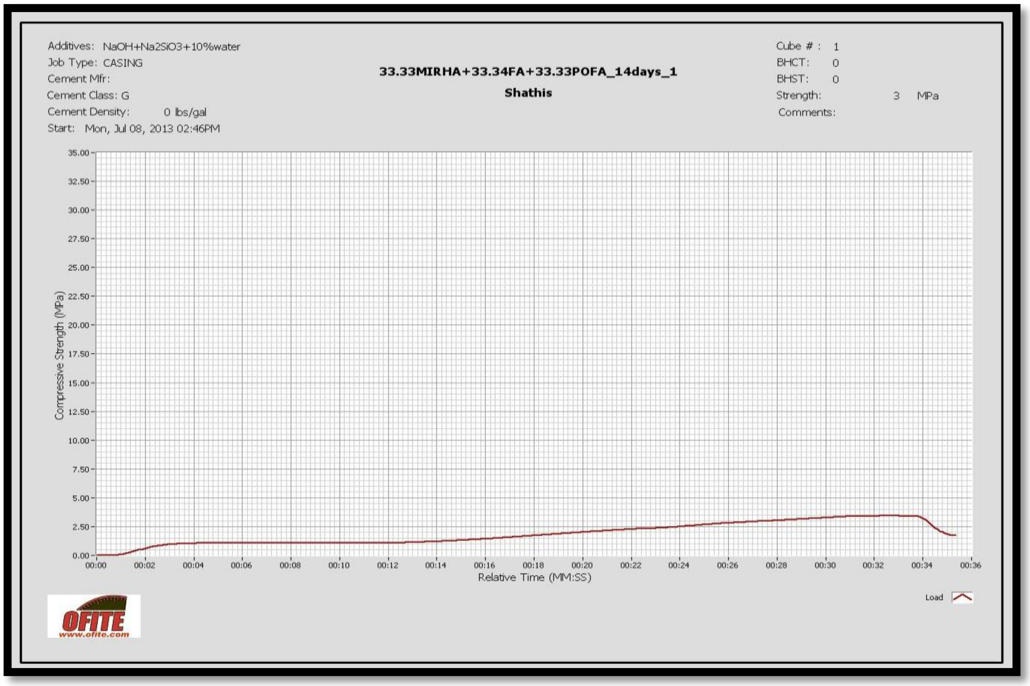
Figure 43 shows a peak value of 3.91 MPa of compressive strength for sample 3 of 7 days curing of Composition 2. The compressive strength value obtained for sample 2 is higher if compared to sample 1 and sample 2.

Figure 44: Crushed cement cubes of 7 days curing of Composition 2.

Figure 44 shows the condition of the cement cubes after compressive strength testing of cubes of 7 days curing of Composition 2.

b) 14 days curing

i) Composition 1



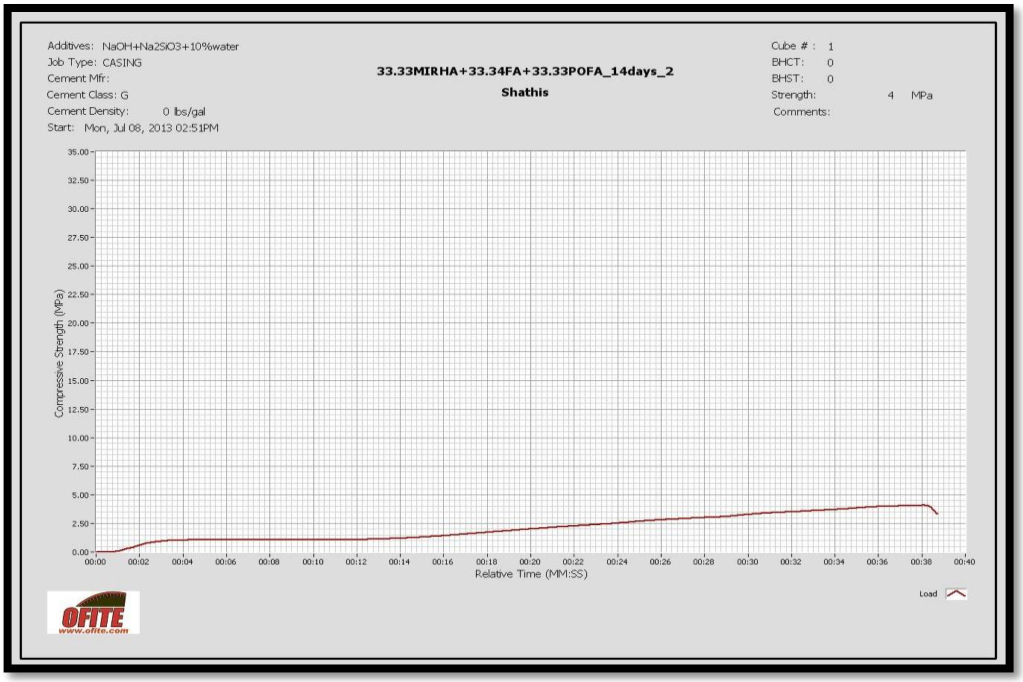
Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 02:46PM

33.33MIRHA+33.34FA+33.33POFA_14days_1
Shathis

Cube # : 1
BHCT: 0
BHST: 0
Strength: 3 MPa
Comments:

Figure 45:Compressive strength result of sample 1 of 14 days curing of Composition 1.

Figure 45 shows a peak value of 3.44 MPa of compressive strength for sample 1 of 14 days curing of Composition 1.

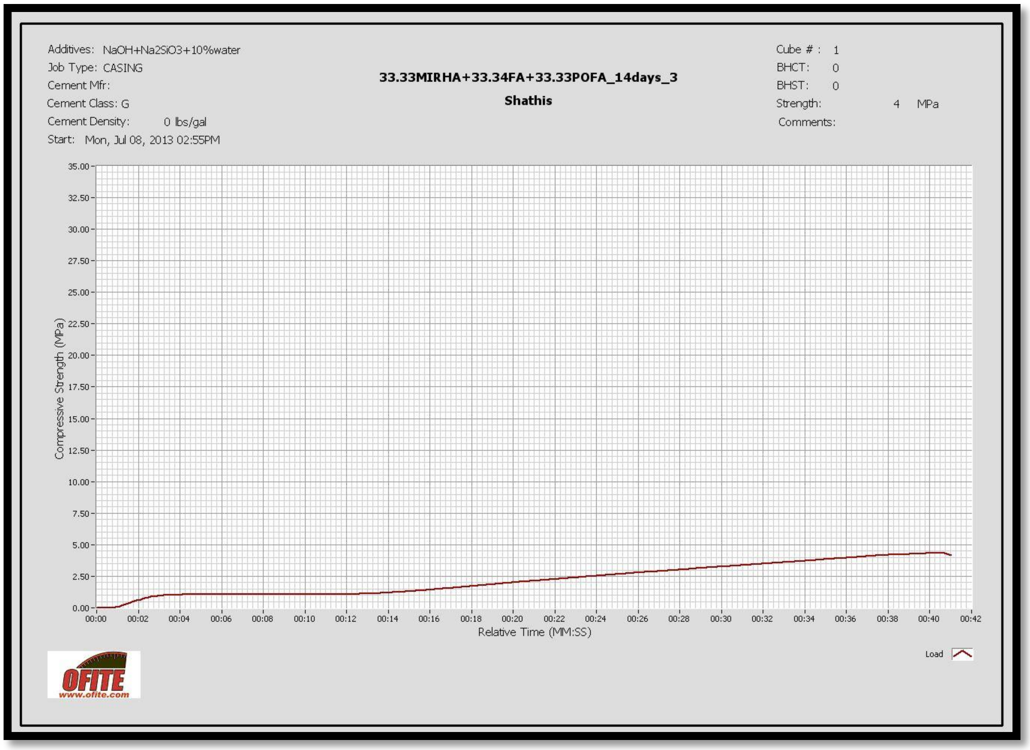

Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 02:51PM

33.33MIRHA+33.34FA+33.33POFA_14days_2
Shathis

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 46:Compressive strength result of sample 2 of 14 days curing of Composition 1.

Figure 46 shows a peak value of 4.08 MPa of compressive strength for sample 2 of 14 days curing of Composition 1. The value of compressive strength obtained for sample 2 is higher than the value obtained for sample 1.


33.33MIRHA+33.34FA+33.33POFA_14days_3

Shathis

Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 02:55PM

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

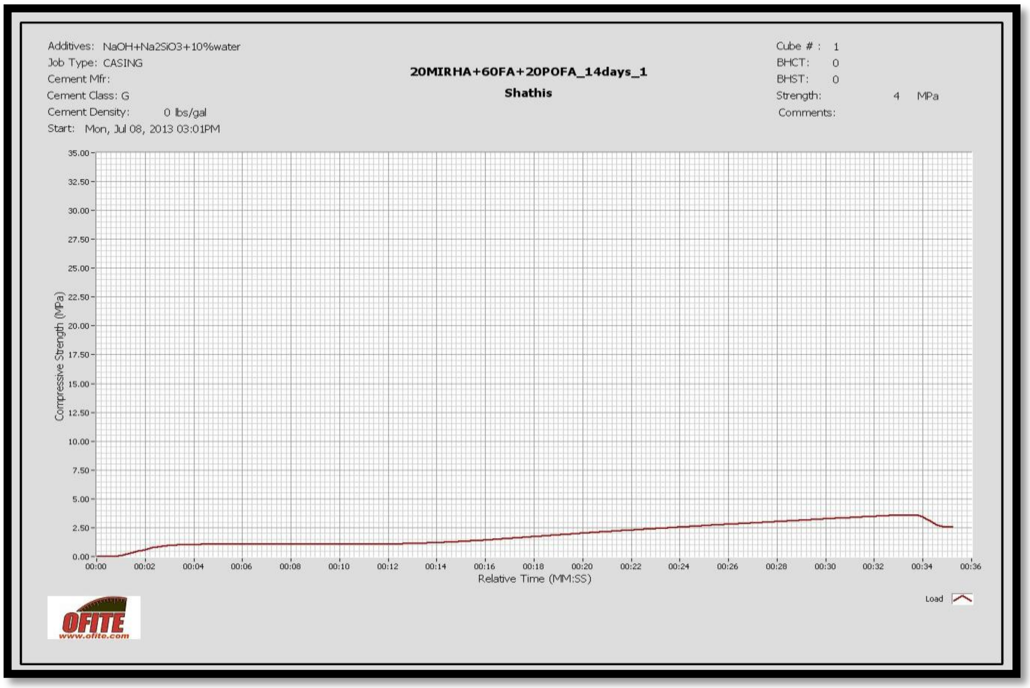
Figure 47:Compressive strength result of sample 3 of 14 days curing of Composition 1.

Figure 47 shows a peak value of 3.95 MPa of compressive strength for sample 3 of 14 days curing of Composition 1. The value of compressive strength obtained for sample 3 is higher than the value obtained for sample 1 but lower than the compressive strength value obtained for sample 2.

Figure 48: Crushed cement cubes of 14 days curing of Composition 1.

Figure 48 shows the condition of the cement cubes after compressive strength testing of cubes of 14 days curing of Composition 1.

ii) Composition 2



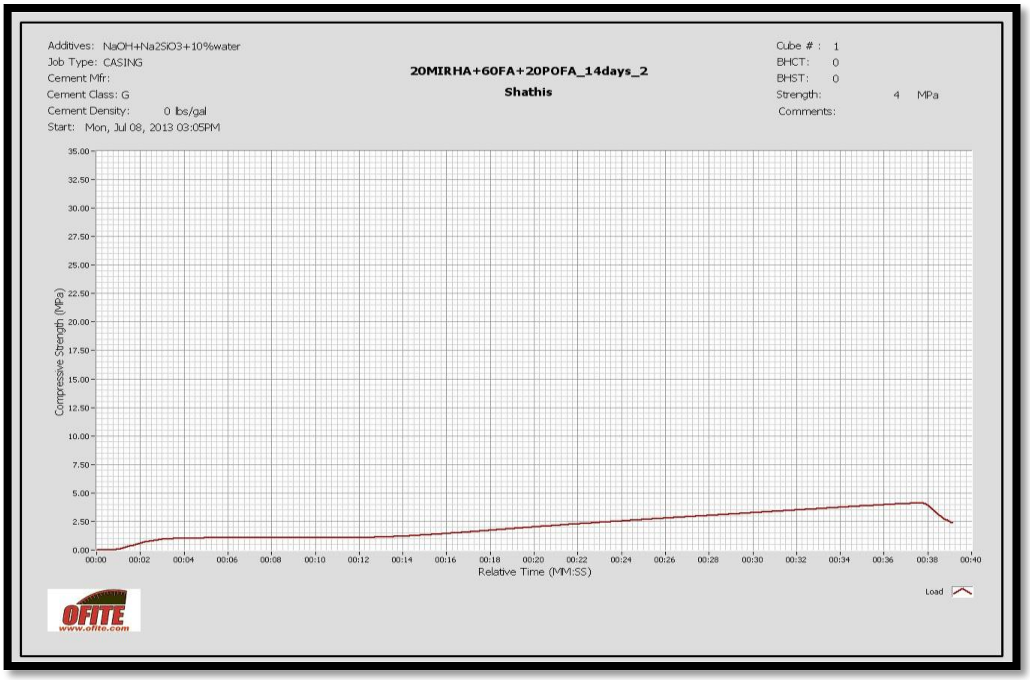
Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 03:01PM

20MIRHA+60FA+20POFA_14days_1
Shathis

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 49:Compressive strength result of sample 1 of 14 days curing of Composition 2.

Figure 49 shows a peak value of 3.59 MPa of compressive strength for sample 1 of 14 days curing of Composition 2.



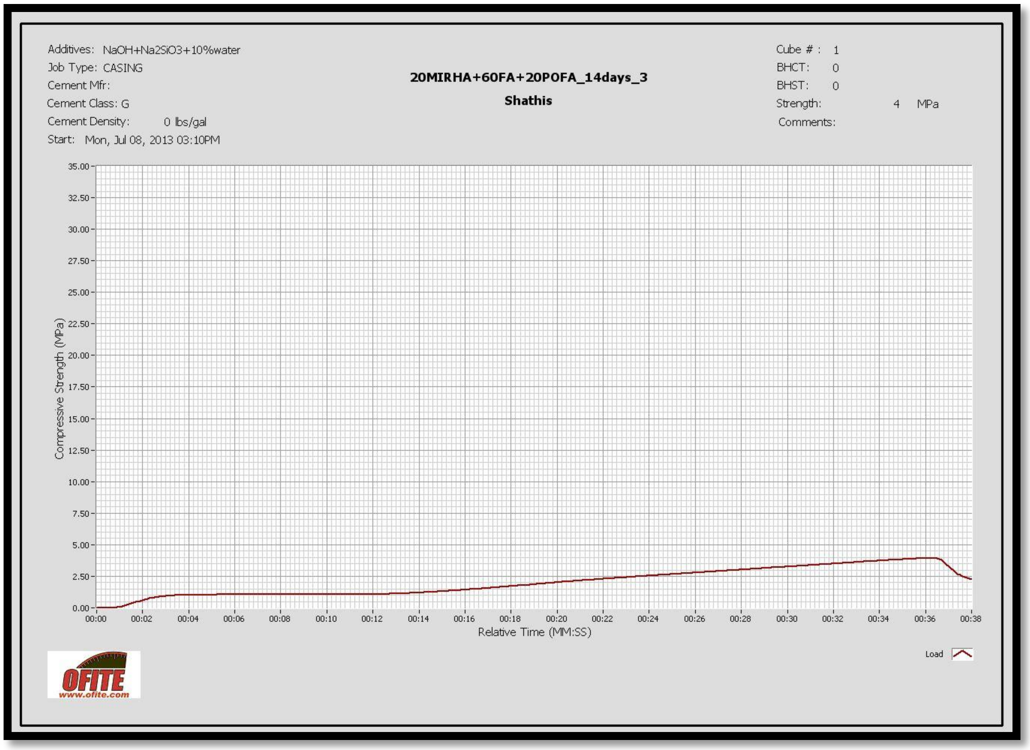
Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 03:05PM

20MIRHA+60FA+20POFA_14days_2
Shathis

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 50:Compressive strength result of sample 2 of 14 days curing of Composition 2.

Figure 50 shows a peak value of 4.09 MPa of compressive strength for sample 2 of 14 days curing of Composition 2. The value of compressive strength obtained for sample 2 is higher than the value obtained for sample 1.



Additives: NaOH+Na2SiO3+10%water
Job Type: CASING
Cement Mfr:
Cement Class: G
Cement Density: 0 lbs/gal
Start: Mon, Jul 08, 2013 03:10PM

20MIRHA+60FA+20POFA_14days_3
Shathis

Cube # : 1
BHCT: 0
BHST: 0
Strength: 4 MPa
Comments:

Figure 51:Compressive strength result of sample 3 of 14 days curing of Composition 2.

Figure 51 shows a peak value of 4.33 MPa of compressive strength for sample 3 of 14 days curing of Composition 2. The value of compressive strength obtained for sample 3 is higher than the value obtained for sample 1 and also sample 2.

Figure 52: Crushed cement cubes of 14 days curing of Composition 2.

Figure 52 shows the condition of the cement cubes after compressive strength testing of cubes of 14 days curing of Composition 2.

4.2.2 Average Compressive Strength Calculations

Based on the results obtained from the compressive strength testing, the average compressive strength of the geopolymer cements of different compositions and respective curing days were calculated and presented in the following tables.

a) 7 days curing

i) Composition 1

Table 11 : Compressive strength testing results of Comp. 1 under 7 days curing

Cement Sample	Compressive Strength (MPa)	Average (MPa)
1	**3.87**	**3.10**
2	**2.32**	

Table 11 shows the average compressive strength value obtained for Composition 1 under 7 days curing which is 3.10 MPa.

ii) Composition 2

Table 12 : Compressive strength testing results of Comp. 2 under 7 days curing

Cement Sample	Compressive Strength (MPa)	Average (MPa)
1	**3.63**	**3.76**
2	**3.73**	
3	**3.91**	

Table 12 shows the average compressive strength value obtained for Composition 2 under 7 days curing which is 3.76 MPa. This value is greater than the value obtained for the same curing period which is 7 days but using composition 1.

b) 14 days curing

i) Composition 1

Table 13 : Compressive strength testing results of Comp. 1 under 14 days curing

Cement Sample	Compressive Strength (MPa)	Average (MPa)
1	**3.44**	**3.82**
2	**4.08**	
3	**3.95**	

Table 13 shows the average compressive strength value obtained for Composition 1 under 14 days curing which is 3.82 MPa. This value is greater than the value obtained for the same composition but with 7 days of curing period.

ii) Composition 2

Table 14 : Compressive strength testing results of Comp. 2 under 14 days curing.

Cement Sample	Compressive Strength (MPa)	Average (MPa)
1	**3.59**	**4.00**
2	**4.09**	
3	**4.33**	

Table 14 shows the average compressive strength value obtained for Composition 2 under 14 days curing which is 4.00 MPa. This value is greater than the value obtained for the same composition but with 7 days of curing period. This value is also greater than the compressive strength value obtained for the same curing period but with composition 1.

4.2.3 Graph of Compressive Strength vs Curing Time for both Comp. 1 and 2.

Graph in **Figure 53** were plotted based on the average compressive strength results obtained from **Table 11-14**.

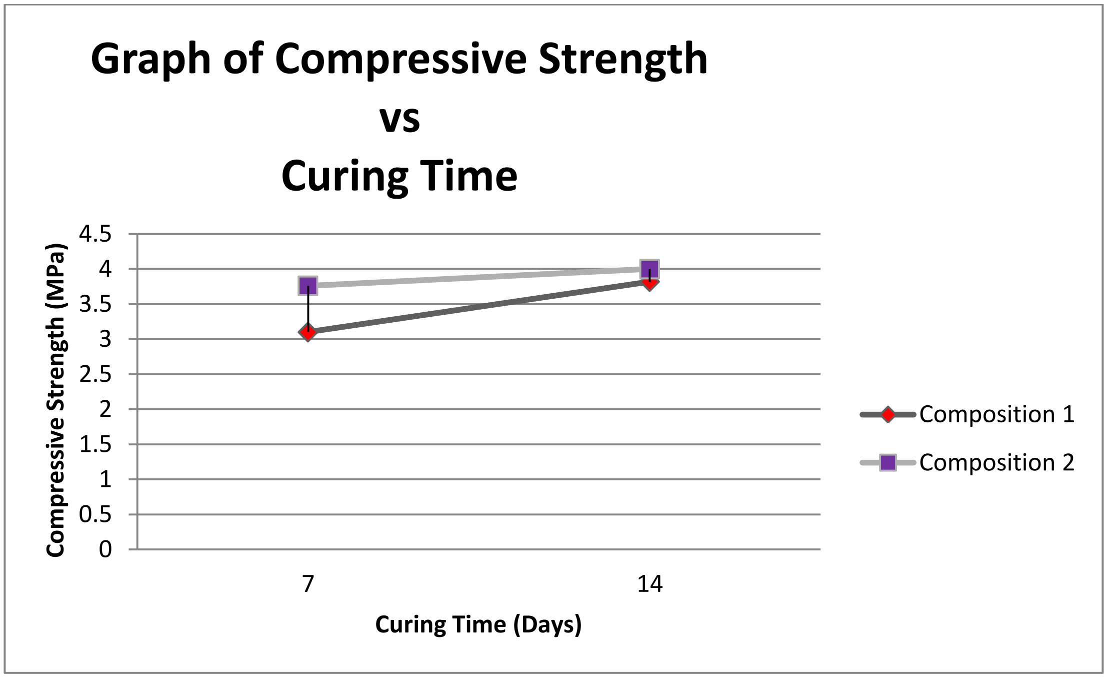


Figure 53: Graph of compressive strength vs curing time for both Composition 1 and 2.

Referring to **Figure 53**, it can be clearly stated that the compressive strength of geopolymer cement is significantly influenced by both the curing period and also the composition of the cement. The average compressive strength value of geopolymer cement of Composition 1 under 7 days curing which is 3.10 MPa is less than the average compressive strength value of geopolymer cement of Composition 2 under 7 days of curing which is 3.76 MPa. Meanwhile, under 14 days curing condition, the average compressive strength value of Composition 1 which is 3.82 MPa is less than the average compressive strength value of Composition 2 which is 4.00 MPa.

4.2.3 Fourier Transform Infra-Red (FTIR)

Infrared spectroscopy has been a widely used method for material analysis in the laboratory since the early 1930s. An infrared spectrum represents an identity of a sample with different absorption peak that correspond to the frequency of vibrations between the bonds of the atoms making up the material. There are no any compounds that share the same exact infrared spectrum, just like the uniqueness of fingerprints for each human being. This is owing to the fact that for different material, it is made up of distinct combination of atoms. Thus, it is of no surprise that infrared spectroscopy has been widely used in qualitative analysis of almost all kind of material. Besides that, the peaks in the spectrum are directly indication of the amount of the material present. With the advancement in modern software algorithms, infrared is an excellent tool for quantitative and qualitative analysis (Adiff Nafillah, 2013).

FTIR is commonly known as Fourier Transform Infra-Red, which is an outstanding method of infrared spectroscopy. Normally, an IR radiation is passed through a sample. The analyzed sample will absorbed some of the infrared radiations and allow some of the radiation to pass through it. The resulting spectrum will be detected by the detector and will be sent to a computer to perform the analysis on the said sample. Fourier Transform Infrared (FTIR) commonly used to identify type of elements contained in a sample or organic compound. The compound identification based on resulting spectrum represents the molecular absorption and transmission, creating a unique molecular fingerprint where no two elements can share the same infrared spectrum. For this instrument, the source used is laser beam according to the technician. Laser beam can enhance the accuracy for element identification compare to other type of source (Adiff Nafillah, 2013). **Appendix 12** shows the IR chart that is widely used to determine the functional groups of a sample.

4.2.4 FTIR Results

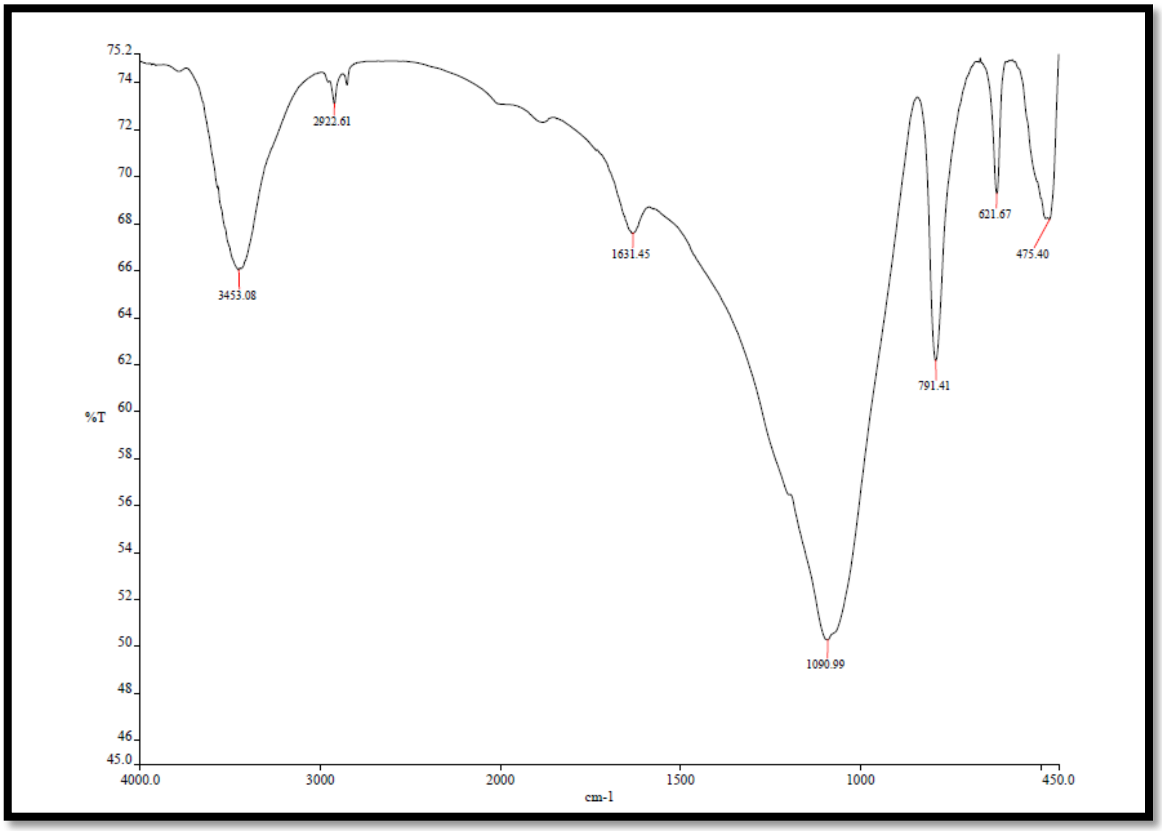


Figure 54: Result of FTIR testing of MIRHA.

Table 15: Functional groups of MIRHA

Peak No	Wavelength (cm^{-1})	Functional Group
1	3453.08	Alcohols
2	2922.61	Alkanes
3	1631.45	Amines
4	1090.99	Aliphatic amines
5	791.41	Alkyl halides
6	621.67	Alkynes
7	475.40	Alkyl halides

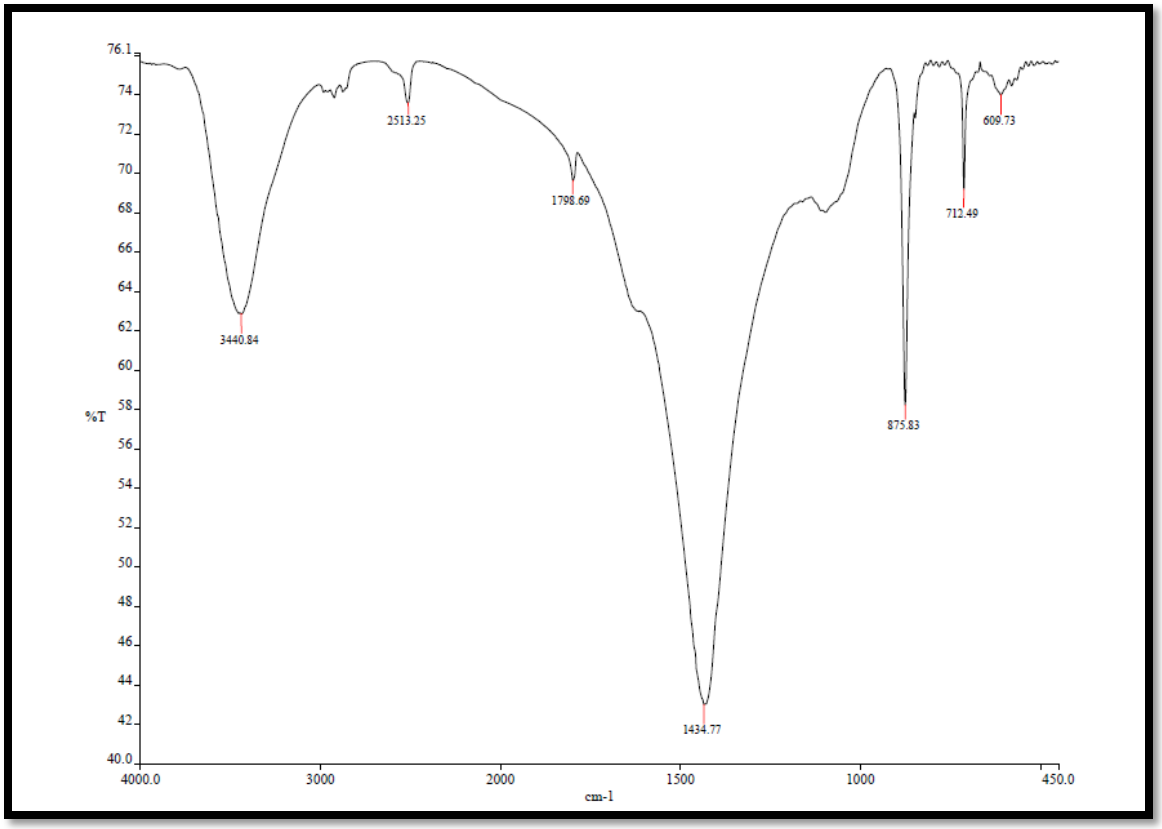


Figure 55: Result of FTIR testing of Fly Ash.

Table 16: Functional groups of Fly Ash.

Peak No	Wavelength (cm^{-1})	Functional Group
1	3440.08	Alcohols
2	2513.25	Carboxylic acids
3	1798.69	Alkynes
4	1434.77	Aromatics
5	875.83	Amines
6	712.49	Alkenes
7	609.73	Alkyl halides

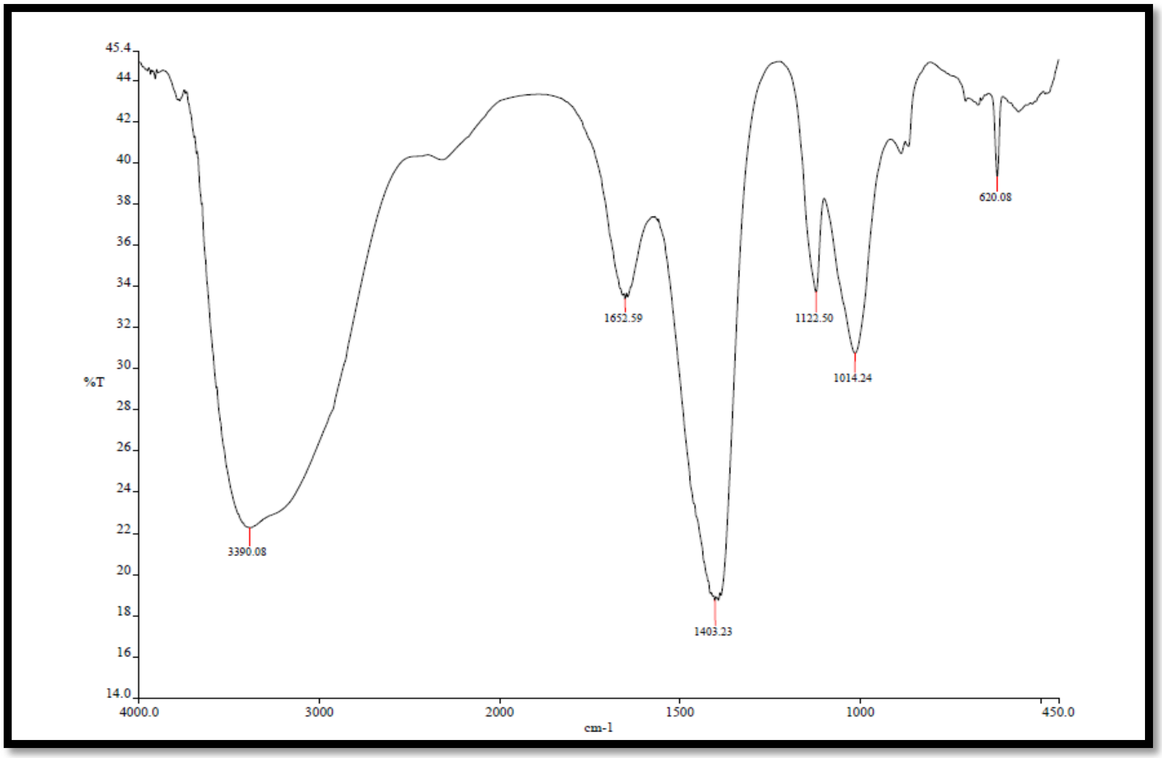


Figure 56: Result of FTIR testing of POFA.

Table 17: Functional groups of POFA.

Peak No	Wavelength (cm^{-1})	Functional Group
1	3390.08	Amines
2	1652.59	Alkenes
3	1403.23	Alkyl halides
4	1122.50	Aliphatic amines
5	1014.24	Alcohols
6	620.08	Alkynes

Figure 54-56 shows the results obtained from FTIR analysis of MIRHA, fly ash and POFA respectively. **Table 15-17** shows the corresponding functional groups of those three materials by referring to **Appendix 12**

4.3 Discussions

4.3.1 Discussion on Compressive Strength Testing

This results shows that the composition of the cement plays a role in determining the compressive strength of the geopolymer cement. This different occurred due to the increased percentage of fly ash used in Composition 2 which is 60% compared to 33.33% in Composition 1. This is attributed to the gradual hardening of the geopolymer cement by a substantially fast chemical reaction under alkaline condition on silicon and aluminium minerals present in fly ash. This situation also is due to the low alumina content in MIRHA and POFA compared to fly ash which triggered a higher average compressive strength value in Composition 2 when the percentage of MIRHA and POFA were reduced from 33.33% to 20% (Azreen, 2011).

The results also clearly indicate that the curing period is proportional to the compressive strength of geopolymer cement. This situation is explainable by referring to the higher pozzolanic reactions that has occurred in the geopolymer cements in the term of 14 days curing compared to 7 days curing (Kamal, 2008). Referring to **Figure 53,** there is a higher increment in the compressive strength value from 7 days curing to 14 days curing of Composition 1 compared to slight increment of compressive strength value from 7 days curing to 14 days curing of Composition 2. Thus, it is believed that the adequate amount of water and high pozzolanic reactivity were the reasons why there is higher strength acceleration in Composition 1 compared to Composition 2 (Kamal, 2008).

4.3.2 Discussion on FTIR Testing

As been discussed earlier, inclusions of higher percentage of fly ash in Composition 2 have increased the compressive strength of the geopolymer cement compared to Composition 1. Comparing the functional groups of fly ash with those of MIRHA and POFA, it can be stated that the presence of aromatics plays a vital role in the compressive strength of the geopolymer cement since it is only present in fly ash. An aromatic compound refers to the arrangement of carbon atoms in a ring which gives the compound higher bond strength compared to linear arrangement of same number of carbons (Wikipedia, 2013). This is a reasonable explanation on the increase of compressive strength when the percentage of fly ash was increased from 33.33% in Composition 1 to 60% in Composition 2.

4.3.3 Discussion Based on Comparison with Conventional Cement

Class G cement is used in oil well cementing. Class G is sulfate resistant cement used in primary and remedial cementing applications. Class G or oil well G is manufactured according to strict API guidelines with respect to setting times, compressive strength development and free water content and is a consistent product that meets the demands of oil well cementing. Class G cement has a very good compressive strength development for quick drill out times (Canyon, 2011). According to previous researches, the compressive strength of Glass G cement after 2 days and 4 days curing under ambient temperature and pressure are 10.95 MPa and 16.55 MPa respectively (Mojtaba Labibzadeh, 2010). Thus, for 7days and 14 days curing, the compressive strength would be much higher than 16.55 MPa.

Based on previous researches done on geopolymer cements, the compressive strength under ambient temperature and pressure after 7 days curing is in the range of 6 MPa – 13 MPa and after 14 days curing is in the range of 7 MPa – 16 MPa (Azreen, 2011). Therefore, the compressive strength of geoplymer cement obtained in this research using MIRHA, fly ash and POFA is much lower compared to that of Class G cement and also of geopolymer cements in previous studies. However this scenario occurs because in this research only the three aforementioned materials were used as raw substance whereas in other studies including Class G cement other substances like crushed granite and aggregates were used to strengthen the cement. Furthermore, to increase the workability, a high range water reducer super plasticizer was used (Azreen, 2011). This is the primary factor for low compressive strength obtained in this research compared to Class G cement and other previous geopolymer cement production.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Relevancy to the Objectives

In this research on geopolymers and also based on previous researches, it is acceptable that in term of reducing the global warming, the geopolymers could reduce the carbon dioxide emission to the atmosphere caused by cement and aggregate industries by about 80%. Geopolymers have emerged as novel engineering materials with the potential to form a substantial element of environmentally sustainable oil well cements (Azreen, 2011). Based on the research done and the obtained results, it can be concluded that the compressive strength of geopolymer cement is significantly influenced by both curing period and also the composition. The compressive strength gradually increases when the curing period is extended and increment in the percentage of fly ash in the composition of the cement also increases the compressive strength. However, it will not be applicable for real life oil well cementing purposes without the addition of aggregates and plasticizers which could give the optimum compressive strength as Class G cement for oil well cementing.

5.2 Suggested Future Work for Expansion and Continuation

This research has a high potential to be continued in the future by undertaking research on different parameters. The research can be repeated with the inclusion of aggregates and plasticizers in the cement. Different molarity of sodium hydroxide solution also could be used to study the effect of alkaline molarity on the compressive strength. The effect of curing temperature also could be studied by selecting different curing conditions of different temperature to study its effect on the compressive strength of the geopolymer cement. The research also could be continued in the future by using different compositions of raw material other than used in this research for a more reliable conclusion on the compressive strength of produced geopolymer cement.

REFERENCES

Adiff Nafillah, C. Y. (2013). *Fourier Transform Infrared Analysis.*

Amir H. Mahmoudkhani, D. N. (2008). New Environment Friendly Cement Slurries.

Andri Kusbiantoro, M. F. (2012). The effest of microwave incinerated rice husk ash on the compressive and bond strength of fly ash based geopolymer concrete. *Construction and Building Material* .

Azreen, W. H. (2011). Mix Design and Compressive Strength of Geopolymer Concrete containing Blended Ash from Agro-Industrial Wastes.

Bao, G. J. (2005). Am Ceram Soc. p. 88:3287.

Barsoum, A. G. (2006). Microstructural Evidence of Reconstituted Limestone Blocks in the Great Pyramids of Egypt. *Journal of The American Ceramics Society* , 89.

Berkhout, F. (2013). *Biority*. Retrieved June 10, 2013, from Turning Oil Palm Waste into Valuale Products: http://www.biority.com/?page_id=4

Bouzoubaa, F. (2001). Compressive Strength and Chloride-Ion Penetrability. In *Concrete Incorporating Rice Husk Ash.*

Business Dictionary. (2013). Retrieved May 18, 2013, from Portland Cement: http://www.businessdictionary.com/definition/Portland-cement.html

Canyon, T. S. (2011). Class G. *Product Data Sheet* .

Clean Coal. (2013). Retrieved June 9, 2013, from (Clean Coal Technology Offered as a Practical and Affordable Solution to Save the Environment and Saving Money, 2013)l: http://cleancoal.pro/cleancoaltechnology/

Conner. (1990). *Chemical Fixation and Solidification of Hazardous Waste.* New York: Van Nostrand Reinhold.

Consoli. (2000). Influence of Curing Under Stress on the Tri-Axial Response of Cemented Soils. *Geotechnique* , 99.

Corotis, O. X. (2007). The Effect of Rice Husk Ash On Mechanical Properties of Concrete Under High Temperatures. In *18th Engineering Mechanics Divison Conference.*

D.Bapat, J. (2012). Pulverised Fuel Ash. In *Mineral Admixtures in Cement and Concrete* (p. 80). Florida, US: CRC Press, Taylor and Francis Group.

D.D. Bui, P. S. (2001). Gap Graded Concrete Blended with Rice Husk Ash and Fly Ash. In S. D. Concrete. Michigan: Library of Congress.

Dam, T. J. (March 2010). Gopolymer Concrete. *Tech Brief* .

David Mack, R. D. (2012). Cement:How tough is tough enough? A Laboratory and Field Study.

Davidovits. (2008). *Geopolymer Chemistry and Applications.* France: Institut Geopolymere.

Davidovits. (1984). *Pyramids of Egypt Made of Man Made Stone, Myth or Fact?* Washington DC: Smithsonian Institution.

Davidovits, J. (January 2013). Geopolymer Cement. 2.

Davidovits, J. (July 2011). *Geopolymer Chemistry and Applications.* France: Institut Geopolymere.

Davidovits. (1991). Thermal Analysis 37:1633.

Diggbuyer. (2011). Retrieved June 10, 2013, from Oil Palm Empty Fruit Bunch Fiber: http://www.diggbuyer.com/Oil-Palm-Empty-Fruit-Bunch-Fiber-h2641956.html

Divya Khale, R. C. (2007). Mechanism of geopolymerization and factors influencing its development: a review.

Duxson, L. V. (2005). Ind Eng Chem Res. 44.

Farlex. (2013). *The Free Dictionary*. Retrieved May 17, 2013, from http://www.thefreedictionary.com/crush

Feng, Q. L. (2004). Adsorption of Lead and Mercury by Rice Husk Ash. *Journal Colloid Interf* , 1.

Fiseha Mekonnen Guangul, S. A. (2011). *AIP Conference Proceedings*. Retrieved May 17, 2013, from Elemental and thermo-chemical analysis of oil palm fronds for biomass energy conversion: http://proceedings.aip.org/resource/2/apcpcs/1440/1/1197_1?isAuthorized=no

G.C.Bye. (1999). *Portland Cement.* London: Thomas Telford Limited.

Girard, J. (2011, October 23). *The Concrete Countertop Institute*. Retrieved May 16, 2013, from The use of pozzolans in concrete: http://www.concretecountertopinstitute.com/blog/2011/10/the-use-of-pozzolans-in-concrete/

Hardjito, W. R. (2003). George Hoff Symposium. Las Vegas, USA: ACI.

Hermann E, K. C. (1999). Proceedings of Geopolymers. In K. C. Hermann E, *Proceedings of Geopolymers* (p. 211).

Hewlette. (1998). Chemistry of Cement and Concrete. New Delhi: Butterworth Heinmann.

Hos JP, M. P. (2002). Material Science.

Hwang, C. L. (1996). The Use of Rice Husk Ash in Concrete. In *Waste Materials Used in Concrete Manufacturing* (p. 184). William Andrew Publication.

Institute, A. C. (2001). Cementitious Materials for Concrete. *ACI Education Buletin* , E3-01.

Institute, G. (2010). *What is a Geopolymer? Introduction*. Retrieved May 16, 2013, from http://www.geopolymer.org/science/introduction

Instron. (2013). Retrieved May 2013, 2013, from Glossary of Materials Testing: http://www.instron.us/wa/glossary/Compressive-Strength.aspx?ref=https://www.google.com.my/

Kamal, N. S. (2008). The Influence of Burning Temperatures and Percentage Inclusion of Microwave Incinerated Rice Husk Ash (MIRHA) on Normal Strength Concrete.

Kim D. Basham, M. C. (2007, December 7). *Concrete Construction*. Retrieved May 17, 2013, from What is Fly Ash?: http://www.concreteconstruction.net/concrete-construction/what-is-fly-ash.aspx

Kumar. (1993). Rice husk ash based cement. In *Mineral Admixtures in Cement and Concrete.* New Delhi, India: ABI Books Private Ltd.

Mallicoat, S. K. (2005). Ceram Eng Sci Proc. p. 26:37.

Marceau, M. N. (2007). *Life Cycle Inventory of Portland Cement Concrete.* PCA R&D Serial No. 3011. Portland Cement Association, Skokie, IL.

Masanobu Kanaoka, T. T. (2008). Relationships Between The Compressive Strength and The Testing Method for Cemented Soils. 584.

Mojtaba Labibzadeh, B. Z. (2010). Early age compressive strength of oil well class G cement due to borehole pressure and temperature changes. 43.

Nasvi, R. S. (2012). Comparison of mechanical behaviors of geopolymers and class G cement as well cement at different curing temperatures for geological sequestration of carbon dioxide.

Palomo A, D. L. (2003). *Cem Conc Res 33:281.*

Palomo, L. (2003). Cement Concrete. 33.

Paul, R. (2011, March 30). *Anna University Lab Manuals For Engineering Students*. Retrieved May 17, 2013, from Compressive Strength Test on Cement: http://labmanual.blogspot.com/2011/03/compressive-strength-test-on-cement.html

Pauler. (2009, October 1). *The Modern Green*. Retrieved June 9, 2013, from Fly Ash Concrete: http://themoderngreen.com/2009/10/fly-ash-concrete-eco-friendly-and-lasts-longer/

Phair, S. V. (2003). Mater Lett. p. 57:4356.

PV, K. (1994). Proceedings of the first international conference on alkaline cements, concretes. Ukraine: VIPOL Stock Company.

Qrbiz. (2012). Retrieved May 27, 2013, from The Business Opportunity in China: http://www.qrbiz.com/product/59005/Rice-husk-ash.html

Rahier, V. M. (1996). J Mater Sci 31:71.

Salton, J. (2009, October 2). *New 'green' geopolymer concrete delivers win-win for industry and the planet*. Retrieved May 18, 2013, from http://www.gizmag.com/green-geopolymer-concrete-technology/13016/

Sensale. (2006). Strength Development of Concrete with Rice Husk Ash. In *Cement and Concrete Composites* (pp. 158-160).

Singh, I. (2012, October 13). *Life*. Retrieved June 10, 2013, from Empty Fruit Bunch: http://ish83.blogspot.com/2012/10/empty-fruit-bunch-efb.html

Sofi, V. D. (2006). J Material Science.

Tamano. (2004). Characteristics of Hardened Cement Slurry in Bored Pre-Cast File. 507.

Taylor, H. F. (1997). *Cement Chemistry.* Great Britain: Thomas Telford Publishing.

TechBrief: Geopolymer Concrete. (2010). Retrieved May 21, 2013, from Materials-Concrete: http://www.fhwa.dot.gov/pavement/pub_details.cfm?id=665

Technology, D. o. (2009). *Pop Beton*. Retrieved May 16, 2013, from Microstructure of Aluminosilicate Polymer: http://www.geopolymery.eu/en/photo-gallery/microstructure-of-alumosilicate-polymer/

The Concrete Society. (2006). Retrieved May 17, 2013, from Fly Ash or Pulverized Fuel Ash: http://www.concrete.org.uk/fingertips_nuggets.asp?cmd=display&id=136

The Geopolymerization Process. (n.d.). Retrieved May 24, 2013, from Goepolymer Alliance: http://geopolymers.com.au/science/geopolymerization

Tiemeyer, L. P. (2013). Sealing Quality of Cementing Systems To Be Used On Carbon Capture and Storage Wells.

ToolingU. (2012). Retrieved May 17, 2013, from Ferrous Metals and Alloys 210: http://www.toolingu.com/definition-500210-15801-compressive-strength.html

Vaan Jaarsveld, V. D. (2002). Chemical Engineering. 89.

Van Deventer, X. (2002). *Cement Concrete Res 32:1705.*

Viet Cargo. (n.d.). Retrieved May 27, 2013, from Save Environment Your Way: http://vietcargo.com.vn/product/Rice%20husk%20pellets%20-10/

Vishie, A. K. (2009, June 13). *Leo Club*. Retrieved May 28, 2013, from Outing to Recycle Factory: http://leoclubsmkdl.blogspot.com/2009/06/hiwavetm-oxidizer-or-also-called-hiwox.html

Wesche, K. (1991). *Fly Ash in Concrete.* Great Britain: E & FN SPON.

Whitfiled. (1953). Pressure Pre-hydration Increases Strength of Hydraulic Cement Mortar Specimens. 611.

Wikipedia. (2013, March 24). Retrieved June 11, 2013, from Aromaticity: http://en.wikipedia.org/wiki/Aromaticity

Wiles. (1988). Standard Handbook of Hazardous Waste Treatment and Disposal. New York: McGraw Hills.

Woolard CD, P. K. (2000). Water SA 26:531.

Xiong CJ, P. X. (2004). *International Workshop on Sustainable Development and Concrete Technology.* Beijing.

Xu H, V. D. (2000). Miner Process. 59:247.

Xu, V. D. (2002). *Miner Eng 15:1131.*

Yoshimoto. (1976). Strength of Mortar Hardened under High Pressure. 240.

APPENDICES

APPENDIX 1: Compressive strength testing results for Sample 1 of Composition 1 for 7 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 33.33MIRHA+33.34FA+33.33POFA_7days_Sample 1
Cube Number: 1
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathiskumar
Additives:
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Tue, Jul 02, 2013 10:25AM

Test Duration: 00:00:38

Elap Time   Load (MPa)

00:00:34    3.75
00:00:35    3.76
00:00:35    3.77
00:00:35    3.78
00:00:35    3.79
00:00:35    3.80
00:00:35    3.81
00:00:35    3.82
00:00:35    3.83
00:00:35    3.84
00:00:36    3.84
00:00:36    3.85
00:00:36    3.86
00:00:36    3.87
00:00:36    3.87
00:00:36    3.87
00:00:36    3.87
00:00:36    3.87
00:00:36    3.86
00:00:36    3.84
00:00:36    3.79
00:00:37    3.69
00:00:37    3.56
00:00:37    3.38
00:00:37    3.19
```

APPENDIX 2: Compressive strength testing results for Sample 2 of Composition 1 for 7 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 33.33MIRHA+33.34FA+33.33POFA_7days_Sample 2
Cube Number: 2
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathiskumar
Additives:
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Tue, Jul 02, 2013 10:47AM

Test Duration: 00:00:24

Elap Time   Load (MPa)

00:00:21    2.14
00:00:21    2.15
00:00:21    2.16
00:00:21    2.17
00:00:21    2.18
00:00:22    2.19
00:00:22    2.20
00:00:22    2.21
00:00:22    2.22
00:00:22    2.23
00:00:22    2.24
00:00:22    2.25
00:00:22    2.26
00:00:22    2.27
00:00:22    2.28
00:00:22    2.29
00:00:23    2.29
00:00:23    2.30
00:00:23    2.31
00:00:23    2.31
00:00:23    2.32
00:00:23    2.31
00:00:23    2.31
00:00:23    2.30
00:00:23    2.28
00:00:24    2.25
00:00:24    2.21
00:00:24    2.16
00:00:24    2.10
```

APPENDIX 3: Compressive strength testing results for Sample 1 of Composition 2 for 7 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_7days_Sample 1
Cube Number: 1
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathiskumar
Additives:
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Tue, Jul 02, 2013 10:52AM

Test Duration: 00:00:38

Elap Time   Load (MPa)

00:00:34    3.73
00:00:34    3.73
00:00:34    3.74
00:00:34    3.75
00:00:35    3.76
00:00:35    3.77
00:00:35    3.78
00:00:35    3.79
00:00:35    3.81
00:00:35    3.82
00:00:35    3.83
00:00:35    3.84
00:00:35    3.85
00:00:36    3.86
00:00:36    3.87
00:00:36    3.88
00:00:36    3.89
00:00:36    3.90
00:00:36    3.90
00:00:36    3.91
00:00:36    3.91
00:00:36    3.91
00:00:36    3.90
00:00:36    3.88
00:00:37    3.86
00:00:37    3.83
00:00:37    3.79
00:00:37    3.75
00:00:37    3.70
```

APPENDIX 4: Compressive strength testing results for Sample 2 of Composition 2 for 7 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_7days_Sample 2
Cube Number: 2
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathiskumar
Additives:
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Tue, Jul 02, 2013 10:57AM

Test Duration: 00:00:36

Elap Time   Load (MPa)

00:00:32    3.53
00:00:32    3.55
00:00:33    3.56
00:00:33    3.57
00:00:33    3.58
00:00:33    3.59
00:00:33    3.60
00:00:33    3.61
00:00:33    3.62
00:00:33    3.63
00:00:33    3.64
00:00:34    3.65
00:00:34    3.66
00:00:34    3.67
00:00:34    3.68
00:00:34    3.69
00:00:34    3.70
00:00:34    3.71
00:00:34    3.72
00:00:34    3.73
00:00:34    3.73
00:00:34    3.73
00:00:35    3.72
00:00:35    3.71
00:00:35    3.69
00:00:35    3.67
00:00:35    3.64
00:00:35    3.58
00:00:35    3.49
```

APPENDIX 5: Compressive strength testing results for Sample 3 of Composition 2 for 7 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_7days_Sample 3
Cube Number: 3
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathiskumar
Additives:
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Tue, Jul 02, 2013 11:01AM

Test Duration: 00:00:36

Elap Time   Load (MPa)

00:00:32    3.52
00:00:32    3.53
00:00:32    3.54
00:00:33    3.55
00:00:33    3.56
00:00:33    3.57
00:00:33    3.58
00:00:33    3.59
00:00:33    3.60
00:00:33    3.61
00:00:33    3.62
00:00:33    3.62
00:00:34    3.63
00:00:34    3.63
00:00:34    3.63
00:00:34    3.63
00:00:34    3.63
00:00:34    3.63
00:00:34    3.62
00:00:34    3.60
00:00:34    3.58
00:00:34    3.56
00:00:34    3.53
00:00:35    3.49
00:00:35    3.44
00:00:35    3.38
00:00:35    3.31
00:00:35    3.23
00:00:35    3.13
```

APPENDIX 6: Compressive strength testing results for Sample 1 of Composition 1 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 33.33MIRHA+33.34FA+33.33POFA_14days_1
Cube Number: 1
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 02:46PM

Test Duration: 00:00:35

Elap Time   Load (MPa)

00:00:32    3.41
00:00:32    3.41
00:00:32    3.41
00:00:32    3.41
00:00:32    3.41
00:00:32    3.41
00:00:32    3.42
00:00:32    3.42
00:00:32    3.43
00:00:32    3.44
00:00:33    3.44
00:00:33    3.44
00:00:33    3.43
00:00:33    3.42
00:00:33    3.42
00:00:33    3.41
00:00:33    3.41
00:00:33    3.41
00:00:33    3.42
00:00:34    3.42
00:00:34    3.41
00:00:34    3.40
00:00:34    3.37
00:00:34    3.31
00:00:34    3.21
00:00:34    3.08
00:00:34    2.92
00:00:34    2.74
```

APPENDIX 7: Compressive strength testing results for Sample 2 of Composition 1 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 33.33MIRHA+33.34FA+33.33POFA_14days_2
Cube Number: 2
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 02:51PM

Test Duration: 00:00:39

Elap Time   Load (MPa)

00:00:36    3.95
00:00:36    3.96
00:00:36    3.97
00:00:36    3.97
00:00:36    3.98
00:00:36    3.98
00:00:36    3.99
00:00:37    4.00
00:00:37    4.00
00:00:37    4.01
00:00:37    4.01
00:00:37    4.02
00:00:37    4.02
00:00:37    4.03
00:00:37    4.03
00:00:37    4.03
00:00:38    4.04
00:00:38    4.04
00:00:38    4.05
00:00:38    4.06
00:00:38    4.07
00:00:38    4.08
00:00:38    4.08
00:00:38    4.07
00:00:38    4.02
00:00:38    3.92
00:00:38    3.76
00:00:39    3.55
00:00:39    3.30
```

APPENDIX 8: Compressive strength testing results for Sample 3 of Composition 1 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 33.33MIRHA+33.34FA+33.33POFA_14days_3
Cube Number: 3
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 03:10PM

Test Duration: 00:00:38

Elap Time   Load (MPa)

00:00:34    3.78
00:00:34    3.79
00:00:35    3.80
00:00:35    3.81
00:00:35    3.82
00:00:35    3.83
00:00:35    3.84
00:00:35    3.85
00:00:35    3.86
00:00:35    3.87
00:00:35    3.88
00:00:36    3.88
00:00:36    3.89
00:00:36    3.90
00:00:36    3.91
00:00:36    3.92
00:00:36    3.92
00:00:36    3.93
00:00:36    3.94
00:00:36    3.95
00:00:36    3.95
00:00:36    3.93
00:00:37    3.87
00:00:37    3.77
00:00:37    3.64
00:00:37    3.47
00:00:37    3.30
00:00:37    3.13
00:00:37    2.97
```

APPENDIX 9: Compressive strength testing results for Sample 1 of Composition 2 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_14days_1
Cube Number: 1
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 03:01PM

Test Duration: 00:00:35

Elap Time   Load (MPa)

00:00:32    3.42
00:00:32    3.43
00:00:32    3.44
00:00:32    3.45
00:00:32    3.46
00:00:32    3.47
00:00:32    3.48
00:00:32    3.49
00:00:32    3.50
00:00:32    3.51
00:00:32    3.52
00:00:33    3.54
00:00:33    3.55
00:00:33    3.56
00:00:33    3.57
00:00:33    3.58
00:00:33    3.58
00:00:33    3.58
00:00:33    3.59
00:00:33    3.59
00:00:34    3.59
00:00:34    3.59
00:00:34    3.59
00:00:34    3.57
00:00:34    3.53
00:00:34    3.46
00:00:34    3.35
00:00:34    3.23
```

APPENDIX 10: Compressive strength testing results for Sample 2 of Composition 2 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_14days_2
Cube Number: 2
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 03:05PM

Test Duration: 00:00:39

Elap Time   Load (MPa)

00:00:36    3.92
00:00:36    3.93
00:00:36    3.95
00:00:36    3.96
00:00:36    3.97
00:00:36    3.98
00:00:36    3.99
00:00:36    4.00
00:00:36    4.01
00:00:37    4.03
00:00:37    4.04
00:00:37    4.05
00:00:37    4.05
00:00:37    4.06
00:00:37    4.07
00:00:37    4.07
00:00:37    4.08
00:00:37    4.08
00:00:38    4.08
00:00:38    4.09
00:00:38    4.09
00:00:38    4.08
00:00:38    4.03
00:00:38    3.95
00:00:38    3.82
00:00:38    3.65
00:00:38    3.46
00:00:38    3.28
00:00:38    3.10
```

APPENDIX 11: Compressive strength testing results for Sample 3 of Composition 2 for 14 days of curing.

```
Compessive Strength Export
Version 2.03 beta

Test Name: 20MIRHA+60FA+20POFA_14days_3
Cube Number: 3
Cement Class: G
Job Type: CASING
BHCT: 0.0
BHST: 0.0
Customer: Shathis
Additives: NaOH+Na2SiO3+10%water
Cement Desity: 0.00 lbs/gal
Cement Mfr.:
Comments:

Start Time: Mon, Jul 08, 2013 02:55PM

Test Duration: 00:00:41

Elap Time   Load (MPa)

00:00:38    4.19
00:00:38    4.19
00:00:38    4.20
00:00:38    4.20
00:00:38    4.21
00:00:38    4.21
00:00:39    4.22
00:00:39    4.23
00:00:39    4.23
00:00:39    4.24
00:00:39    4.25
00:00:39    4.26
00:00:39    4.27
00:00:39    4.28
00:00:39    4.28
00:00:40    4.29
00:00:40    4.30
00:00:40    4.30
00:00:40    4.31
00:00:40    4.32
00:00:40    4.33
00:00:40    4.33
00:00:40    4.33
00:00:40    4.33
00:00:40    4.33
00:00:40    4.33
00:00:41    4.32
00:00:41    4.31
00:00:41    4.29
```

APPENDIX 12: Table of IR Chart.

Functional Group	**Molecular Motion**	**Wavenumber (cm^{-1})**
alkanes	C-H stretch	2950-2800
	CH_2 bend	~1465
	CH_3 bend	~1375
	CH_2 bend (4 or more)	~720
alkenes	=CH stretch	3100-3010
	C=C stretch (isolated)	1690-1630
	C=C stretch (conjugated)	1640-1610
	C-H in-plane bend	1430-1290
	C-H bend (monosubstituted)	~990 & ~910
	C-H bend (disubstituted - E)	~970
	C-H bend (disubstituted - 1,1)	~890
	C-H bend (disubstituted - Z)	~700
	C-H bend (trisubstituted)	~815
alkynes	acetylenic C-H stretch	~3300
	C,C triple bond stretch	~2150
	acetylenic C-H bend	650-600
aromatics	C-H stretch	3020-3000
	C=C stretch	~1600 & ~1475
	C-H bend (mono)	770-730 & 715-685
	C-H bend (ortho)	770-735
	C-H bend (meta)	~880 & ~780 & ~690
	C-H bend (para)	850-800
alcohols	O-H stretch	~3650 or 3400-3300
	C-O stretch	1260-1000
ethers	C-O-C stretch (dialkyl)	1300-1000
	C-O-C stretch (diaryl)	~1250 & ~1120

aldehydes	C-H aldehyde stretch	~2850 & ~2750
	C=O stretch	~1725
ketones	C=O stretch	~1715
	C-C stretch	1300-1100
carboxylic acids	O-H stretch	3400-2400
	C=O stretch	1730-1700
	C-O stretch	1320-1210
	O-H bend	1440-1400
esters	C=O stretch	1750-1735
	C-C(O)-C stretch (acetates)	1260-1230
	C-C(O)-C stretch (all others)	1210-1160
acid chlorides	C=O stretch	1810-1775
	C-Cl stretch	730-550
anhydrides	C=O stretch	1830-1800&1775-1740
	C-O stretch	1300-900
amines	N-H stretch (1 per N-H bond)	3500-3300
	N-H bend	1640-1500
	C-N Stretch (alkyl)	1200-1025
	C-N Stretch (aryl)	1360-1250
	N-H bend (oop)	~800
amides	N-H stretch	3500-3180
	C=O stretch	1680-1630
	N-H bend	1640-1550
	N-H bend (1^o)	1570-1515
alkyl halides	C-F stretch	1400-1000
	C-Cl stretch	785-540
	C-Br stretch	650-510
	C-I stretch	600-485

nitriles	C,N triple bond stretch	~2250
isocyanates	-N=C=O stretch	~2270
isothiocyanates	-N=C=S stretch	~2125
imines	R_2C=N-R stretch	1690-1640
nitro groups	$-NO_2$ (aliphatic)	1600-1530&1390-1300
	$-NO_2$ (aromatic)	1550-1490&1355-1315
mercaptans	S-H stretch	~2550
sulfoxides	S=O stretch	~1050
sulfones	S=O stretch	~1300 & ~1150
sulfonates	S=O stretch	~1350 & ~11750
	S-O stretch	1000-750
phosphines	P-H stretch	2320-2270
	PH bend	1090-810
phosphine oxides	P=O	1210-1140