Solidification of Industrial Effluents into Geopolymer Matrix

by

Mohd Afzan Bin Abdullah
15472

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

Universiti Teknologi PETRONAS,
32610 Bandar Seri Iskandar,
Perak Darul Ridzuan.

CERTIFICATION OF APPROVAL

Solidification of Industrial Effluents into Geopolymer Matrix

by

Mohd Afzan Bin Abdullah
15472

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Dr Muhammad Rashid B Shamsuddin)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

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.

MOHD AFZAN BIN ABDULLAH

ABSTRACT

In this work, geopolymers were produced by reacting metakaolin with industrial effluent from different sources. Instead of directly treating the raw effluent, it would be useful to utilize the effluent and turn it into a value-added substance such as geopolymer, thus will sustain the environment. The right compositions of the materials were determined before mixing to form a cubic shape of geopolymer composite. Each composite will undergo several tests to investigate its properties and characteristics. Such tests include density, Scanning Electron Micrograph (SEM), Thermogravimetric Analysis (TGA), and compressive strength. All samples labeled G1, G2, G3, and G4 which comprises of mixture of metakaolin with KOH solution, OGT effluent, batik effluent, and paper & pulp effluent respectively. They were cured in an oven at temperature of 60^{o}C for 24 hours, and later cooled down for three days at room temperature. Sample G1 showed the best characteristics of density and compressive strength compared to other samples. Similar with TGA, significant weight loss was observed in sample G1, but the other three samples experienced gain in weight after initial exposure to elevated temperature before the weight loss occurred. The reason was due to chemical reactions occurred during the heating process. As for SEM, the microstructural images of all samples were not much different.

ACKNOWLEDGEMENT

Firstly, my utmost gratefulness goes to the Almighty Allah for giving me strength and empowered me to complete my Final Year Project. He was always there for me whenever I feel lost, vulnerable and doubt about myself. Second, I would like to convey my gratitude to my supervisor, Dr Muhammad Rashid for providing me continuous support and encouragement throughout my project. I would like to say thank you for the precious advice and guidance you had given to me.

Third, my gratitude goes to my beloved family and friends for always being by my side. They had been my motivation to pursue the project harder. They were truly my strength and my backbone. Whenever I was in doubt, they will be there for me to cheer me up and boost my spirit in completing the project. Fourth, I would like to thank Mr Irfan, Mr Ahmer, and Mr Rizwan, PhD students who I seek for consultation and advice regarding my project. They were too generous to spend their time sharing their knowledge with me. Their guidance, wisdom, and assistance had made this project on the right path towards completion.

Fifth, I also would like to articulate my thanks to Mr Marzuky, operator Industrial Effluent Treatment System (IETS) of Onshore Gas Terminal (OGT) and Mr Fauzi, owner of Kilang Batik Fauzi for letting me to get effluents from their facilities. Their kindness and cooperation will never be forgotten. Finally, I would like to express my thanks to all the lab technicians who have helped me to obtain apparatus and chemicals, letting me to use lab equipment, ran tests for my samples, and giving guidance whenever I needed it. From the bottom of my heart, thanks for all the assist and support.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Geopolymer is a solid substance which is formed by combining aluminosilicate-reactive materials with strong alkaline solutions, followed by curing at room temperature. It is a member of inorganic polymers group (Rangan, 2010). The discovery of geopolymers was first reported in 1950s by a Soviet Union's scientist named Prof. V. D. Glukhovsky (Tavor, Wolfson, Shamaev, & Shvarzman, 2007). The name "geo-polymer" came out several decades later by Prof. J. Davidovits and it has been investigated as an alternative to organic composit matrix.

The matrix is based on polymineral resins, which are alumino-silicate binders (Sheppard, 2003). The advantages of geopolymer compared to other organic composites include; easy to make, can be combined with various different materials, lower emission of carbon dioxide during the production process, can withstand high temperature and pressure, insoluble in water and organic solvents (but only affected by strong hydrochloric acid), and fire proof.

Despite of being inherently brittle, the unique combination of properties and low temperature processing has considerable potential in developing cost effective inorganic composite materials. However, it might not be sustainable to completely substitute the Ordinary Portland Cement (OPC) which is currently being used as universal concrete in construction industry.

There are wide range of applications of geopolymer had been developed worldwide such as aircraft cabin materials, casing for electronic flight recorder, thermal shields in the exhaust system for Formula 1 racing cars, air filter in jets, and molds to be used in metal processing.

1.2 Problem Statement

Nowadays, most industrial plants straightforwardly discharge their wastewater upon undergoing treatment (Tavor et al., 2007). If it is not treated properly, the unfavorable condition such as its acidity or alkalinity and contamination of hazardous substances, may lead to damage of ecosystem.

Commonly used application to treat industrial wastewater includes chemical and biological treatments (Tavor et al., 2007). The most widely applied method is biological degradation of organic matters aerobically by using bacteria. However, there are flaws of using this method such as unpleasant smell, and large amount of sludge to be removed, existence of non-degradable organic matters. These flaws will eventually limit the ability to optimize the level of concentration of organic compounds.

Therefore, lot of studies has been conducted in searching for the best solution to deal with industrial effluent for the sake of environment. The focus around the world is to exploit the raw effluent from industries for the preparation of materials such as glass and ceramics (Perná & Hanzlíček, 2014). The reuse of raw industrial effluent to be solidified using geopolymerization technique is studied for potential practical application and to reduce environmental impact.

Moreover, the abundant amount of metakaolin available which comes from variety of sources containing kaolinite should be utilized. Its nature as a synthetic artificial aggregate is beneficiary new source of structural aggregate material to be solidified into geopolymers (Alida et al., 2013).

1.3 Objectives and Scope of Study

The following are the main objectives to be achieved:

i. To find suitable effluent from different industries to be used as raw material for geopolymers
ii. To form geopolymer composites by mixing industrial effluent and metakaolin
iii. To analyze and compare the characteristics of the geopolymer composites derived from different industrial effluents

A broad objective was chosen for this project to allow direct comparison of the effects of different variables on the composite properties in one comprehensive study. An amount of raw effluent will be obtained from different industrial companies, and be used as activator in producing geopolymer composites.

The properties of the geopolymer to be investigated are the external morphology (texture) of the geopolymer by using SEM, loss of mass upon heating at high temperature (using TGA), compressive strength, and density. The depth to which individual parameters could be investigated is limited within the scope of this project. The project flow chart and key milestone of the study are attached in Appendix A and Appendix B for the detail of the project work.

CHAPTER 2

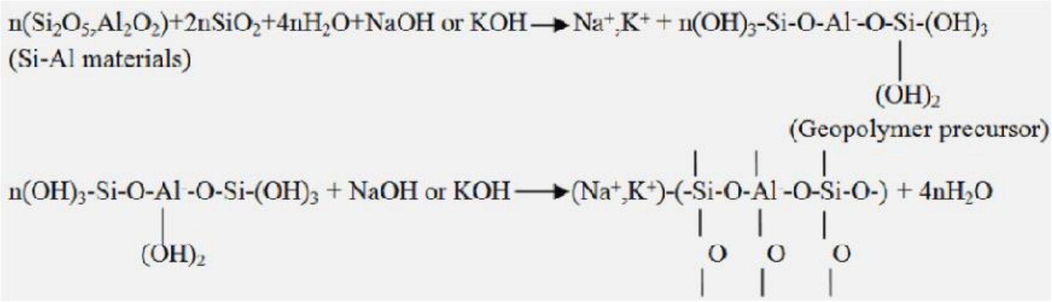
LITERATURE REVIEW

In this chapter, a brief introduction of geopolymer is provided. Furthermore, relevant information about the properties, applications, and characterization of geopolymer are also presented in order to establish the basic background for this project.

2.1 Theories of Geopolymers

Geopolymers and inorganic (aluminosilicate) polymers are the two widely used terms among researchers today (Welter, 2013). However, the term geopolymer is adopted more predominantly. The reactions that take place during the geopolymer formation and solidification processes are described as ‘geopolymerization’.

The main theory of geopolymer is the polymerization of the Si-O-Al-O bond (Das, Mohapatra, & Rath, 2014). It is developed when Al-Si source materials like fly ash or metakaolin is mixed with alkaline activating solution (NaOH or KOH solution). It can be formed as -Si-O-Al-O- or –Si-O-Al-O-Si-O- or –Si-O-Al-O-Si-O-Si-O-. Below are the chemical reactions for the formation of geopolymer:



$$\underset{\text{(Si-Al materials)}}{n(Si_2O_5,Al_2O_2)+2nSiO_2+4nH_2O+NaOH\text{ or }KOH} \longrightarrow Na^+,K^+ + \underset{\text{(Geopolymer precursor)}}{n(OH)_3\text{-Si-O-}\underset{\displaystyle (OH)_2}{\underset{|}{Al^-}}\text{-O-Si-}(OH)_3}$$

$$n(OH)_3\text{-Si-O-}\underset{\displaystyle (OH)_2}{\underset{|}{Al^-}}\text{-O-Si-}(OH)_3 + NaOH\text{ or }KOH \longrightarrow (Na^+,K^+)\text{-(-}\overset{|}{\underset{\underset{|}{\underset{O}{|}}}{Si}}\text{-O-}\overset{|}{\underset{\underset{|}{\underset{O}{|}}}{Al^-}}\text{-O-}\overset{|}{\underset{\underset{|}{\underset{O}{|}}}{Si}}\text{-O-)} + 4nH_2O$$

FIGURE 2.1 Formation of geopolymer (Das et al., 2014)

Based on the above equation, water is expelled from the chemical reaction and has no role in the polymerization process. Addition of water will form porosity in the concrete due to evaporation during curing process (Das et al., 2014).

2.2 Synthesis of Geopolymer

Tavor et al. (2007) had reported that geopolymers are synthesized via the reaction of metakaolin or fly ash, sodium silicate, and alkaline solution at room temperature. Under such a strong alkaline solution, the aluminosilicates form free SiO_4 and AlO_4 tetrahedral clusters, which are linked together to yield polymeric precursors.

According to Tavor et al. (2007), the dry materials were weighed, added to a mixer, and mixed for 2 min. The liquid materials then were weighed and added to the mixture. The mixture was mixed for 6 min and then placed into a mold of 12 cubes (with dimensions of 25 cm × 25 cm × 25 cm) that were placed on vibrating table. The moulds were covered and cured at 50 °C for 24 h and then dried in the oven or in the air.

The most vital factor is the temperature for curing the geopolymer (Al Bakri et al., 2012). The increasing of curing temperature will cause the setting time of the concrete to decrease. During the curing process, the geopolymer concrete experiences the polymerization process.

There are two types of mixing of geopolymer; normal mixing and separate mixing (Das et al., 2014). For normal mixing, the fly ash, sodium hydroxide solution and sodium silicate solution and aggregate are mixed at once, whereas for separate mixing, the fly ash was first mixed with the sodium hydroxide solution for at least 10 minutes before adding sodium silicate solution with aggregate.

2.3 Applications of Geopolymers

Ferone et al. (2013) had reported that geopolymer-based materials are applied in the fields of binders, matrices for stabilization of hazardous waste, new ceramics, materials which are resistant to fire, asbestos-free products, and high-tech materials.

Development of low-cost, environmental-friendly, fire-resistant materials for the application of aircraft composite and cabin interior is being investigated (Sheppard, 2003). The objective of the study is to eradicate cabin fire as reason of death in accidents related to aircraft. Ignition, burnt or release of smoke after exposed to heat flux does not occur to geopolymer. Hence, its materials are applicable to be used as aircraft cabin component for cargo liners, floor panels, ceiling, sidewalls and partitions.

According to Sheppard (2003), geopolymer composites have replaced titanium in Formula 1 racing cars as thermal protections in the exhaust system. Other applications of geopolymer which currently being used worldwide include fire-resistant geopolymer casing flight recorder, highly advanced fireproof air filter in jets, and molds in metal processing.

These days, scientists are inventing railway sleepers (Ferdous, Manalo, Khennane, & Kayali, 2015). The sleepers are subjected to a very huge number of cyclic freights. The railway sleepers have to be electrically insulated. Hence, geopolymer concrete is the best material to be used as it does not conduct electricity.

2.4 Properties and Characterization

Geopolymer-based materials is attractive due to its ability to achieve tremendous mechanical properties, high strength, high resilience, can resist freeze-thaw, low diffusion rate of chloride, can resist abrasion, thermal stability, and resistant to fire (Ferone et al., 2013). Since the content of calcium in it is low, acid attack has no effect on geopolymer as compared to Portland cement-based materials. The unique properties of geopolymers resulted in their rapid development as alternative materials which are environmentally friendly in building constructions.

2.4.1 Density

Archimedes Principle states that the buoyant force on a submerged object is equal to the weight of the fluid that is displaced by the object. Density can be measured using the Archimedes buoyancy technique with dry weights, soaked weights and immersed weights in water (Berger, 2010). Density of geopolymer can be measured by water displacement method (Kumar & Kumar, 2010).

2.4.2 Compressive Strength

The compressive strength of the geopolymer was determined by using a press (Tavor et al., 2007). The property of compressive strength is important for concretes as it also depends on curing period and temperature (Al Bakri et al., 2012). When the curing time and temperature increase, the compressive strength also increases. With curing temperatures ranging from 60 to 90 °C within a time ranging from one day or two, the compressive strength of concrete can be obtained at approximately 400 to 500 kg/cm^2 (Al Bakri et al., 2012).

Drying time of geopolymer also gives a significant impact on the compressive strength (Welter, 2013). Geopolymer sample which had been dried for 28 days gives higher compressive strength compared to the one dried for only seven days. It is believed that letting the geopolymer to dry a little longer will enhance its compressive strength.

2.4.3 Scanning Electron Micrograph (SEM)

SEM applies a focused ray of high-energy electrons to create a variety of signals at the surface of solid samples (Swapp, 2015). The signals that derived from electron-sample interactions will reveal information about the specimen including texture, chemical composition, crystalline structure and orientation of materials making up the sample. It was used to analyze the pore network microstructure and products formation in the geopolymer (Aguilar, Melo, & Olivares, 2013). For that purpose, a little amount of geopolymer samples were dried up and metallized with gold.

Most of the fly ash particles are naturally in spherical shape (Al Bakri et al., 2012). The ash consists of a series of spherical vitreous particles of diameters ranges (from 200 to 10 Am). Few spheres may contain other particles of a smaller size in their interiors.

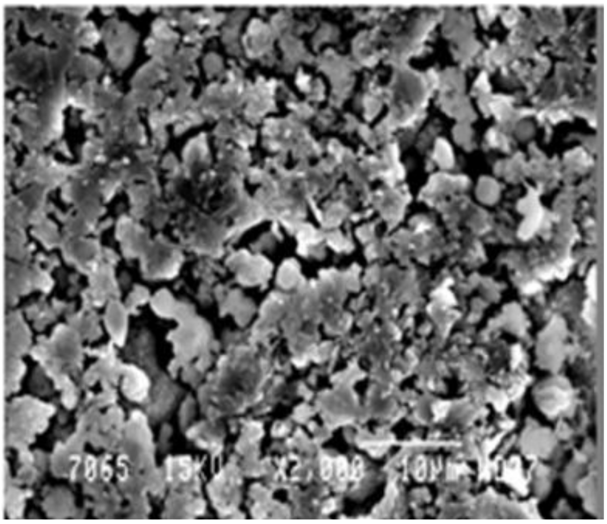


FIGURE 2.2 SEM image of geopolymer (Kumar & Kumar, 2010)

2.4.4 Thermal Analysis

In the Thermal Gravimetric Analysis (TGA) test, the loss of weight was measured while the specimens were gradually exposed to increasing temperatures (Al Bakri et al., 2012). Powdered specimens of geopolymer were used in TGA to ensure the attainment of thermal equilibrium during transitory heating.

According to Rosas-Casárez et al. (2014), TGA can be used to determine evaporation of water mechanisms causing loses of material weight as a result of regulated heating. Sample prepared in fine powder form are slid and put inside the analysis device for testing (Marín-López et al., 2009). They are later calcined to temperature of 1000^{o}C by 10^{o}C increment per minute.

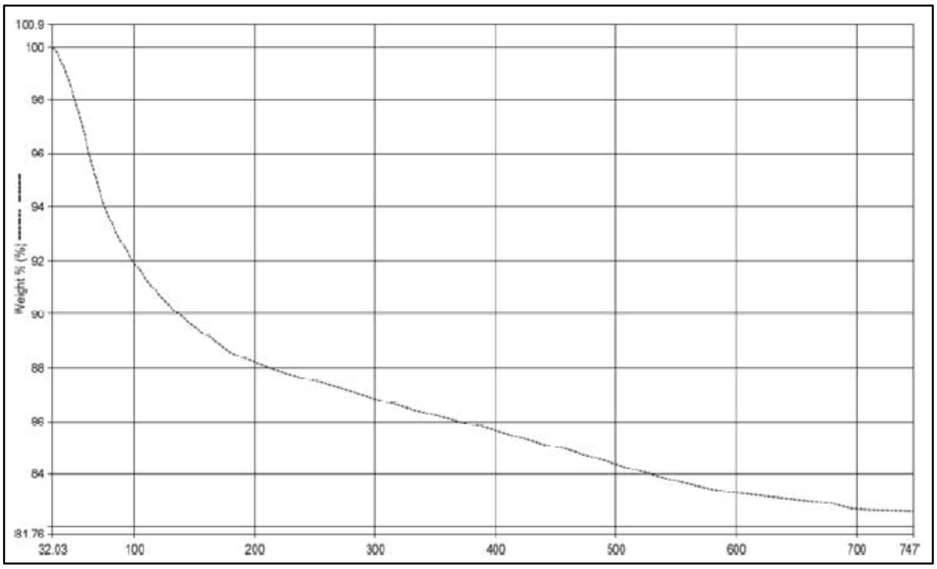


FIGURE 2.3 TGA of fly ash geopolymer paste (Al Bakri et al., 2012)

2.5 Solidification of Industrial Effluent

There has been very limited study on solidification of industrial wastewater, let alone applying raw wastewater for production other added-value materials. Tavor et al. (2007), in their work had reported that they were the first to do recycling of effluent with left over organic compound by its solidification into a geopolymer matrix.

Their work however focused on the effect of phenol concentration in the effluent for production of fly ash-based geopolymer to yield variation of compressive strengths. Result obtained from the study had made it feasible to introduce new concept of reusing wastewater from industries by immobilizing them into geopolymer (Tavor et al., 2007).

For the FYP scope of study, this research will mainly focus on the properties and characterization of geopolymers which made up of different industrial effluents. The effect of different compositions making up the effluent and its pH to be mixed with metakaolin to form geopolymer will be analyzed within this project.

CHAPTER 3

METHODOLOGY

3.1 Materials and Apparatus

Kaolin was provided by Kaolin (M) Sdn Bhd; kaolin products manufacturer located in Tapah, Perak. The powder undergone dehydroxylated process to remove the chemically bonded hydroxyl ions by heating it at 700^{o}C in a furnace for three hours. Hence, calcined kaolin or metakaolin (MK) is produced as the aluminosilicate-reactive material for this study. Table 3.1 shows the chemical composition of major oxides making up the metakaolin (determined by researchers using different sources).

TABLE 3.1 Chemical composition of metakaolin

Chemical	MK composition (wt %)			
	Marín-López et al. (2009)	Welter (2013)	Ferone et al. (2013)	Sanjayan et al. (2015)
SiO_2	51.55	56.61	52.90	55.9
Al_2O_3	44.79	40.96	41.90	37.2
K_2O	0.16	0.01	0.77	0.18
Fe_2O_3	0.49	0.34	1.60	1.70
TiO_2	1.61	0.08	1.80	2.40
MgO	0.13	0.02	0.19	0.24
CaO	0. 05	0.01	0.17	0.11
Na_2O	0.20	<0.01	-	0.27
P_2O_5	0.01	0.19	-	0.17
LOI	0.06	1.43	-	0.8

*LOI = loss on ignition at 1000^{o}C for 1 hour

As for the alkaline activator (AA), two types of industrial effluent were obtained. Each came from Onshore Gas Terminal (OGT), which is a gas processing plant located in Terengganu and Kilang Batik Fauzi (textile industry) which is located in Chemor, Perak. Meanwhile effluent from paper & pulp industry was simulated in the laboratory.

Potassium hydroxide (KOH) solution with molarity of 4M had also been prepared as the standard alkaline solution for the experiment. To make the hydroxide solution, first the potassium hydroxide flakes are weighed at 164g and put in a clean beaker. Then, distilled water is added to dissolve the flakes before 1 liter of the solution is prepared. The pH of the solution is 13.29.

Effluent from OGT is colourless and has pungent odour. It is basically acidic in nature. The pH of the effluent recorded a value of 6.26. Among the major substances contained in it are cyanide, chlorine, heavy metals such as zinc, ferum, boron, manganese, and mercury. On the other hand, effluent from Kilang Batik Fauzi recorded a pH reading of 10.74. Substances included in the wastewater are sodium carbonate, wax, and colouring dye. The colour of the effluent is dark maroon.

A simulated effluent of paper & pulp industry was produced in the laboratory. Chemicals added to make up the solution are carbon powder, sodium hydroxide, sodium carbonate, calcium carbonate, calcium oxide, aluminum oxide, zinc chloride, and tap water. The pH of the solution is recorded at 12.30. Table below shows the apparatus and materials used in producing the geopolymer:

TABLE 3.2 Apparatus and materials

Apparatus	**Materials**
1. Hand stirrer 2. Beaker 3. Measuring cylinder 4. Electronic balance 5. pH meter 6. Cube mold (5 mm × 5 mm × 5 mm) 7. Spatula 8. Oven	1. Metakaolin 2. KOH solution 3. Industrial effluents 4. Sodium silicate (Na_2SiO_3) solution

3.2 Samples Preparation

The compositions of geopolymers needed to be formulated to ensure that the MK/AA ratio can provide a favorable mixture. The amount of MK and AA was measured accordingly so that the mixing ratio of 0.9 which corresponded to composition design given by Ferdous et al. can be met. A mixture weighing 500 g was produced with respect to the MK/AA ratio for each type of solution. Sodium silicate (Na_2SiO_3) solution, in the amount of 1% of total AA was added to improve the strength of the composite.

TABLE 3.3 Weight of materials to be mixed

Sample	Weight of material (g)						
	Metakaolin	KOH solution	OGT effluent	Batik effluent	Simulated effluent	Na_2SiO_3 solution	Total
1	260	230	-	-	-	10	500
2	260	-	230	-	-	10	500
3	260	-	-	230	-	10	500
4	260	-	-	-	230	10	500

The MK and AA were mixed at constant speed for 10 minutes and a further 10 minutes were required for mixture to become thickened. The mixture then poured into cubic steel molds before being cured at 60^oC for 24 hours in an oven. After curing, the specimens were retrieved from their casting mold to cool down for three days at room temperature before undergoing physical properties test and characterization. Since this procedure dealt with untreated wastewater from industries, proper personal protective equipment (PPE) such as mask, goggle, and rubber gloves were applied for extra protection.

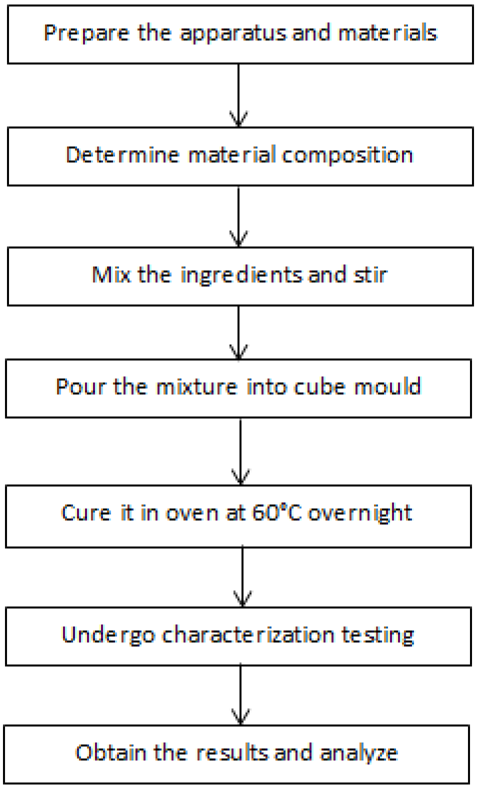


FIGURE 3.1 Flow chart for mix design procedure

3.3 Characterization Tests

For density test, it was conducted in Geopolymer Lab at Block 5. Compressive strength was done at Block 13, SEM analysis at Block 17, and TGA at Block 4. The results for each test will later be explained in the next chapter.

3.3.1 Density

It was tested by applying water displacement method. The weight of the composites was weighed and recorded before being submerged in a beaker of water. The volume of water inside the beaker is 1000ml. The initial and final (after submerging the geopolymer) volumes of water inside the beaker will be recorded accordingly. The unit of the density is g/cm^3. Formula to calculate density is as follow:

$$Density = \frac{m}{V}\ (g/cm^3) \tag{1}$$

3.3.2 Compressive Strength

The capacity of the specimens to withstand loads was to be determined. Compressive strength measurements of specimens were performed using ADR Touch 2000 BS EN Compression Machine in load control mode with a loading rate of 20 MPa/min. The specimens were tested at the age of 3 days after casting. It is calculated by dividing the peak load to the cross-sectional area of the composite (N/m^2 @ MPa). Formula below is designed to calculate the compressive strength of the specimen.

$$\sigma_c = \frac{P_{max}}{A_s} \tag{2}$$

σ_c = compressive strength (MPa)
P_{max} = maximum applied load (N)
A_s = cross-sectional area of the composite (m^2)

3.3.3 Scanning Electron Micrograph (SEM)

The purpose is to analyze the microstructure and products formation in the geopolymer. The samples were crushed into fine powder form and dried overnight before undergoing the analysis. The analysis was carried out by using the Phenom ProX desktop scanning electron microscope with magnification of 5000×. The voltage used was 10kV with full Backscattered Detector (BSD) electron. The size of the microstructure which can be seen was approximately 54 µm. Table of EDS analysis for each sample was also provided with the SEM result.

3.3.4 Thermal Gravimetric Analysis (TGA)

The purpose was to study the weight loss (%) against temperature. The samples were crushed into fine powder form and dried overnight prior the test. The analysis was conducted using Perkin Elmer TGA (Pyris 1) system under 20 ml/min of N_2 flow, from 30 – 800°C at ramp rate of 20°C/min.

CHAPTER 4

RESULTS AND DISCUSSION

After several series of attempts, four types of cubic geopolymer composites with different ingredients were selected for further characterization processes. Each sample type was prepared in duplicates (3 solid structures per type). From this point onward, the four samples will be coded as G1 for MK + KOH mixture, G2 (MK + OGT effluent), G3 (MK + Batik effluent), and G4 (MK + Paper & pulp effluent), respectively. Figure 4.1 below shows a sample of geopolymer which had been produced.

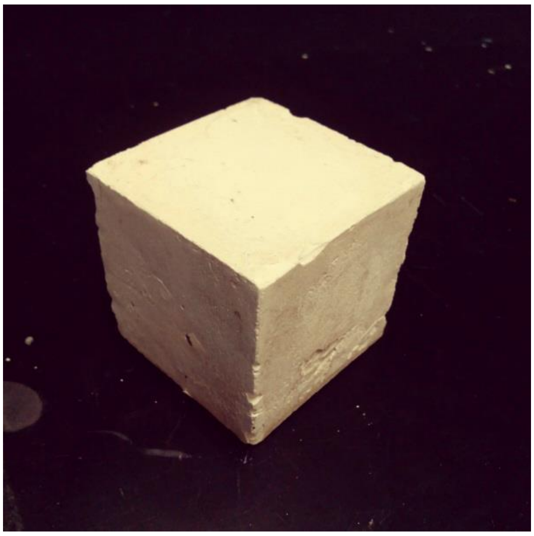


FIGURE 4.1 Geopolymer solid

4.1 Density

The density of the different type of geopolymers was determined prior to compressive strength testing. The weight and volume of all samples were measured respectively and the densities were calculated based on the formula given in earlier section. Table 4.1 below shows the result of the density test.

TABLE 4.1 Densities of geopolymers measured on cubical specimens

Sample	**Density (g/cm^3)**			
	1	**2**	**3**	**Average**
G1	1.9369	1.9362	1.9475	1.9402
G2	1.7385	1.7053	1.7167	1.7202
G3	1.5439	1.5693	1.5820	1.5651
G4	1.6771	1.7201	1.7885	1.7286

The densities of all three solid structures for each sample were measured, and an average reading was recorded. All four compositions showed almost similar value of average densities and ranged between approximately 1.72 to 1.95 g/cm^3. There is also variation of the density between each batch of different samples.

Sample G1 shows the highest average density with a value of 1.9402 g/cm^3 whereas sample G3 which comprises of MK and batik effluent possesses the lowest density with average of 1.5652 g/cm^3. Sample G4 and G2 were second and third with average densities of 1.7286 g/cm^3 and 1.7202 g/cm^3 respectively.

The reason might be due to the composition of components making up the sample. Since the molarity and concentration of KOH solution in sample G1 is greater compared to the solutions in other samples, hence it enhance the density of the solid structure.

4.2 Compressive Strength

All samples were tested after being dried for three days. The compressive strength was measured on cubical solids with dimension of 5 mm × 5 mm × 5 mm. However, the height of the solids would not influence the compressive strength. Before testing, the end surfaces of all samples were leveled parallel to ground.

Three batches of specimens for each type of sample were tested their compressive strength, and the average reading was recorded. Table 4.2 below represents the result of the compressive strength test for all samples.

TABLE 4.2 Compressive strengths of all specimens

Sample	**Strength (MPa)**			
	1	**2**	**3**	**Average**
G1	5.14	4.94	6.02	5.34
G2	4.69	4.74	5.14	4.86
G3	4.40	4.20	4.44	4.35
G4	4.74	4.44	4.89	4.69

The highest compressive strengths are notable on each specimen of sample G1 compared to others, which made up an average strength of 5.34 MPa. The second highest was attained by sample G2 with an average strength of 4.86 MPa followed by sample G4 which recorded average strength of 4.69 MPa. Sample G3 ranked last with recorded average strength of 4.35 MPa. Figure 4.2 below shows the chart of compressive strengths of the geopolymer samples.

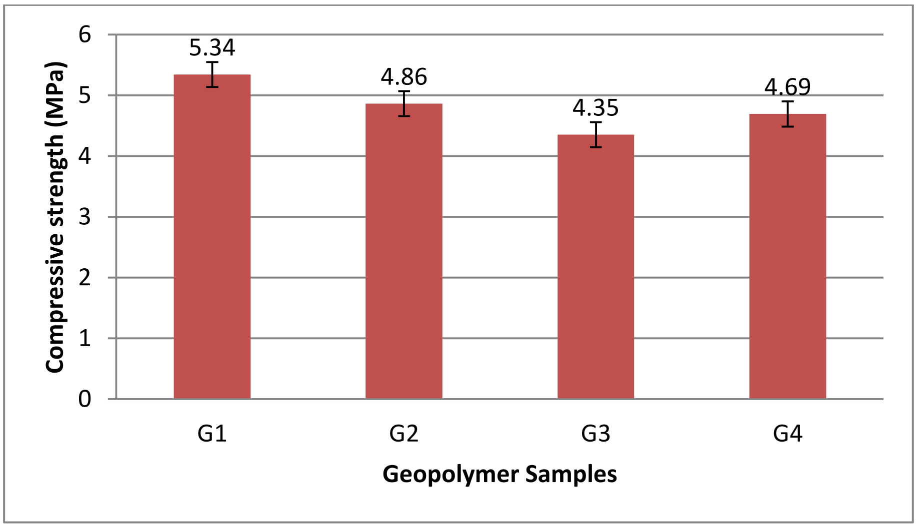


FIGURE 4.2 Compressive strengths of the geopolymers

The resulting strength of each batch of the samples was at random and generally unpredictable. Since all batches were fabricated according to the same process and from the same materials (for each type of sample), the significant variation between the batches has no obvious explanation.

The compressive strengths measured of all samples were unexpectedly lower than they were supposed to be. One reason could be the effect of drying time. Extending the time for geopolymer to cool down will result in an increase of compressive strength.

Increasing the concentration of alkaline solution also can improve the mechanical strength of a geopolymer. As from the result obtained, sample G1 which comprises of mixture of MK and KOH solution with molarity of 4M gave the highest value of compressive strength compared to other samples. If molarity of the solution is increased, the strength of the geopolymer will also be enhanced.

Introduction of Na_2SiO_3 solution into the mixing composition also has a significant impact on the compressive strength of the structure. Sample G2 which made up of MK and effluent from OGT (acidic solution with pH of 6.26) was added with an amount of sodium silicate to increase its alkalinity. And hence, had increased its compressive strength as well compared to samples which made up of batik effluent (pH 10.74) and paper & pulp effluent (pH 12.30). Amount of sodium silicate added to the mixtures prior mixing should also be increased to achieve higher compressive strength.

The strength variation within each sample batches was likely in some way related to the process of producing the geopolymer itself. Although there were some slight dissimilarity in processing and formation procedure used within the study (e.g technique of stirring, sequence of ingredients mixing, accuracy of weight of materials, etc.), the results obtained were not having much gap among all the samples.

4.3 Scanning Electron Micrograph (SEM)

All four different geopolymer samples were crushed into finer form to analyze its microstructure. The SEM images showing the morphology of the samples with magnification of 5000× were obtained. The shapes of the microstructures as observed in Figure 4.3 are irregular and inconsistence in all samples. The red circles in the figure indicate the pores observed within the samples.

The difference in microstructure can be seen in sample G1 as it exhibits a compact and slightly denser structure compared to the other three samples (Figure 4.3a). Sample G2 and G4 (Figure 4.3b,d) possess almost similar structure and less dramatic difference, meanwhile sample G3 (Figure 4.3c) seems to be porous and scarcely compact. The particles of sample G3 also is the least dense among all the samples.

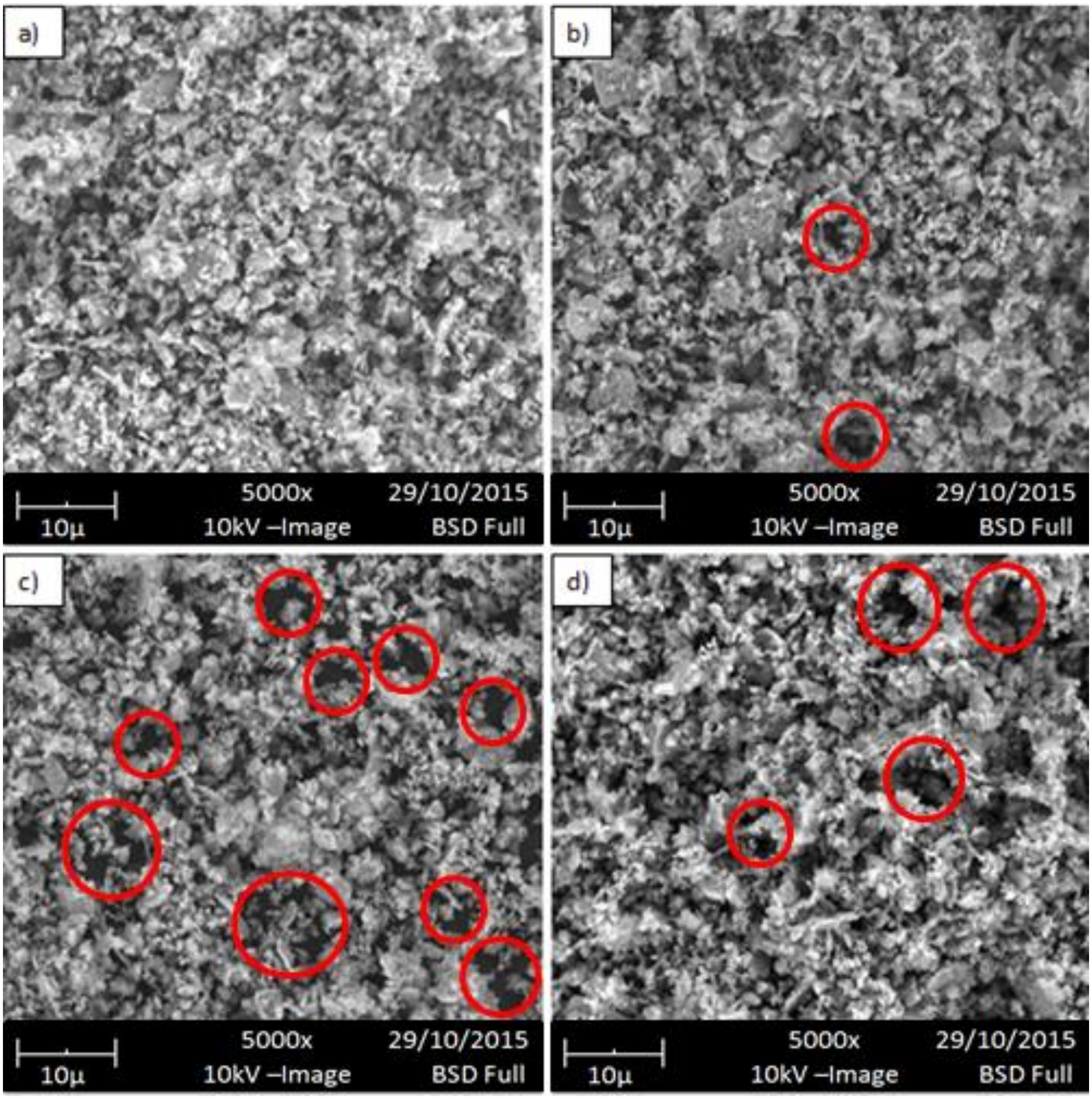


FIGURE 4.3 SEM microstructure of all samples. a) Sample G1, b) Sample G2, c) Sample G3, d) Sample G4.

To obtain more significance result of SEM, the fracture surfaces of the samples should be analyzed. Different types of geopolymer will exhibit a clearer difference in microstructure images, and thus the disparity can be interpreted reasonably.

Tables indicating the weight percentage of elements existing in the sample were also come together with the SEM images result. Table 4.3, 4.4, 4.5, and 4.6 shows the weight concentration of elements in sample G1, G2, G3, and G4 respectively.

TABLE 4.3 Weight concentration of elements in sample G1

Element Symbol	**Element Name**	**Weight Concentration (%)**
Si	Silicon	18.8
Al	Aluminum	18.5
O	Oxygen	56.9

TABLE 4.4 Weight concentration of elements in sample G2

Element Symbol	**Element Name**	**Weight Concentration (%)**
Si	Silicon	24.4
Al	Aluminum	20.8
O	Oxygen	54.5

TABLE 4.5 Weight concentration of elements in sample G3

Element Symbol	**Element Name**	**Weight Concentration (%)**
Si	Silicon	17.6
Al	Aluminum	15.7
O	Oxygen	51.4

TABLE 4.6 Weight concentration of elements in sample G4

Element Symbol	**Element Name**	**Weight Concentration (%)**
Si	Silicon	17.3
Al	Aluminum	15.6
O	Oxygen	51.1

As seen from the table above, the concentration of Si and Al in sample G2 were 24.4% and 20.8% respectively, which are the highest compared to the other samples. Apart from that, the oxygen concentration in sample G1 is the highest as compared with other samples with percentage of 56.9%.

Since the significant percentage of silicon and aluminum are exist in all specimens, this shows that the geopolymer produced are valid and acceptable. However, if the concentration of both elements is higher, the compressive strength and density of the samples would be improved.

4.4 Thermal Gravimetric Analysis (TGA)

The same powdered geopolymer samples which had been used for SEM analysis were later applied for the TGA test. Figure 4.4 below shows the TGA graph of weight percentage versus temperature for sample G1.

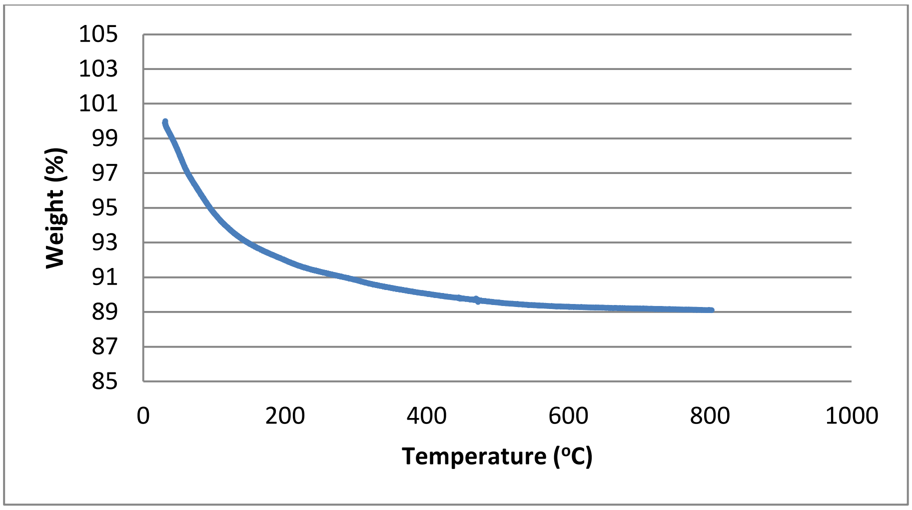


FIGURE 4.4 TGA result of sample G1

The result presented in the above graph indicates a total weight loss of ~ 11% from the sample. Major declined can be seen in between the temperature of 30^{o}C to 150^{o}C. This is due to the dewatering process that removes water and moisture exists in the geopolymer network. Second significant degradation is at temperature ranged between 200^{o}C to 450^{o}C. The weight gradually decreases from 500^{o}C to 800^{o}C.

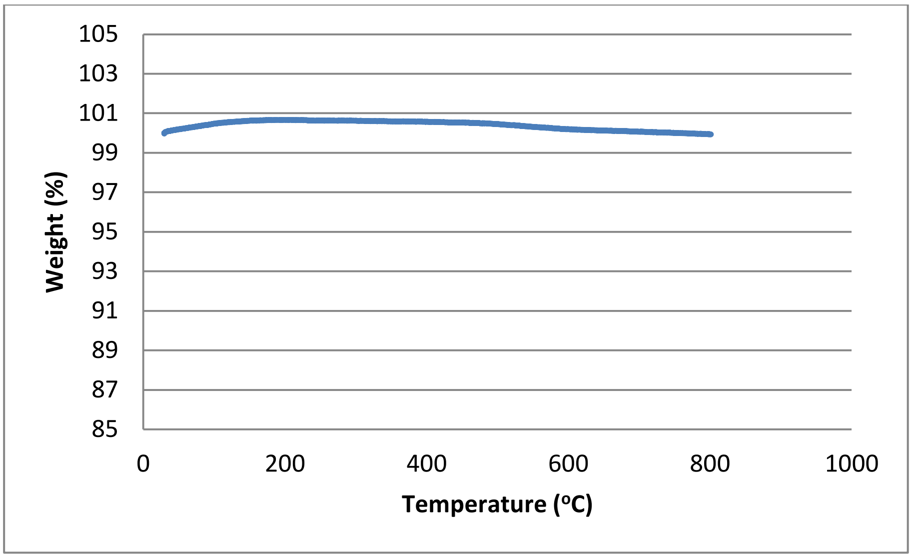


FIGURE 4.5 TGA result of sample G2

The above graph is obtained after testing the sample G2. The pattern shown by graph is really unpredictable. It indicates that the sample had gained its weight about 0.7% after exposed to temperature from 30°C to 200°C. The reason might be due to chemical reactions occurred during the test. Since the exact composition of components making up the effluent is not accurately determined, hence the chemicals involved in such reactions were unknown.

However, the weight began to decrease slightly at temperature of 200°C to 500°C before a steep decrement occurs at temperature 500°C to 600°C. Another significant thermal loss is notable at temperature ranged from 600°C to 800°C. The weight of the sample is expected to decrease with increasing temperature until there is no further weight change.

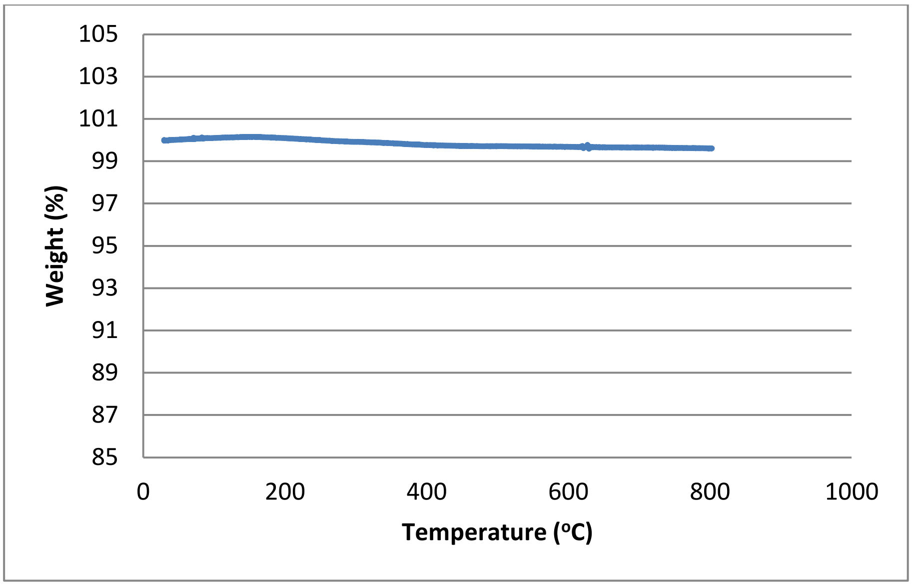


FIGURE 4.6 TGA result of sample G3

Figure 4.6 above shows the TGA graph obtained for sample G3. It seems like the pattern is almost similar to the result from sample G2. There is a little increment of weight (0.15%) recorded after the sample is heated to 180°C. The reason is also might be due to chemical reactions occurred during the process. The actual composition of components presence in the effluent is also not determined, hence will make it impossible to guess what reaction had occurred within that temperature range.

Linear reduction of weight is observed starts between the temperatures of 180°C to 450°C. It continues decreasing from temperature of 450°C and above until there is no change in weight. There is also slight disturbance in weight observed at temperature between 620°C to 640°C. The reason can be due to some interference happened in the surrounding of the room during the process.

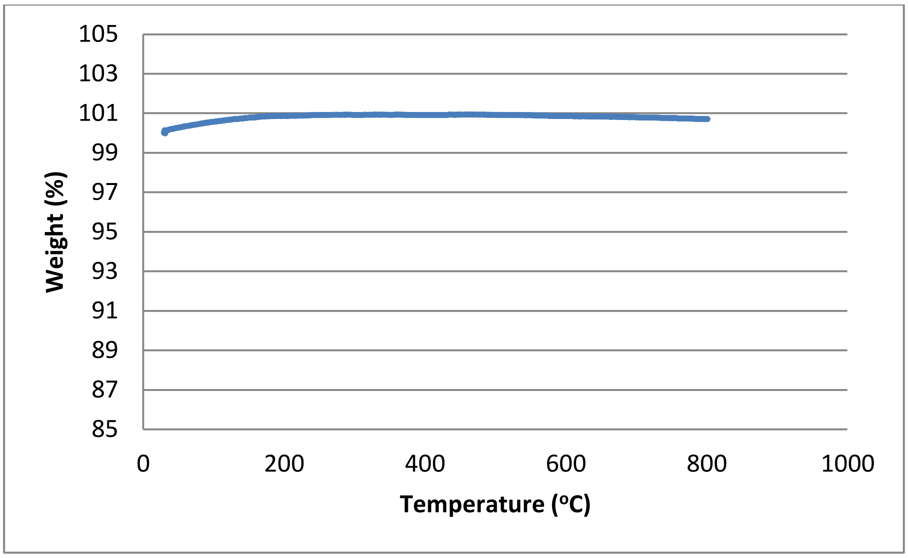


FIGURE 4.7 TGA result of sample G4

The above figure shows the TGA result obtained after analyzing the sample G4. Similar to results of sample G2 and G3, rapid increment in weight is observed for this sample after being heated to 180^{o}C. However, unlike the previous results, the weight continues to ascend until it reaches the temperature of 450^{o}C.

The only logical explanation to this behavior is the occurrence of chemical reactions throughout the heating process. Since the sample comprises of MK and simulated effluent of paper & pulp industry which contains carbon, aluminum oxide, calcium carbonate, zinc chloride, and calcium oxide, the weight gain might be the result of reaction between any of these chemicals with nitrogen to form nitride compound. Loss of weight is notably occurred later from temperature of 500^{o}C and above.

It was clear that the composition of each effluent needed to be identified prior to the mixing with MK to form geopolymer composite. Without knowing the exact amount of component making up the liquid, the reactions occurred during the TGA were also cannot be unraveled. Weight gain during TGA is usually caused by atmospheric reaction within the chamber such as adsorption or absorption, solid-gas reaction, and magnetic transitions.

TGA result of sample G1 possesses no significant abnormality as the KOH solution is made up solely by solving potassium hydroxide pellets into deionized water, hence no reaction has occurred onto the sample. Moreover, the analysis should be extended to higher temperature to further study the pattern of weight loss until the change reaches its maximum (constant weight).

CHAPTER 5

CONCLUSION AND RECOMMENDATION

The aim of this project was to synthesis geopolymer matrix by mixing metakaolin with industrial effluents and performs characterization tests to analyze the properties and characteristics of the specimens. Four characterization techniques were performed; density, compressive strength, SEM and TGA.

It was shown that the density and compressive strength of geopolymer made up of pure KOH solution (sample G1) recorded a value of 1.9402 g/cm^3 and 5.34 MPa which were the highest compared to samples comprised of industrial effluents. The reasons were due to the low molarity of alkaline in the effluents and the variety of chemical composition and concentration compared to pure KOH solution. Increasing the duration of cooling and drying to seven days or longer will also result in high compressive strength.

The SEM images of all samples were slightly similar to each other. However in sample G3, the pores were very obvious and showed the least dense structure compared to other samples. For TGA test, only sample G1 shows considerable weight loss, while the other three samples experienced gain in weight at the initial stage of heating process before they started to decrease at elevated temperature. This was due to chemical reactions occurred within the TGA chamber. The overall results obtained within this project are somehow deviated to other relevance researches.

Reusing industrial wastewater as raw material to be solidified with metakaolin, which is also a waste product from kaolin production plant to form a geopolymer composite is relatively sustainable in preserving the environment. The study of characterization and properties of produced geopolymers is essential for the student to understand and explore the geopolymer technology.

Even though it is almost impossible to be a total replacement of OPC, geopolymer which comprises of aluminosilicate-reactive materials (such as fly ash, slag, metakaolin, etc) and industrial effluent may be useful to be used in making pavement, sculpture, coating material, fish pond, and flooring. Plus, geopolymerization can also be applied to encapsulate hazardous wastewater and make it easier to be disposed compared to undergoing typical wastewater treatment.

However, for such applications to become more realistic, addition of sodium silicate (Na_2SiO_3) should be introduced in the mixing of metakaolin and effluent to increase the compressive strength of the geopolymer. It is also recommended that the duration of drying of geopolymer upon curing process to obtain a rigid structure of geopolymer which can withstand a higher compressive strength. It is also necessary to find out what are the components existing in the wastewater and their respective composition. So that whenever any unexpected reaction ever occurs upon the geopolymer structure, the reason can be foreseeable immediately.

Moreover, determining the concentration of alkalinity of the effluent is also important in analyzing the properties and characteristics of the produced geopolymer. Immobilizing as much wastewater as possible is desirable to reduce the treatment cost. Further study on different technique of recycling raw wastewater should be investigated to sustain a harmonic environment.

REFERENCES

Aguilar, A. S., Melo, J. P., & Olivares, F. H. (2013). Microstructural analysis of aerated cement pastes with fly ash, Metakaolin and Sepiolite additions. *Construction and Building Materials, 47*, 282-292.

Al Bakri, A. M., Kamarudin, H., Bnhussain, M., Nizar, I. K., Rafiza, A., & Zarina, Y. (2012). The processing, characterization, and properties of fly ash based geopolymer concrete. *Rev. Adv. Mater. Sci, 30*, 90-97.

Alida, A., Al Bakri, A. M., Kamarudin, H., Ruzaidi, C., Salleh, M. M., & Chin, K. H. (2013). The Effect of Acidic to the Fly Ash Based Geopolymer Artificial Aggregate. *Australian Journal of Basic and Applied Sciences, 7*(5), 303-307.

Berger, B. (2010). *The importance and testing of density/porosity/permeability/pore size for refractories.* Paper presented at the Proceeding of the Southern African Institute of Mining and Metallurgy Refractories Conference.

Das, S. K., Mohapatra, A. K., & Rath, A. (2014). Geo-polymer Concrete–Green Concrete for the Future—A Review.

Ferdous, W., Manalo, A., Khennane, A., & Kayali, O. (2015). Geopolymer concrete-filled pultruded composite beams–Concrete mix design and application. *Cement and Concrete Composites, 58*, 1-13.

Ferone, C., Colangelo, F., Roviello, G., Asprone, D., Menna, C., Balsamo, A., . . . Manfredi, G. (2013). Application-oriented chemical optimization of a metakaolin based geopolymer. *Materials, 6*(5), 1920-1939.

Kumar, S., & Kumar, R. (2010). Tailoring geopolymer properties through mechanical activation of fly ash.

Marín-López, C., Araiza, J. R., Manzano-Ramírez, A., Avalos, J. R., Perez-Bueno, J., Muñiz-Villareal, M., . . . Vorobiev, Y. (2009). Synthesis and characterization of a concrete based on metakaolin geopolymer. *Inorganic Materials, 45*(12), 1429-1432.

Perná, I., & Hanzlíček, T. (2014). The solidification of aluminum production waste in geopolymer matrix. *Journal of Cleaner Production, 84*, 657-662.

Rangan, B. V. (2010). *Fly ash-based geopolymer concrete.* Paper presented at the Proceedings of the International Workshop on Geopolymer Cement and Concrete.

Sheppard, L. M. (2003). Geopolymer Composites: A Ceramic Alternative to Polymer Matrices. Retrieved June 25, 2015, from http://composite.about.com/library/weekly/aa030529.htm

Tavor, D., Wolfson, A., Shamaev, A., & Shvarzman, A. (2007). Recycling of industrial wastewater by its immobilization in geopolymer cement. *Industrial & Engineering Chemistry Research, 46*(21), 6801-6805.

Welter, M. (2013). *Unidirectional fibre reinforced geopolymer matrix composites.* (Doctor of Philosophy in Chemistry), Victorie University of Wellington.

APPENDICES

APPENDIX A

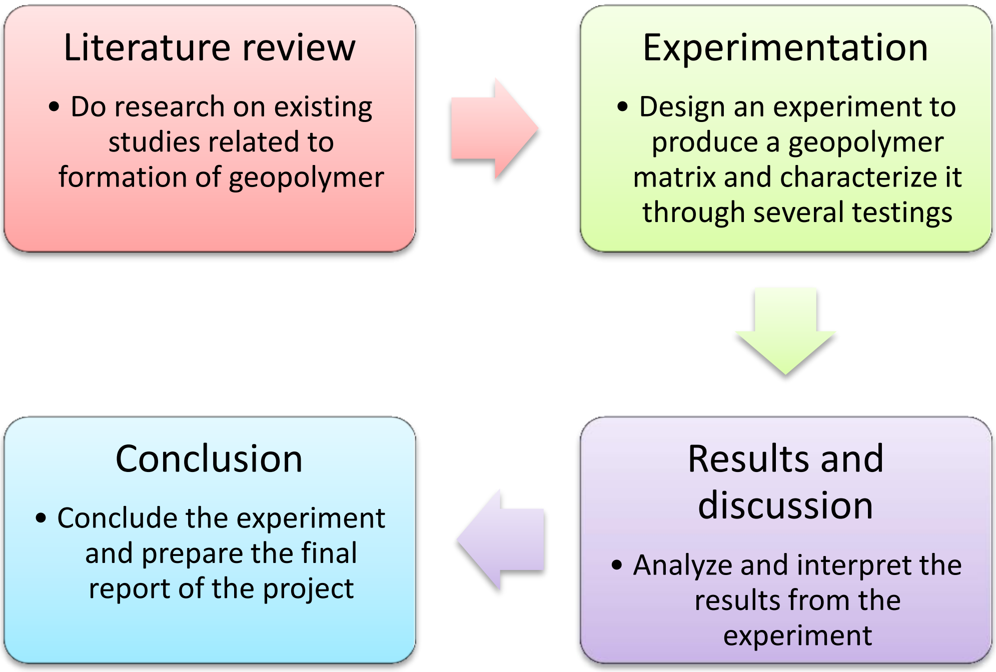


FIGURE A-1 Project flow chart

APPENDIX B

TABLE B-1 Project key milestone for FYP I

Term	No	Key Project Milestone	Expectation	Remarks
FYP 1	1	Understanding the project, consultation with supervisor, proceed with experimental study.	Week 1 - Week 14	Meeting with supervisor once a week
	2	Collection of journals, research papers for better understanding, determining projects gap, preparation of methodology, and preparation of chemicals and apparatus.	Week 2 - Week 7	Guideline from previous research papers to commence with the experimental study
	3	Preparation of extended proposal and propose to supervisor and internal examiner	Week 2 - Week 8	Formal proposal report need to be prepared
	4	Submission of extended proposal	Week 7	For the evaluation by supervisor and internal examiner
	5	Defend the proposal to proceed with project	Week 8	Present the roughly about the project study and progress to supervisor and internal examiner
	6	Proceed with the experimental work	Week 8 - Week 13	Preparation of formal report for the initial result and the progress of the project
	7	Submit draft and final interim report	Week 12 - Week 13	Submission of draft report to supervisor for checking before final report being submitted for evaluation by supervisor and internal examiner

TABLE B-2 Project key milestone for FYP II

Term	No	Key Project Milestone	Expectation	Remarks
FYP 2	1	Obtain effluent from different industries, prepare standard solution, prepare metakaolin	Week 1 - Week 3	Contact person-in-charge first prior getting the effluents.
	2	Proceed with experimental work to produce geopolymer	Week 2 - Week 7	Prepare specimens which are fit enough to undergo characterization
	3	Characterization of produced geopolymer	Week 5 - Week 10	4 characterization tests; bulk density, compressive strength, SEM, and TGA
	4	Outline report for the project work	Week 3 - Week 11	Write formal report according to the given guideline
	5	Submission of progress report	Week 8	Reporting work in progress and preliminary result obtained
	6	Pre-SEDEX evaluation	Week 11	Evaluation to select the best projects to enter SEDEX
	7	Submission of dissertation report and technical paper	Week 12	Final report to be submitted to supervisor and examiners
	8	VIVA evaluation	Week 13	Final oral presentation

APPENDIX C

TABLE C-1 Researches on synthesis and characterization of geopolymer

Year	Author(s)	Research Title	Description
2007	Dorith Tavor, Adi Wolfson, and Anat Shamaev	Recycling of Industrial Wastewater by Its Immobilization in Geopolymer Cement	Report on recycling of industrial wastewater with a residual organic compound via its solidification in a geopolymer matrix. Phenol leaching was measured when solutions that contained values similar to its saturation concentration were used.
2009	C. Marín-López, J. L. Reyes Araiza, A. Manzano-Ramírez, J. C. Rubio Avalos, J. J. Perez-Bueno, M. S. Muñiz-Villareal, E. Ventura-Ramos, and Y. Vorobiev	Synthesis and Characterization of a Concrete Based on Metakaolin Geopolymer	This paper describes the synthesis and characterization of a concrete based on metakaolin geopolymer. In addition, its physical, mechanical and thermal properties are compared to those of a concrete based on portland cement
2010	Sanjay Kumar and Rakesh Kumar	Tailoring Geopolymer Propereties Through Mechanical Activation of Fly Ash	Investigated the influence of mechanical activation of fly ash to the properties of geopolymer. Fly ash was mechanically activated by vibrating samples in an eccentric vibratory mill.
2010	B. Vijaya Rangan	Fly Ash-Based Geopolymer Concrete	Identify the effects of salient factors that influence the properties of the geopolymer concrete in the fresh and hardened states.
2012	A.M. Mustafa Al Bakri, H. Kamarudin, M. Bnhussain, I. Khairul Nizar, A. R. Rafiza, and Y. Zarina	The Processing, Characterization, and Properties of Fly Ash Based Geopolymer Concrete	This paper summarizes the current knowledge about the properties and characteristics of fly ash-based geopolymer by reviewing previous research work.
2012	Alberto Sepulcre Aguilar, Javier Pinilla Melo, and Francisco Hernández Olivares	Microstructural Analysis of Aerated Cement Pastes with Fly Ash, Metakaolin and Sepiolite Additions	Studied products formation in aerated cement pastes, using aluminum powder as expansion agent, in order to determine the effect of metakaolin and sepiolite

			addition as well as cement selection, in pore network.
2012	Claudio Ferone, Francesco Colangelo, Giuseppina Roviello, Domenico Asprone, Costantino Menna, Alberto Balsamo, Andrea Prota, Raffaele Cioffi, and Gaetano Manfredi	Application-Oriented Chemical Optimization of a Metakaolin Based Geopolymer	In this study the development of a metakaolin based geopolymeric mortar to be used as bonding matrix for external strengthening of reinforced concrete beams is reported.
2013	Michael Welter	Unidirectional Fibre Reinforced Geopolymer Matrix Composites	This study investigated several key aspects of fibre reinforced geopolymer matrix composites in order to improve the basic knowledge of geopolymers.
2014	Sourav Kr. Das, Amarendra Kr. Mohapatra, and A.K. Rath	Geo-polymer Concrete–Green Concrete for the Future—A Review	This paper gives an overall view of the process and parameters which affect the geo-polymer concrete till date. It is an inorganic 3D polymer which is synthesized by activation of aluminosilicate source like fly ash.
2014	Ivana Perná, and Tomás Hanzlícek	The Solidification of Aluminum Production Waste in Geopolymer Matrix	The study was on the solidification of waste materials from aluminum production and insulating properties of products when both waste types are reacting with geopolymer precursors.
2015	Wahid Ferdous, Allan Manalo, Amar Khennane, and Obada Kayali	Geopolymer Concrete-Filled Pultruded Composite Beams – Concrete Mix Design and Application	A mix design procedure has been proposed for fly-ash based geopolymer concrete and its use as infill hybrid composite beam is investigated. Then, the structural performance of geopolymer concrete filled hybrid composite beam is investigated to determine their possible application in civil infrastructure.

APPENDIX D

FIGURE D-1 Mixing process of metakaolin and alkaline activator

FIGURE D-2 Device for SEM analysis

FIGURE D-3 Device for compressive strength test