EFFECT OF GEOPOLYMER CEMENT IN ACIDIC WELL

By

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The Dissertation Submitted in Partial Fulfillment of

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Petroleum Engineering Programme

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Approved by,

____

(Ms. Raja Rajeswary Suppiah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

September 2014

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

Roosalee Che-ubong

ABSTRACT

Cement manufacturing industries which release a great amount of CO_2; CO_2 is one of the greenhouse gases which gives high impact to global warming. In this case, it is important to find and develop the environmental friendly cement slurry to reduce the amount of CO_2 to the environment. Geopolymer cement is a geopolymer material in cement slurry that can reduce the CO_2 in the part of manufacture. Furthermore, it has good compressive strength, low cost, stronger resistance to corrosion, acid resistance, and low cost. In the oil well cementing has various parameters that affect the cement properties such as pressure, temperature, acid and etc. This project is aimed to study on Fly-ash based Geopolymer cement properties on compressive strength at various concentrations of Sodium hydroxide (NaOH) and study the effect of Fly-ash based Geopolymer cement and Class G cement in sulfuric acid (H_2SO_4) at various concentrations. This would further on lead to the possibility of substituting Ordinary Portland Cement (OPC) with Fly-ash based Geopolymer cement. By substituting OPC with Fly-ash based Geopolymer cement, we should to find the best formulation of Fly-ash based Geopolymer cement slurry to indicate a high compressive strength than the OPC. This project manipulates several variables mainly the concentrations of NaOH solution, curing time and concentrations of H_2SO_4 solution at various concentrations in order to determine its effect on the Fly-ash Geopolymer compressive strength. The scope of study is focused on preparing the Fly-ash based Geopolymer cement slurry and testing cement slurry according to API-RP-10B. In the experiment, a variable is manipulated and its effect on the Geopolymer compressive strength is observed. From the experiments conducted, we are able to figure out the optimum condition for Fly-ash based Geopolymer cement that would result in a higher compressive strength. It is concluded that 12M of NaOH indicates a higher compressive strength than 10M and 15M. Curing time is directly proportional to compressive strength that means a longer curing time results a high compressive strength. Moreover, H_2SO_4 solution affects to loss compressive strength and the increasing of H_2SO_4 concentration considerably affects the compressive strength of OPC and Geopolymer Cement. All of these results has been presented and discussed. The objectives of the final year project have been achieved.

ACKNOWLEDGEMENT

First and foremost, I would like to express my utmost gratefulness to Allah SWT for giving me the strength and good health during the completion of my project. Without His blessing, I would not be able to complete my FYP.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND STUDY

Nowadays, the world is threatened of climate change by green house gasses. Carbon dioxide (CO_2) is the major greenhouse gas that effects the ozone layer**.** According to the Government of Canada greenhouse gas report, cement manufacturing is the one of industry which releases great amount of CO_2. From this issue, it is important to find and develop an environmental friendly cement slurry to use in the industries to reduce the amount of CO_2 (Amir et al., 2008).

Cement is widely used in construction material (Amir et al., 2008). Portland cement (Class G cement) is a type of cement which is mostly used in oil and gas industries. The component of Portland cements are limestone and either clay or shale. However, Portland cement is the one of major greenhouse gases producer, so it is important to find the new cement that can reduce the CO_2 and have better quality than Portland cement (Nik Khairul & Sonny, 2013).

Geopolymer cement is cement slurry obtain through the activation of aluminosilicates with aqueous alkaline solution which can reduce the greenhouse gases (Amir et al, 2008). Geopolymer cement indicates the better performance such as compressive strength, acid resistance, mass loss, pumpabilty and etc. (Van Jaarsveld et al., 1997; Diaz et al., 2010).

However , the oil well cement is affected by acidizing treatment such as zonal isolation (Brady et al.,1989). According to Silva et al. (1996), stated that the factor affects on zonal isolation depend on surface defect, cement slurry, composition and acid solution composition. For better understanding, this research will focus on acid resistance of Fly-ash based Geopolymer cement toward sulfuric acid.

1.2 PROBLEM STATEMENT

Carbon dioxide (CO_2) is one of the greenhouse gases which gives high impact to global warming issue nowadays (EPA, 2014). Portland cement is the construction material used in the many industries. This cement manufacturing is one of the processes which releases great amount of CO_2 gases into atmosphere to impact the ozone layer that causes global warming.

Geopolymer cement is one of the best environmentally friendly materials to replace the Portland cement. Geopolymer cement indicates the better performance such as compressive strength, mass loss, pumpability and has higher resistance towards corrosion. Due to carbonation of concrete, pH of Portland cement produced from $CaCO_3$ drops from 12-13 to 7-8 reading and this leads to corrosion. However, Geopolymer cement comprises K_2CO_3 or Na_2CO_3 drops from 12.5-11 to 10.5-10. The difference in the drop of Geopolymer cement is not significant. Hence, the Geopolymer cement has higher resistance towards corrosion (Davidovits, 2005).

Furthermore, Geopolymer cement is better than Portland cement in the segment of acid resistance (Uehara, 2010). Comparison study carried out between the Geopolymer and Portland cement shows that Geopolymer cement is better than Portland cement because it emits less CO_2 and energy saving in the process (Hewayde et al., 2006). The cost of Portland cement is 10%-30%higher than Geopolymer cement (Lloyd & Rangan, 2010).

In this project, we will focus on the acid resistance of Fly-ash based Geopolymer cement. Fly-ash based Geopolymer cement will be developed and introduced an alternative cement which has less impact from an acidic condition.

1.3 OBJECTIVES

The main objective of this project is to study the effect of using fly ash in improving the geopolymer properties by adding Sodium hydroxide at various concentrations. A comparison study is also conducted with the Class G cement. A further investigation is also carried out to measure the compressive strength of fly ash based geopolymer cement immersed in various concentrations of sulfuric acid.

1.4 SCOPE OF STUDY

The scope of study is focused on preparing the cement slurry and testing cement slurry according to American Petroleum Institute API-RP-10B in Class G cement and Fly-ash based Geopolymer cement, and to examine the Fly-ash based Geopolymer cement and Class G cement properties on compressive strength at various concentrations of Sodium Hydroxide (NaOH) and sulfuric acid, and compare the results.

CHAPTER 2

THEORY AND LITERATURE REVIEW

2.1 THEORY

2.1.1 Cement

Cement is operated by circulating cement slurry through the inside casing shoe at the bottom of casing string. The main functions of cement are restriction of fluid flow between permeable zones, support the casing string, protect the casing from corrosion, and support the well-bore walls to protect the collapse of formations (Economides, 1990).

2.1.2 Classification of Cementing

Classification of oil well cementing can be divided into two; there are primary cementing and secondary cementing. The main objective of primary cementing is supporting the casing pipe and restricts the movement of formation fluid behind the casing. The primary cementing has many advantages such as seal off zones of lost circulation (fractured formation), protect the casing from shock loads during drilling and protect casing from corrosion (Faiza, 2007).

Furthermore, the common secondary cementing jobs are re-cementing, plug back cementing and squeeze cementing. Re-cementing ensures the cement slurry is circulated into the annulus through perforation. The reasons for re-cementing are to supplement a faulty primary job and extending the casing protection above the cement top. Plug back cementing determine the hole is plugged by cement in order to initiate a new drilling operation and plug back is carried out for a number of reasons. They are abandonment of the hole, sidetracking the hole, seal off lost circulation, shutting off water or gas encroachment. Squeeze cementing is operated during drilling and completion. It involves forcing the cement slurry under pressure into open holes or channels behind the casing or into perforation tunnels. The main purpose of squeeze cementing are to improve a faulty primary cementing job, repairing casing defects, stopping lost circulation in open hole during drilling, supplementing a faulty perforation job and reducing water cut in a producing well (Faiza, 2007).

2.1.3 Type of Cement

The oil industry uses the cement specified by API classification. The table below shows the difference of eight (8) classes of cement.

Table 1: The Difference Class of API Cement for Use at Down-Hole Condition (Dwight, 1989).

API Classification	Water (%)	Mixing Water (gal/sack)	Slurry Weight (lbm/gal)	Well depth (ft)	Temp. (F)
A	46	5.2	15.6	0-6000	80-170
B	46	5.2	15.6	0-6000	80-170
C	56	6.3	14.8	0-6000	80-170
D	38	4.3	16.4	6000-10000	170-260
E	38	4.3	16.4	10000-14000	170-290
F	38	4.3	16.2	10000-16000	230-320
G	38	5.0	15.8	0-8000	80-200
H	38	4.3	16.4	0-8000	80-200

Mix water is the water which is used to make up the cement slurry. Its amount must be carefully controlled because of, if the value of mix water is high so the cement will not set strong. In other hand, the value of mix water is not enough then the value of slurry density and viscosity will increase, pumpability will decrease and less volume of slurry will be produced from each sack of cement. Referring to table above, there are average value and can be changed when it meets the specific temperature and pressure (Dwight, 1989).

Each class of cements has different properties. Class A and B is used when there is no special requirement and it is cheaper than other class. For class B and C, there is moderate to high sulfate resistance and class C has high strength cement. Class D, E and F are good for deep wells under high pressure and high temperature conditions, moderate to high sulfate resistance and high cost. Lastly class G and H, this class is general purpose cement, widely used, moderate to high sulfate resistance, and can be modified using additive to suit application (Dwight, 1989).

2.1.4 Cement Slurry

According to Baker Hughes (2011) revealed that cement slurry can be divided into two (2) types in cementing operation which are lead slurry and tail slurry. Lead slurry is a filler type which contains lower density than tail slurry. But it's greater than the mud and spacer density. This type of slurry is designed to compare with tail slurry for economical matter. The application within the wellbore annulus is intended for isolating weak zones, loss zone, natural fracture and corrosive fluids. Lead slurry is designed to set after tail slurry regarding to the process sequences of cement job. Besides, the cement should set from the bottom hole to the top, since the lead slurry will transmit hydrostatic pressure to the tail slurry while it goes through transition. Lead slurry design is normally applied for cement class G or H to withstand the deeper well and higher temperature at the bottom hole static. For hydrostatic limitations, it's necessary to design the gas tight slurry to resist the damage sheath because of weak formation. Main purposes of lead slurry design are;

- To maintain the hydrostatic column of cement slurry inside the annulus above pore pressure and below fracture gradient.
- To reduce the total cost of cement job while providing hydraulic seal between casing / formation as well as structural support to the casing.

Moreover, Tail slurry is higher density than lead slurry. It's required for zonal isolation of critical zones or hydrocarbon bearing formation. Tail slurry will be designed for higher and rapid compressive strength developments for main reason are;

- To reduce Waiting-On-Cement times (WOC).
- To enhance shoe integrity.
- To provide hydraulic seal between the casing/formation to isolate low pressure zones from high pressure zones.

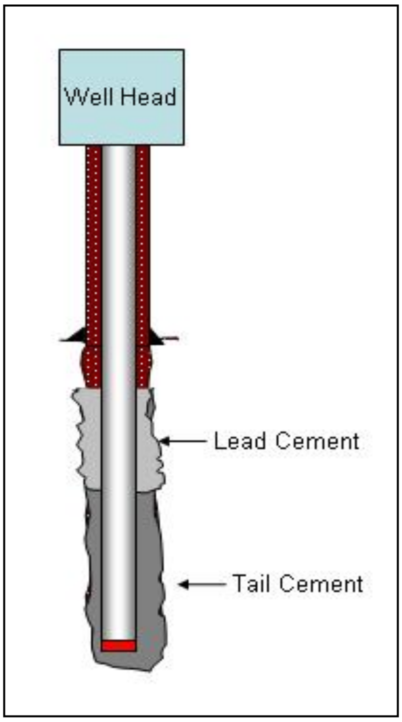


Figure1: Lead Cement and Tail Cement

(Source: http://www.drillingformulas.com/what-are-lead-and-tail-cement/).

2.1.5 Cement Properties

- *Compressive Strength*

This property determines the static and dynamic stresses in the cement in oil wells. Dead weight of pipe is the value of static stress and the action of fluid and formations is the value of compressive stresses. Moreover, the value of dynamic stress is coming from drilling operation. This cement property is supporting casing string / wellhead etc. Cement sheath must develop the minimum compressive strength ~ 500 psi and strength retrograde between 80ºC to 120ºC (Faiza, 2007).

- *Fluid Loss*

Water can lost from slurry before it reaches the intended place and its amount should be determined from lab tests and the amount can be tolerated depending on type of cement job and cement slurry formulation. Control fluid loss additives are used to control the fluid leak-off to the formation. The main function of fluid loss can be divided into two. Main functions are on rheological properties, thickening time and to reduce the risk of wellbore intrusion. Secondly, cement slurries is maintained by constant solid: liquid ratio during placement and the setting time (Faiza, 2007).

- *Thickening Time*

This property determines the length of time the slurry can be pumped. It is measured by cement consistomer. Sufficient time to allow cement slurry to be mixed, pumped into casing and displaced into annulus approximately 2-3 hours. Moreover, retarders are used for cementing deep and hot wells where as accelerators are used to cement shallow wells and surface casings and calcium chloride is the accelerator which decreases thickening time but for retarders, it increases the thickening time. (Faiza, 2007).

2.1.6 Portland Cement

Portland cement is a type of cement which is mostly used in oil and gas industries. It is made from limestone and either clay or shale (Smith, 1989). Calcium-Silicates-Hydrate (C-S-H) and Calcium Hydroxide ($Ca(OH)_2$) are the products of primary hydration which is coming from the cement mix with water (Hewlett, 1998; Taylor, 1997). Moreover, Portland cement manufacturing is one of the processes which emit a great amount of CO_2 into atmosphere to impact the ozone layer that is causing of global warming. So, Geopolymer cement is one of the environments friendly cement that can replace the Portland cement because of the many advantages compared with Portland cement. Furthermore, the basic components of Portland cement are shown in Table 2 below;

Table 2: Basic Components of Portland Cement (Source: Mehta and Monteiro, (n.d.))

Component	Formula	Trade name	Amount (%)	Function
Tricalcium Silicate	CaO_3SiO_2	C_3S	50%	- Fastest hydration - Overall and early strength - Protect a sulphate attack
Dicalcium Silicate	CaO_2SiO_2	C_2S	25%	- Slow reacting - Responsible for gradual increase in strength
Tricalcium Aluminate	$CaO_3Al_2O_3$	C_3A	10%	- Initial set and early strength
Tetracalcium Aluminum	-	-	-	-
Ferrite	$CaO_4Al_2O_3$ Fe_2O_3	C_4AF	10%	- Low heat of hydration
Other oxides such as gypsium, sulphate magnesia, free lime	-	-	5%	-

2.1.7 Geopolymer Cement

Geopolymer cement is one of the best environmentally friendly materials to replace the Portland cement. There are many advantages such as reduce CO_2 emission, use less energy in process, give stronger resistance to corrosion, low cost and acid resistance compared to Portland cement(Mohamed & Ranjith, 2011). Due to carbonation of concrete, pH of Portland cement produced from $CaCO_3$ drops from 12-13 to 7-8 and this leads to corrosion. However, Geopolymer cement comprises K_2CO_3 or Na_2CO_3 drops from 12.5-11 to 10.5-10. The difference in the pH drop of Geopolymer cement is not significant. Hence, the Geopolymer cement has higher resistance towards corrosion (Davidovits, 2005).

Furthermore, Geopolymer cement is better than Portland cement in the segment of acid resistance (Uehara, 2010). Geopolymer cement is better than Portland cement because Geopolymer cement releases less CO_2 and save energy during the manufacturing (Hewayde et al., 2006). The cost of Portland cement is 10%-30% higher than Geopolymer cement (Lloyd & Rangan, 2010).

In additional, Geopolymerization process is the mechanism of geopolymer at pH greater than 12 when alkaline activation of fly ashes in aqueous environment. According to the research of Frantisek Skvara et al. showed the geopolymerization process started from dissolving fly ash and got the formation of geopolymer structure from solution. The next step, Si-O-Al-O skeleton structure is presented by calcium atoms and replaces a charge on aluminum atoms play an important role. To further enhance the understanding, Figure 2 shows the conceptual model for geopolymerization.

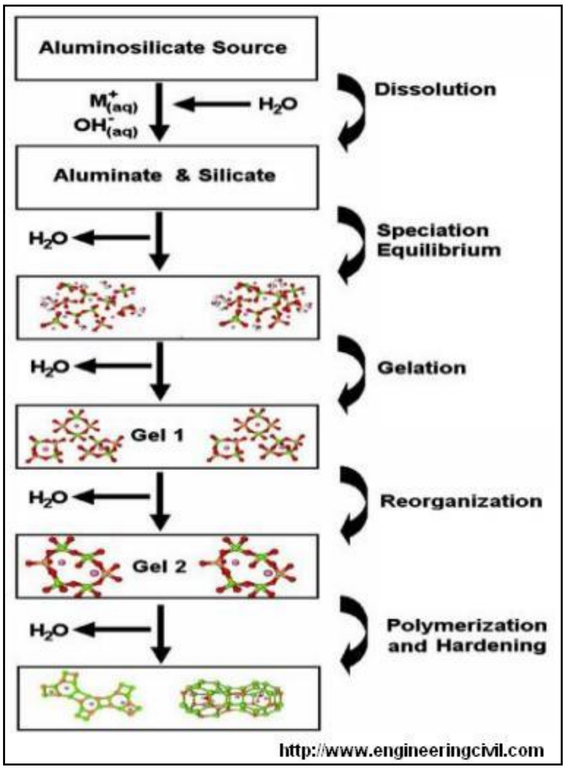


Figure 2: The Conceptual Model for Geopolymerization

(Source: http://www.engineeringcivil.com).

2.2 LITERATURE REVIEW

Portland cement is a major construction material used in the industries. Portland cement manufacturing is the one of industry which is release a great amount of CO_2 (Refer to Figure 3), so we must find the material that is friendly with world. Geopolymer cement is the geopolymer material in cement slurry that can reduce the gas CO_2, enhance mechanical property in cement system, stronger resistance to corrosion, low cost and stronger in acid resistance. Robustness and versatility is a key attribute of Geopolymer system (Amir et al., 2008).

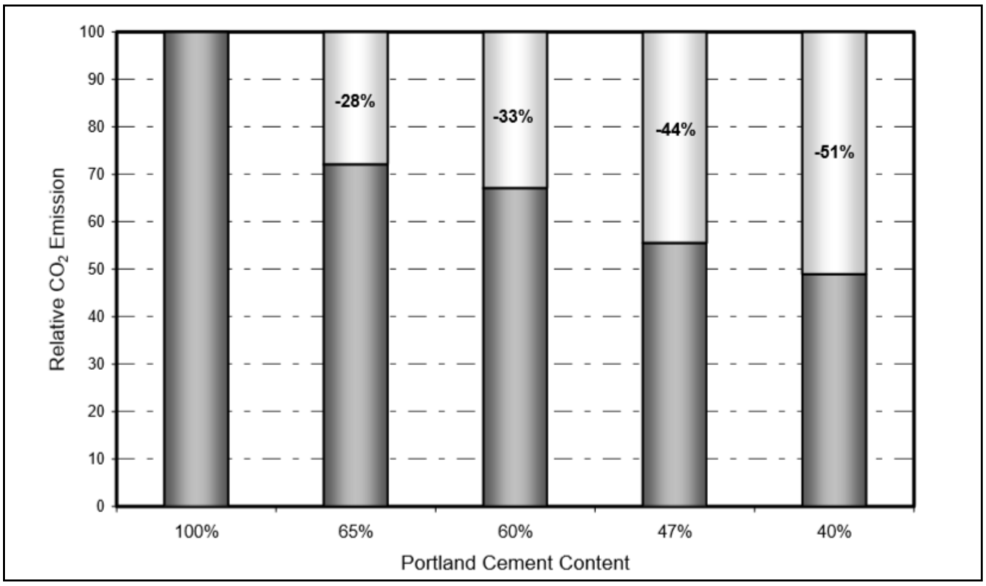


Figure 3: Resulted CO_2 Emission (Amir et al., 2008).

2.2.1 Compressive Strength

According to Amir et al. (2008), the result of compressive strength shows that conventional lightweight neat cement blend over 48 hours, while Geopolymer cement blends perform significantly better. Moreover, the Geopolymer cement shows superior early and late compressive strength development. The graph of compressive strength development for Geopolomer cement and neat cement is shown in the Figure 4.

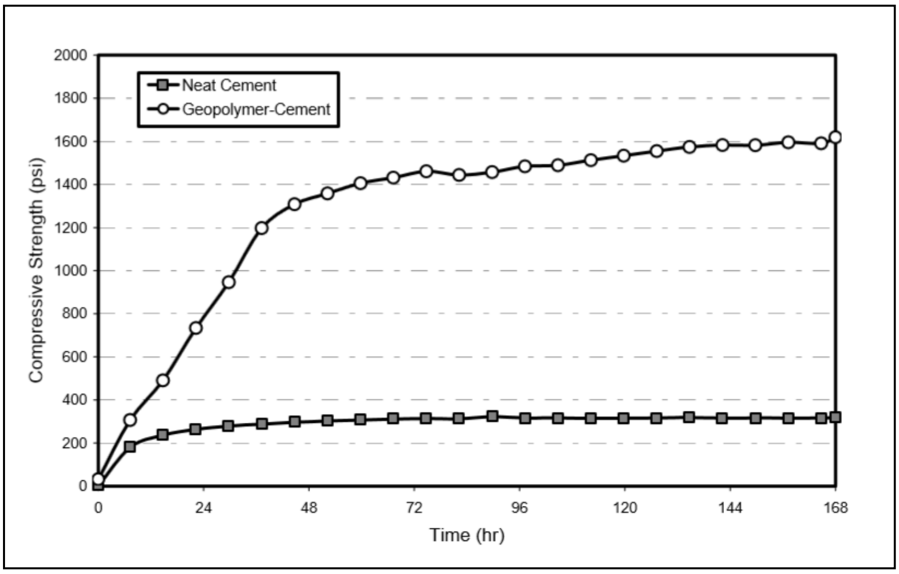


Figure 4: Compressive Strength Development between Geopolomer Cement and Neat Cement (Amir et al., 2008).

According to Frantisek Skvara (2007) revealed the tensile force is the cause of cracking and other problem in the concrete structure. From his research that refer to Figure 5, it shows the ratio of compressive strength and tensile strength in Ordinary Portland Cement (OPC) is around 10:1 and fly-ash based Geopolymer cement is around 10:5.5. This result shows the Geopolymer cement has strong resistance to tensile forces.

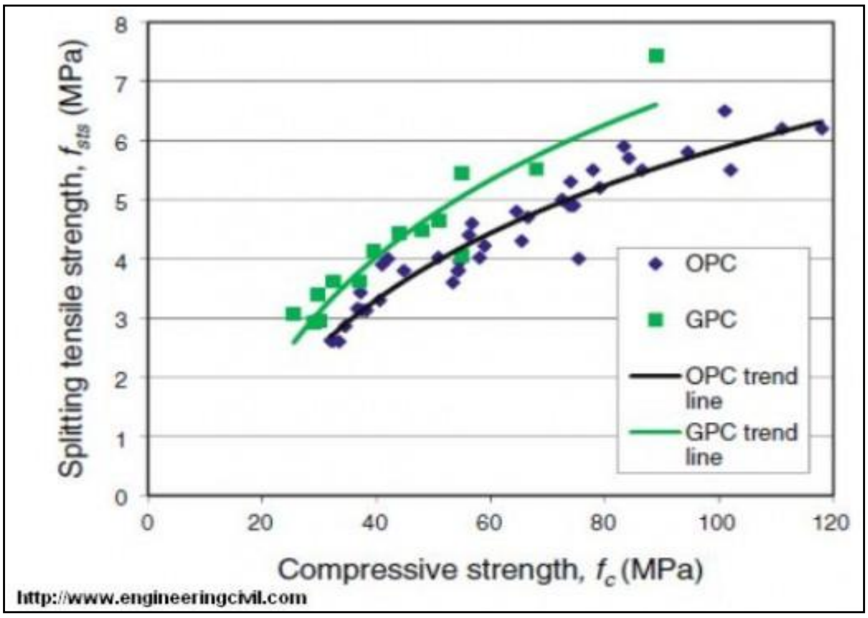


Figure 5: The Comparison Tensile Strength of GPC and OPC with Compressive Strength (Source: http://www.engineeringcivil.com).

According to Nik Khairul & Sonny (2013), it shows that the compressive strength loss of class G cement depend on the curing condition (pressure and temperature) which is shown in Figure 6. At constant pressure, the compressive strength loss decreased rapidly from 90°F-200°F. However, the value of compressive strength loss in constant temperature is lower than constant pressure. Therefore, we can conclude that the increasing of pressure has more impact to compressive strength than increasing the temperature.

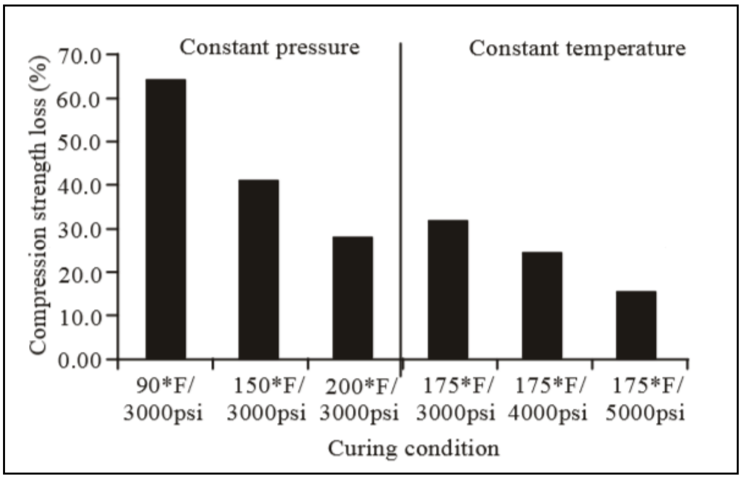


Figure 6: Compressive Strength Loss with Different Curing Condition (Nik Khairul & Sonny, 2013).

2.2.2 Acid Resistance of Geopolymer Cement toward Sulfuric Acid

According to research conducted by Rangan (2005), Davidovits (2011). and Song et al. (2005) revealed the fly ash based geopolymer concrete immerse in sulfuric acid solution and result illustrate the OPC concrete shows sign of severe damage but the fly ash based geopolymer concrete remain structurally inert except development of some fine crack on surface.

Geocistem (1997) & Davidovits et al. (1999) showed the result from testing Geopolymer cement immersed in 5% sulfuric acid solution (Figure 7). They divided into 2 tests which are H_2SO_4 24 hours and H_2SO_4 28 days of hardening. From the test after 28 days, weight change of Geopolymer Carbunculus Cement remain stable but 50 % Portland Cement CEM I 42.5 R is destroyed by acid. For second test after 56 days, Geopolymer Carbunculus Cement loss the weight change less than 5% but -63% of Portland Cement CEM I 42.5 R losses the weight change. We can conclude that the Geopolymer cement yield acid resistance more than Portland cement.

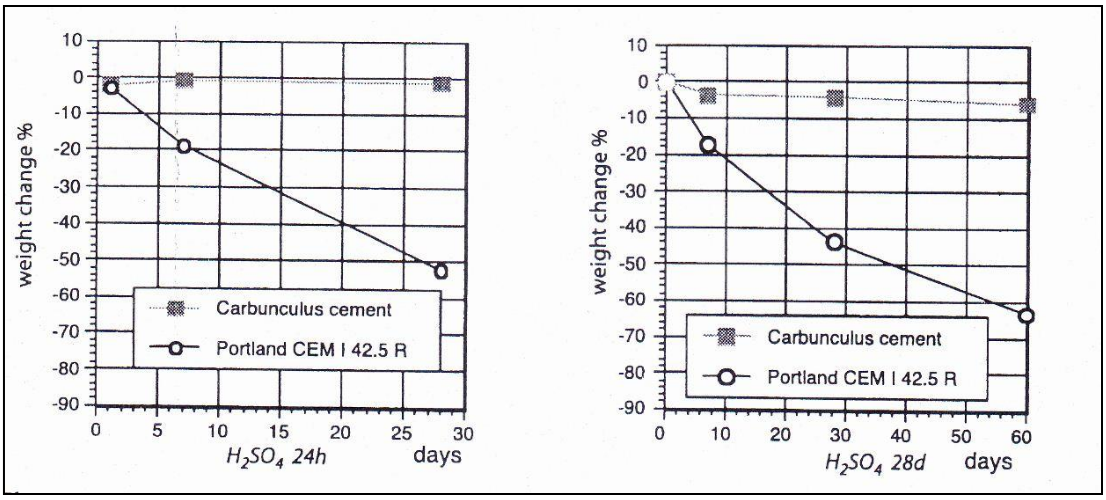


Figure 7: Comparative Test Carbunculus (Geopolymer Cement) vs. Portland Cement I.42.5 R in Sulfuric Acid Solution (5%) (Geocistem 1997; Rinaldi et al., 1999).

Wallah et al. (2005) studied the effect of compressive strength when sulfuric acid attacks on fly ash concrete at various concentrations which are 0.5%, 1% and 2% (Figure 8). Compressive strength remains stable at 0.5% sulfuric acid and start to decrease slightly after 20 weeks. At 1.0% and 2.0% sulfuric acid, the compressive strength is rapidly decreased from week 1 until week 25. Therefore, we can conclude that residual compressive strength is inversely proportional with various sulfuric acid concentrations.

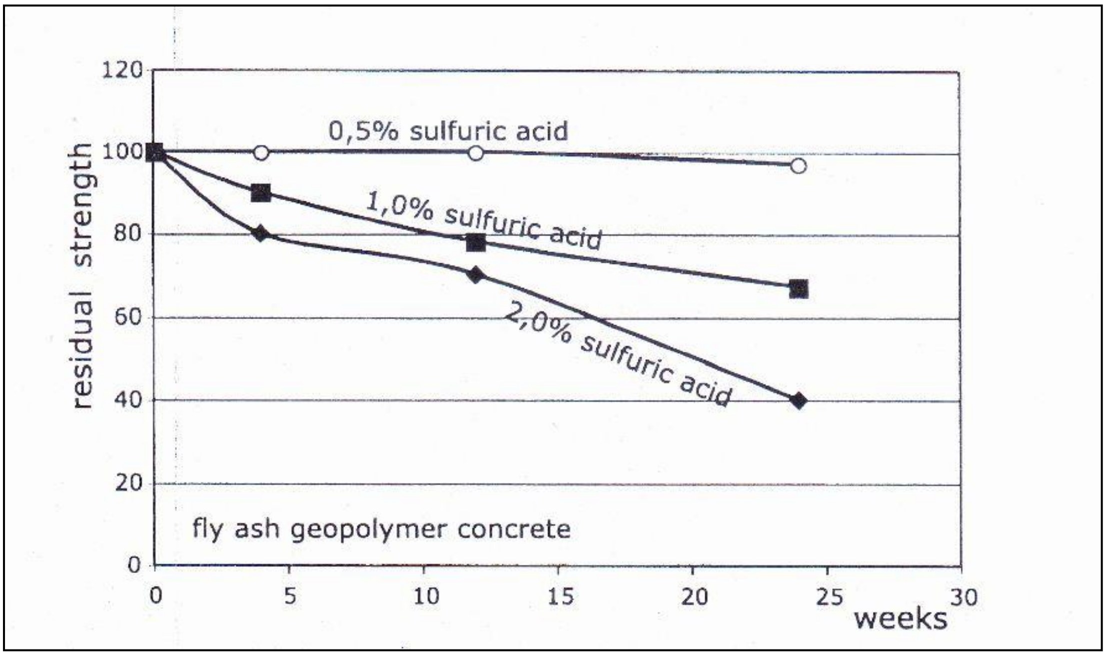


Figure 8: Compressive Strength of Fly-ash Based Geopolymer Concrete at Various Sulfuric Acid Concentrations (Wallah et al., 2005).

CHAPTER 3

METHODOLOGY

3.1 PROCESS FLOW

The process flow is important for student that is planning the project to complete on time. Figure 9 shows the sequence of work which starts from problem statement and ends with conclusion of this project.

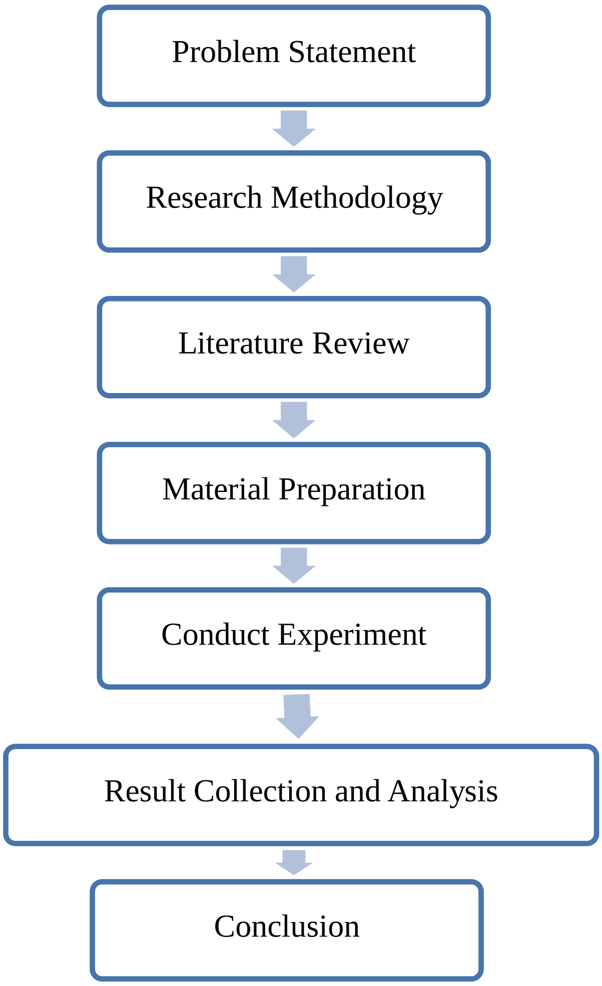


Figure 9: The Sequence of Work.

3.2 GANTT CHART/KEY MILESTONE

The project was expected to complete within the duration of two semesters. The project schedule were planned to start in semester May 2014 and to be completed in semester September 2014. Table 3 shows the project Gantt chart/Key Milestone and work details with respective timeline/duration.

Table 3: Gantt Chart /Key Milestone for FYP I.

Description of Planning	Weeks													
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
Selection of Project Topic	■	■	■											
Preliminary Research Work			■	■	■	■	■							
Submission of Extended Proposal								*						
Proposal Defense									■					
Project work continues										■	■	■		
Submission of Interim Draft Report													*	
Submission of Interim Report														*

Table 4: Gantt Chart /Key Milestone for FYP II.

Description of Planning	Weeks														
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*
Experimentation	■	■	■	■	■	■	■								
Progress Report Submission							*								
Continue the Experiment							■	■	■						
Pre-SEDEX Presentation									*						
Prepare the Report										■	■				
Final Draft Report Submission												*			
Technical Paper Submission												*			
Viva														*	
Final Report Submission (Hard Bound)															*

■ = Process * = Milestone

3.3 MATERIALS AND TOOLS

3.3.1 Materials

- Fly-ash (Brown Color) Powder.
- Class G Cement Powder.
- Distilled Water.
- Sodium Silicate (Na_2SiO_3).
- Sodium Hydroxide (NaOH) 10M, 12M and 15M.
- Grease.
- Sulfuric Acid (H_2SO_4).

3.3.2 Tools

- Cement Moulds 50mm x 50mm x 50mm.
- Constant Speed Mixer.
- Compressive Strength Tester.
- Oven.
- Beakers.
- Weighing Machine.

3.4 PROCEDURES

3.4.1 Preparation of Cement Slurry and Cement Cubes

Before the cement samples are formed into cube in shapes, cement slurry samples will be made based on American Petroleum Institute API-10B-2 procedure by using Constant Speed Mixer. Two (2) types of cement will be used in this study which are class G cement (GC) and Geopolymer cement (GPC) (Figure 10) and Table 5 shows the formulation of cement slurries composition. Moreover, this project used the Sodium Hydroxide (NaOH) at various concentrations there are 10M, 12M and15M.

Table 5: Cement Slurries Composition.

Samples	Cement (792 g)		Mix Liquid (349 g)		
	Class G	*Fly Ash*	*NaOH (10,12,15M.)*	*Na_2SiO_3*	*H_2O*
GC	100%	-	-	-	349 g
GPC (1)	-	100%	42.57 g	106.43 g	200 g
GPC (2)	-	100%	349 g	-	-

Figure 10: Type of Cements.

Table 6: Cement Slurry and Cement Cube Sample Preparation.

Cement Slurry and Cement Cube Samples Preparation	
No.	**Procedure**
1	Weigh amount of cement and water needed.
2	Pour the appropriate amount of water into the mixer container.
3	Pour the amount of chemical additive (liquid) into the mixer container.
4	Turn the power on.
5	Pour the amount of cement and additive (powder) into the mixer container.
6	Blend the cement and the liquid material around 60 seconds in the cement mixer (Figure 11).
7	Pour the cement slurry that was prepared earlier into two inch squared cement moulds (Figure 12). Make sure all the moulds are greased first before filling in the slurry.
8	After the moulds have been filled and covered with the top plate, immediately place them in the oven.
9	Set the temperature of oven at 60 Celsius, 24 hours.

Figure 11: Cement Mixer.

Figure 12: Cement Moulds.

3.4.2 Curing Time

After the mold is released from oven, it would be cured for 1 day, 3 days and 5 days at room temperature respectively. Next step is doing the compressive strength test that will be described in step 3.3.3 and choose the sample which has optimum compressive strength to immerse in sulfuric acid.

3.4.3 Determination Compressive Strength of Cement Cubes

Determination compressive strength of cement cubes can be determined by Compressive Strength Tester (Figure 13). The compressive strength give the result in the display monitor when the maximum loading at which the cement fails. The procedures of this method are as below:

Table 7: Compressive Strength Test.

Compressive Strength Test	
No.	**Procedure**
1	Place the cement specimen on the lower platen of the hydraulic cylinder.
2	Adjust the layer of steel at the bottom.
3	Turn on the Compressive Strength Tester.
4	Press the blue button to push the upper base of hydraulic cylinder so that it is touching the specimen.
5	Close the safety shield before beginning the test.
6	Push up the “Controlling Handle” to start the pump.
7	Hold down the “Controlling Handle” while observing the specimen. When the specimen fails, push down the “Controlling Handle” to stop the test and the pump.
8	The “Maximum Compressive Strength (KN)” indicates when the maximum load at which the cement fails.

Figure 13: Compressive Strength Tester.

3.4.4 Preparation of Acid Solution

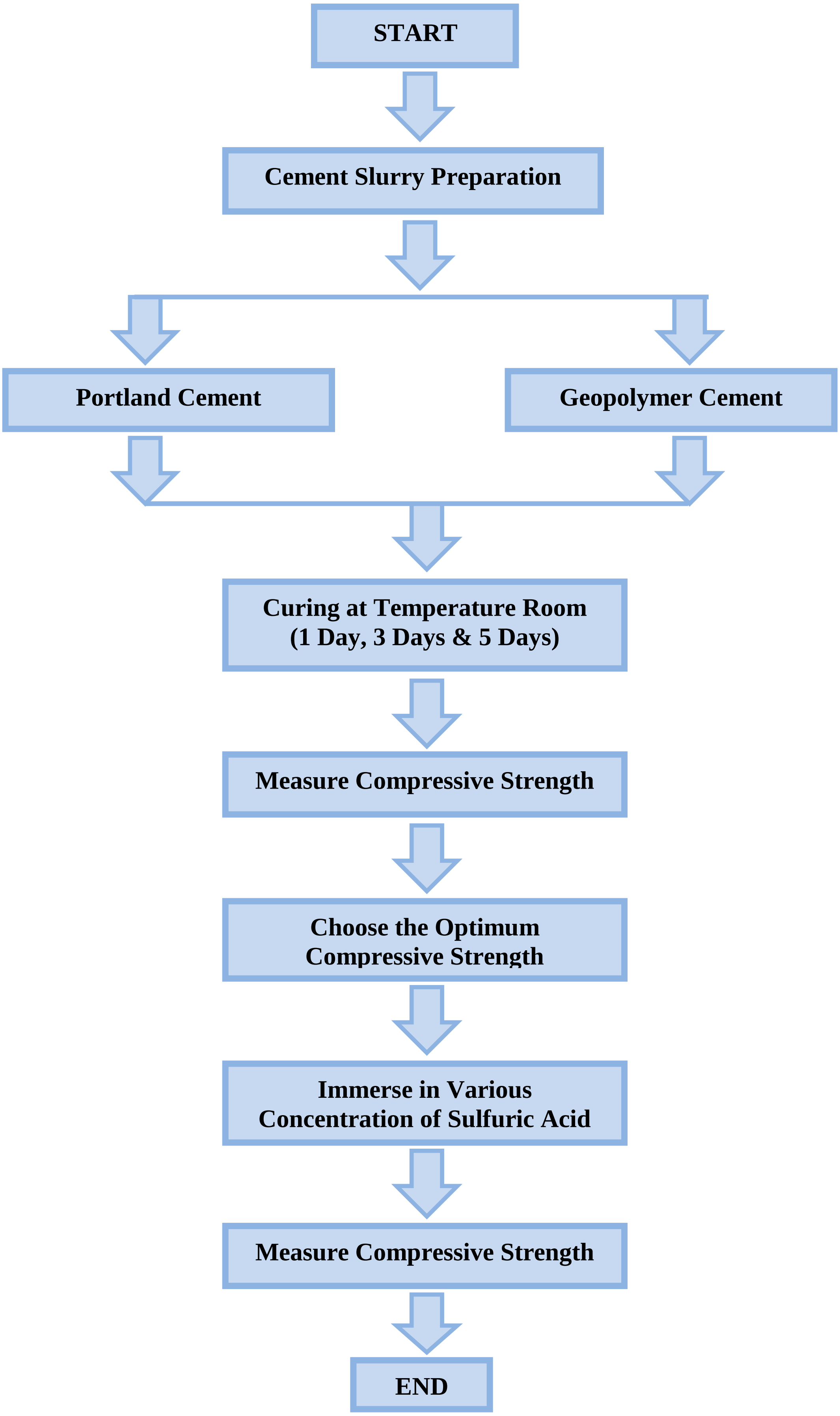
Sulfuric acid will be used for this study. We use Sulfuric acid at various concentrations which are 1M (approximately to 5%) and 0.2M (approximately to 1%) and then, expose of cement cubes in the acid solution.

Figure 14: Preparation of Sulfuric Acid Solution.

3.4.5 Characteristic of the Exposed Cement Cubes

After all of the experiments are conducted, then remove the cement cubes from sulfuric acid and measure the compressive strength in step 3.3.3 again.

3.5 BREAKTHROUGH METHODOLOGY



CHAPTER 4

RESULTS AND DISCUSSION

4.1 EXPERIMENTATION DESIGN

This project is focused on preparing the cement slurry, testing cement slurry and compressive strength of fly-ash based Geopolymer Cement at various curing time, various molarities of sodium hydroxide (NaOH) and various concentrations of sulfuric acid. According to the methodology part, this project can divided into 5 parts. Firstly, we started from preparation of cement slurry and cement cubes. The formulation to test in this project can divided into 3 parts there are Class G Cement (Base Case), Fly-ash based Geopolymer Cement (1) and Fly-ash based Geopolymer Cement (2).

- Class G Cement (Base Case).

This formulation refers to the lab manual American Petroleum Institute (API-RP-10B) stated that the ratio of water to cement is 44%, so the amount of cement is 792g and liquid is 349g. This formulation uses only distilled water only to mix with the Class G Cement.

Table 8: Formulation for Class G Cement.

Samples	Cement (792 g)	Mix Liquid (349 g)
	Class G	H_2O
GC	100%	349 g

- Fly-ash Based Geopolymer Cement (1).

Formulation 1 for Fly-ash Based Geopolymer Cement also refer to API-RP-10B that use the Fly-ash (brown color) and various type of liquids such as distilled water, Sodium Silicate (Na_2SiO_3) and various concentrations of Sodium Hydroxide (NaOH) 10M, 12M and 15M. Moreover, the ratio of sodium hydroxide solution to sodium silicate will be maintained at 1:2.5 proportions based on Frantisek Skvara (2007) research.

Table 9: Formulation 1 for Fly-ash Based Geopolymer Cement.

Samples	**Cement (792 g)**	**Mix Liquid (349 g)**				
	Fly Ash	*NaOH (10M)*	*NaOH (12M)*	*NaOH (15M)*	*Na_2SiO_3*	*H_2O*
GPC (1)	100%	42.57 g	-	-	106.43 g	200 g
GPC (2)	100%	-	42.57 g	-	106.43 g	200 g
GPC (3)	100%	-	-	42.57 g	106.43 g	200 g

- Fly-ash Based Geopolymer Cement (2)

This formulation also refers to API-RP-10B same as the previous formula. We use the Fly-ash (brown color) and use Sodium Hydroxide (NaOH) only as a liquid at various concentrations of 10M, 12M and 15M.

Table 10: Formulation 2 for Fly-ash Based Geopolymer Cement.

Samples	**Cement (792 g)**	**Mix Liquid (349 g)**		
	Fly Ash	*NaOH (10M)*	*NaOH (12M)*	*NaOH (15M)*
GPC (4)	100%	349 g	-	-
GPC (5)	100%	-	349 g	-
GPC (6)	100%	-	-	349 g

Secondly, we pour the cement slurry into a two inch squared cement moulds. Then, the cement cubes were cured for 24 hours in an oven and at atmospheric temperature for 1, 3 and 5 days. Once the cubes have been completely cured, they were tested for compressive strength and the cube samples with optimum compressive strength will be immersed in the sulfuric acid solution.

When we got the optimum compressive strength for each formulation at various curing time and then we repeat the experiment again and curing again at curing time that indicates the optimum compressive strength. After that, we immerse the samples in Sulfuric acid 1 day at various concentrations and test compressive strength again. Lastly, the results obtained were compared against the Class G Ordinary Portland Cement.

4.2 FINDINGS AND DATA GATHERING

4.2.1 Calculations

The preparations of materials are divided into 4 parts.

1. Sodium Hydroxide (NaOH) at various concentrations.
2. The ratio of Sodium Hydroxide (NaOH) to Sodium Silicate (Na_2SiO_3).
3. Sulfuric acid (H_2SO_4) at various concentrations.
4. Compressive Strength.

4.2.1.1 Sodium Hydroxide (NaOH) at Various Concentrations

- Calculating Molarity (M)

(1). Find the amount of moles solute (Solid NaOH) in grams to stir in the distilled water 1000 ml.

(2). 1 Mol NaOH = 40 g. NaOH

$$Molarity\ (M) = \frac{Moles\ Solute}{Milliliters\ Solution}$$

- At 10 M.

$$Molarity\ (M) = \frac{Moles\ \ Solute}{ml\ .Solution}$$

10 M = (X/1000 ml.) * (1 mol/40 g.) * (1000 ml/1L)

X = (10 M * 40 g.)/ (1 mol/1L)

X = (10 M * 40 g.)/ (1 M)

X = 400 g.

Where;

X = Amount of moles solute (g.)

Mol/L = M.

- <u>At 12 M.</u>

$$Molarity\ (M) = \frac{Moles\ \ Solute}{ml\ .Solution}$$

12 M = (X/1000 ml.) * (1 mol/40 g.) * (1000 ml/1L)

X = (12 M * 40 g.)/ (1 mol/1L)

X = (12 M * 40 g.)/ (1 M)

X = 480 g.

Where;

X = Amount of moles solute (g.)

Mol/L = M.

- <u>At 15 M.</u>

$$Molarity\ (M) = \frac{Moles\ \ Solute}{ml\ .Solution}$$

15 M = (X/1000 ml.) * (1 mol/40 g.) * (1000 ml/1L)

X = (15 M * 40 g.)/ (1 mol/1L)

X = (15 M * 40 g.)/ (1 M)

X = 600 g.

Where;

X = Amount of moles solute (g.)

Mol/L = M.

4.2.1.2 The Ratio of Sodium Hydroxide (NaOH) to Sodium Silicate (Na_2SiO_3).

According to Frantisek Skvara (2007) indicated the 1:2.5 proportions is the best ratio of sodium hydroxide (NaOH) solution to sodium silicate (Na_2SiO_3). Hence, in the formulation 1 for Fly-ash based Geopolymer cement used the NaOH 42.57 g. and Na_2SiO_3 106.43 g.

4.2.1.3 Sulfuric Acid (H_2SO_4) at Various Concentrations.

The Sulfuric acids in one bottle have the concentration at 95-97% but this project used only 0.2M (approximately to 1%) and 1M (approximately to 5%). Hence, we should to dilute it by adding slowly acid into water 1000 ml. and stir it together. The volume of acid can calculate by 2 methods are as below and we choose method 2 to calculate the volume of acid.

- <u>Method 1</u>

$$M_1V_1 = M_2V_2$$

Where;

M_1 = The percentage of acid concentration that will be used in the project (%).

V_1 = Volume of water (1000 ml.)

M_2 = The concentration of acid in bottle (95-97%)

V_2 = Volume of acid (ml.)

- Method 2

$$V = M/D$$

Where;

M = Molar mass (98.08 g/M)

V = Volume of acid (ml.)

D = Density (1.84 g/ml.)

- At 1 M.

Step 1;

1 M *98.08 g/M = 98.08 g.

Step 2;

V = M/D

V = (98.08 g.)/(1.84 g/ml.)

V = 53.30 ml.

- At 0.2 M.

Step 1;

0.2 M * 98.08 g/M = 19.616

Step 2;

V = M/D

V = (19.616 g.)/(1.84 g/ml.)

V = 10.66 ml.

4.2.1.4 Compressive Strength.

From the experiment, the compressive strength tester gives the maximum load in kN. The cross section area for two inch squared cement moulds is 0.0025 mm^2 and Compressive strength value can find in the formula below;

$$F_{ci} = F_i/A_{ci}$$

Where;

F_{ci} = Compressive Strength (kN/mm^2)

F_i = Maximum Load (kN)

A_{ci} = Cross Section Area (mm^2)

Note: 1 kN/mm^2 is equal to 0.001 MPa

4.2.2 Results

4.2.2.1 Class G Cement (Base Case)

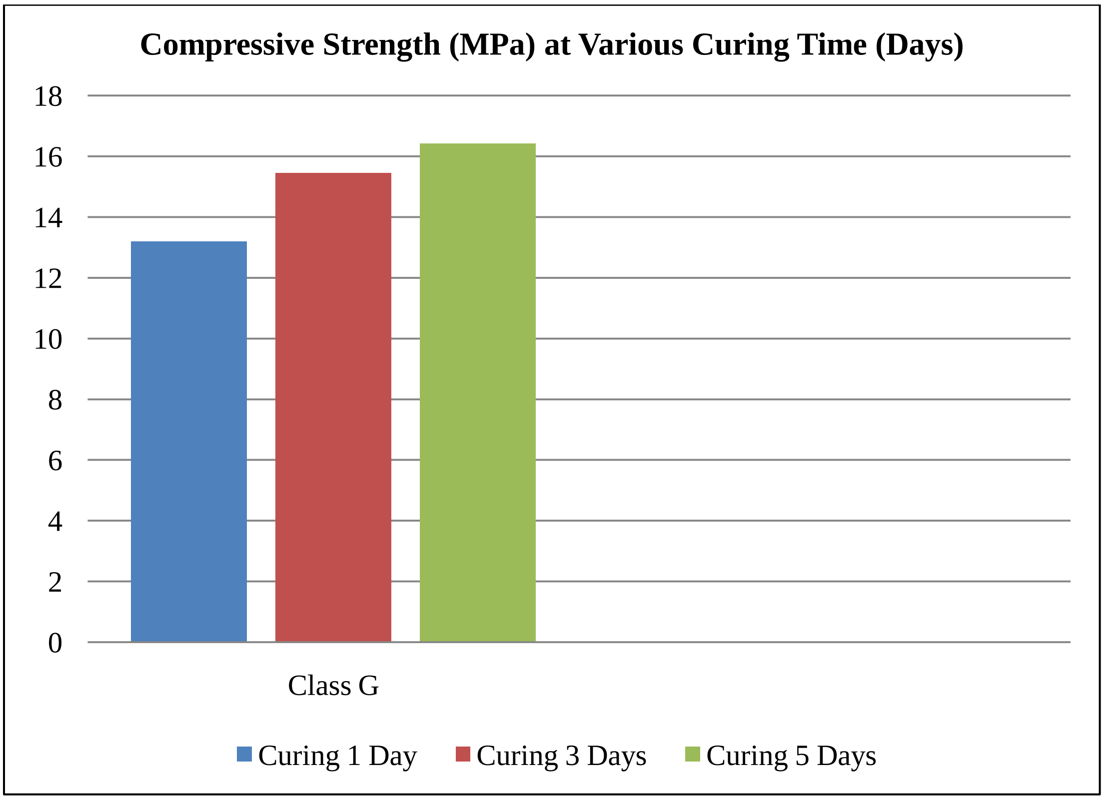


Figure 15: Compressive Strength (MPa) of Class G Cement at Various Curing Time (Days)

The graph above indicate the compressive strength of Class G cement at various curing time there are 1 day, 3 days and 5 days. The results of each compressive strength is shown in the Table 11. Curing for 5 days results the optimum compressive strength that is 16.41 MPa. The experiment is repeated at different curing time and various acid concentration.

Table 11: Compressive Strength (MPa) Results for Class G Cement at Various Curing Time (Days)

Cement Types	Curing 1 Day	Curing 3 Days	Curing 5 Days
Class G	13.2 MPa	15.44 MPa	16.41 MPa

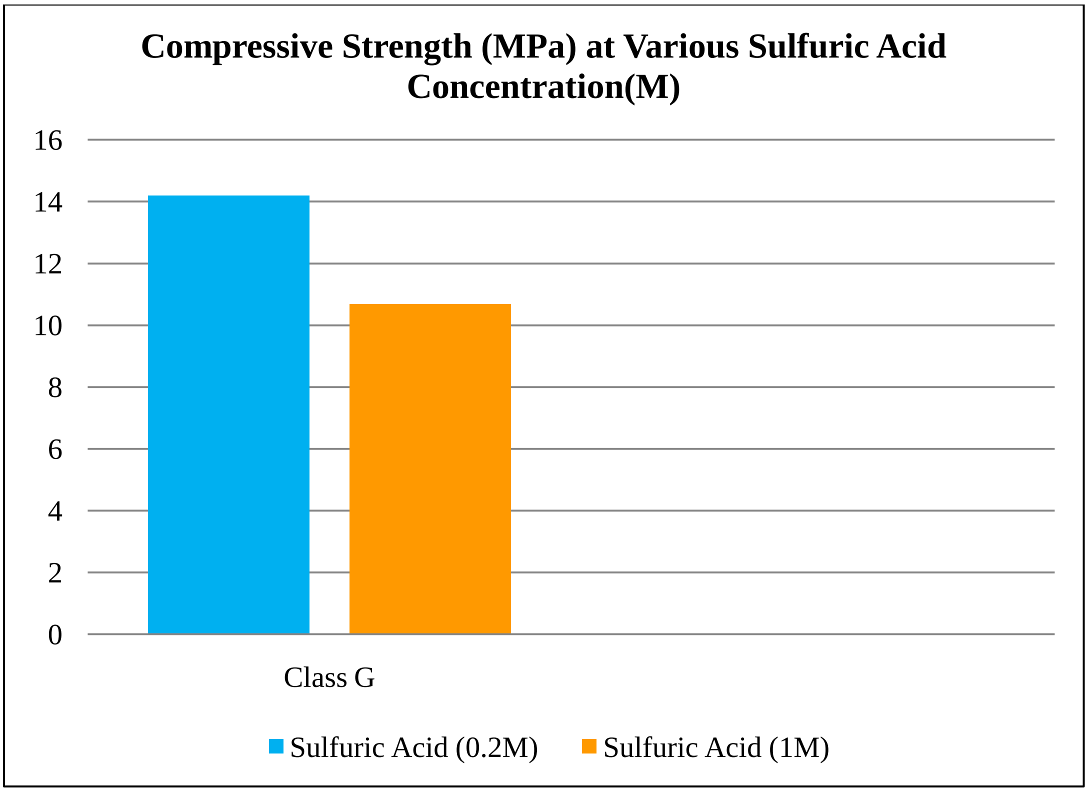


Figure 16: Compressive Strength (MPa) of Class G Cement at Various Sulfuric Acid Concentrations (M)

After we immersed the sample in sulfuric acid and then, testing the compressive strength again. The graph above shows the compressive strength of Class G cement at various Sulfuric acid there are 0.2 M (approximately to 1%) and 1 M (approximately to 5%). The results of each compressive strength is shown in the Table 12. Moreover, **Appendix A** shows the physical characteristics of class G cement after immersing in sulfuric acid at 0.2 M and 1 M.

Table 12: Compressive Strength (MPa) Results for Class G Cement at Various Sulfuric Acids (M)

Cement Types	Sulfuric Acid (0.2M)	Sulfuric Acid (1M)
Class G	14.2 MPa	10.68 MPa

4.2.2.2 Fly-ash Based Geopolymer Cement (Formulation 1)

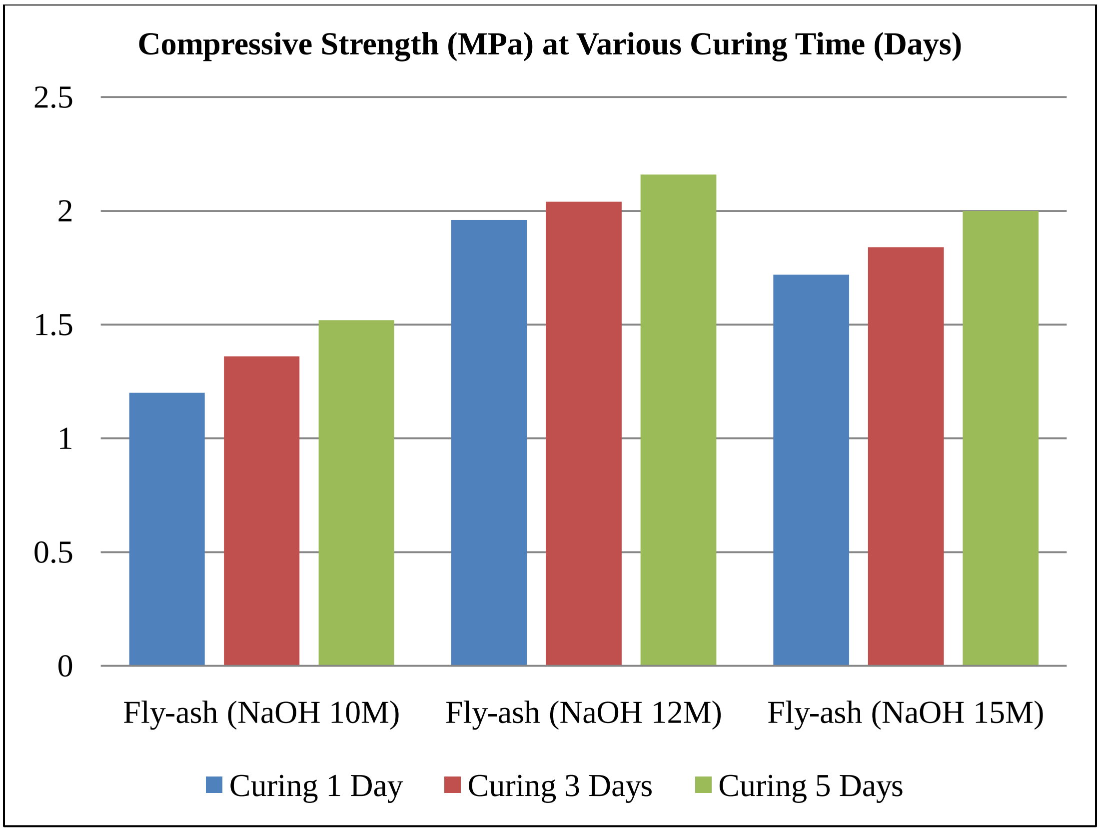


Figure 17: Compressive Strength (MPa) of Fly-Ash Based Geopolymer Cement (1) at Various Curing Time (Days)

The graph above indicates the compressive strength of Fly-ash based Geopolymer cement (1) at various curing time there are 1 day, 3 days and 5 days. Curing time of 5 days resulted in optimum compressive strength. This experiment used the various NaOH concentration there are 10M, 12M and 15M. Fly-Ash Based Geopolymer Cement with 10M, 12M and 15M of NaOH results the compressive strength 1.52 MPa, 2.16 MPa and 2 MPa respectively (Table 13) and 12M of NaOH results the highest compressive strength. The next step is repeat the experiment again and immerse it in the sulfuric acid at various concentrations.

Table 13: Compressive Strength (MPa) Results for Fly-Ash Based Geopolymer Cement (Formulation 1) at Various Curing Time (Days)

Cement Types	Curing 1 Day	Curing 3 Days	Curing 5 Days
Fly-ash (NaOH 10M)	1.2	1.36	1.52
Fly-ash (NaOH 12M)	1.96	2.04	2.16
Fly-ash (NaOH 15M)	1.72	1.84	2

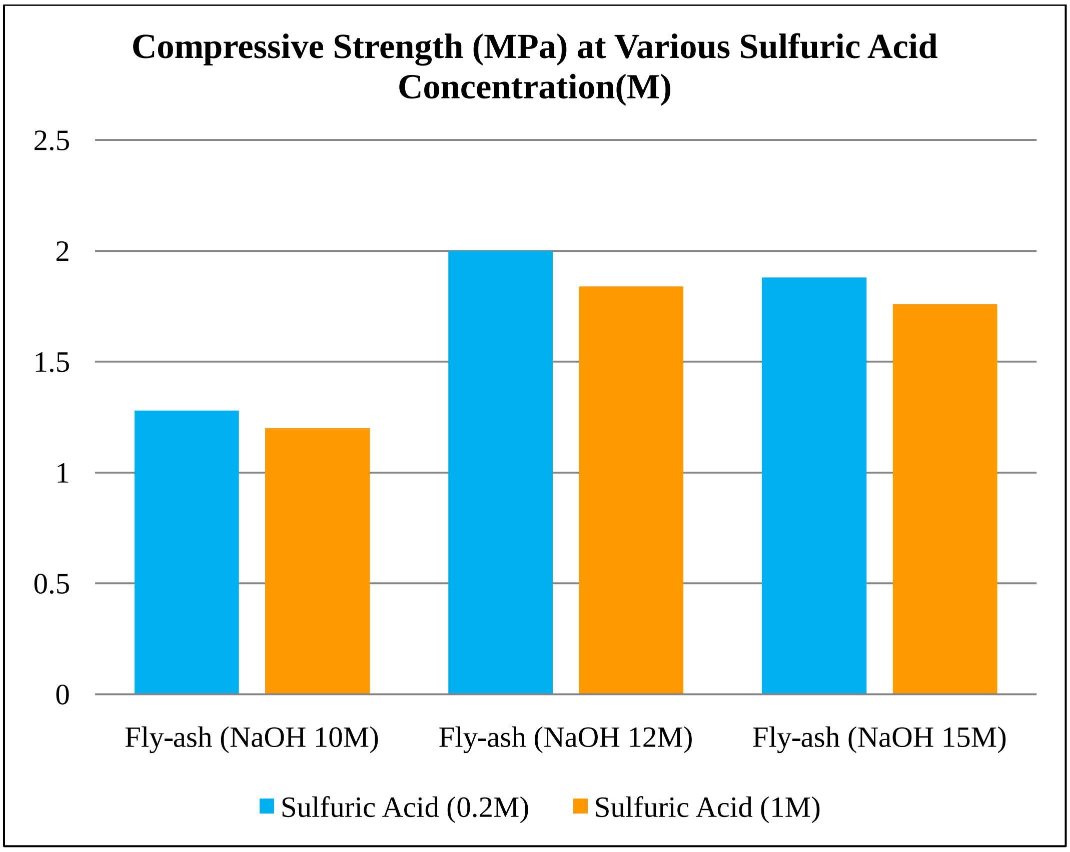


Figure 18: Compressive Strength (MPa) of Fly-Ash Based Geopolymer Cement (1) at Various Sulfuric Acid Concentrations (M)

The graph above indicate the compressive strength of Fly-ash based Geopolymer cement (1) at various Sulfuric acid there are 0.2 M. (approximately to 1%) and 1 M. (approximately to 5%). The results of each compressive strength shows in the Table 14. The samples used 12 M. of NaOH maintained a higher compressive strength but loss in strength initially and the samples used 10 M. and 15 M. of NaOH also loss in strength. Moreover, **Appendix B** shows the physical characteristics of Fly-ash based Geopolymer cement (Formulation 1) after immerse in sulfuric acid at 0.2 M and 1 M.

Table 14: Compressive Strength (MPa) Results for Fly-Ash Based Geopolymer Cement (Formulation 1) at Various Sulfuric Acids (M)

Cement Types	Sulfuric Acid (0.2M)	Sulfuric Acid (1M)
Fly-ash (NaOH 10M)	1.28	1.2
Fly-ash (NaOH 12M)	2	1.84
Fly-ash (NaOH 15M)	1.88	1.76

4.2.2.3 Fly-ash Based Geopolymer Cement (Formulation 2)

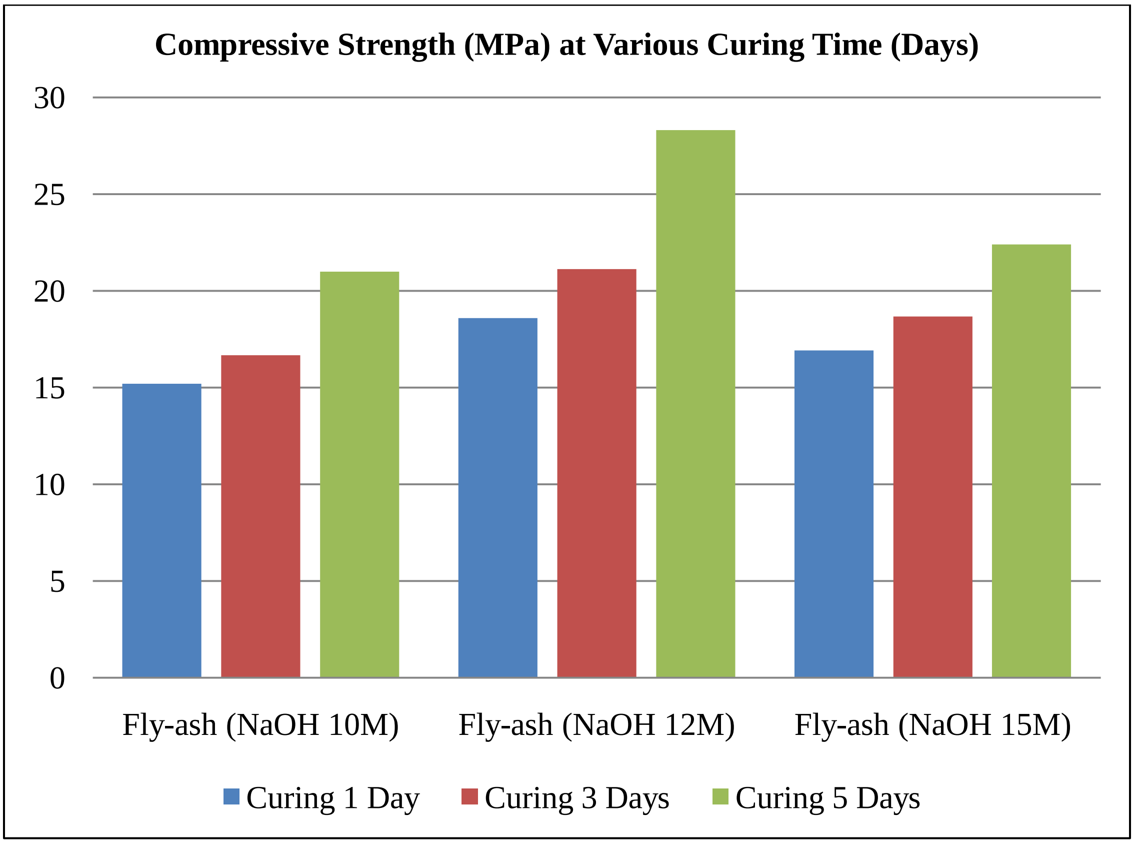


Figure 19: Compressive Strength (MPa) of Fly-Ash Based Geopolymer Cement (2) at Various Curing Time (Days)

The graph above indicates the compressive strength of Fly-ash based Geopolymer cement (Formulation 2) at various curing time. The all of 5 days curing time cements result the optimum compressive strength. This experiment also used the various NaOH concentration same as previous formulation but this experiment using liquid NaOH only. Fly-Ash Based Geopolymer Cement with 10M, 12M and 15M of NaOH results high compressive strength than formulation 1 there are 21 MPa, 28.32 MPa and 22.4 MPa respectively (Table 15) and 12M of NaOH results the highest compressive strength. The next step is repeat the experiment again and immerse it in the sulfuric acid at various concentrations.

Table 15: Compressive Strength (MPa) Results for Fly-Ash Based Geopolymer Cement (Formulation 2) at Various Curing Time (Days)

Cement Types	**Curing 1 Day**	**Curing 3 Days**	**Curing 5 Days**
Fly-ash (NaOH 10M)	15.2	16.68	21
Fly-ash (NaOH 12M)	18.6	21.12	28.32
Fly-ash (NaOH 15M)	16.92	18.68	22.4

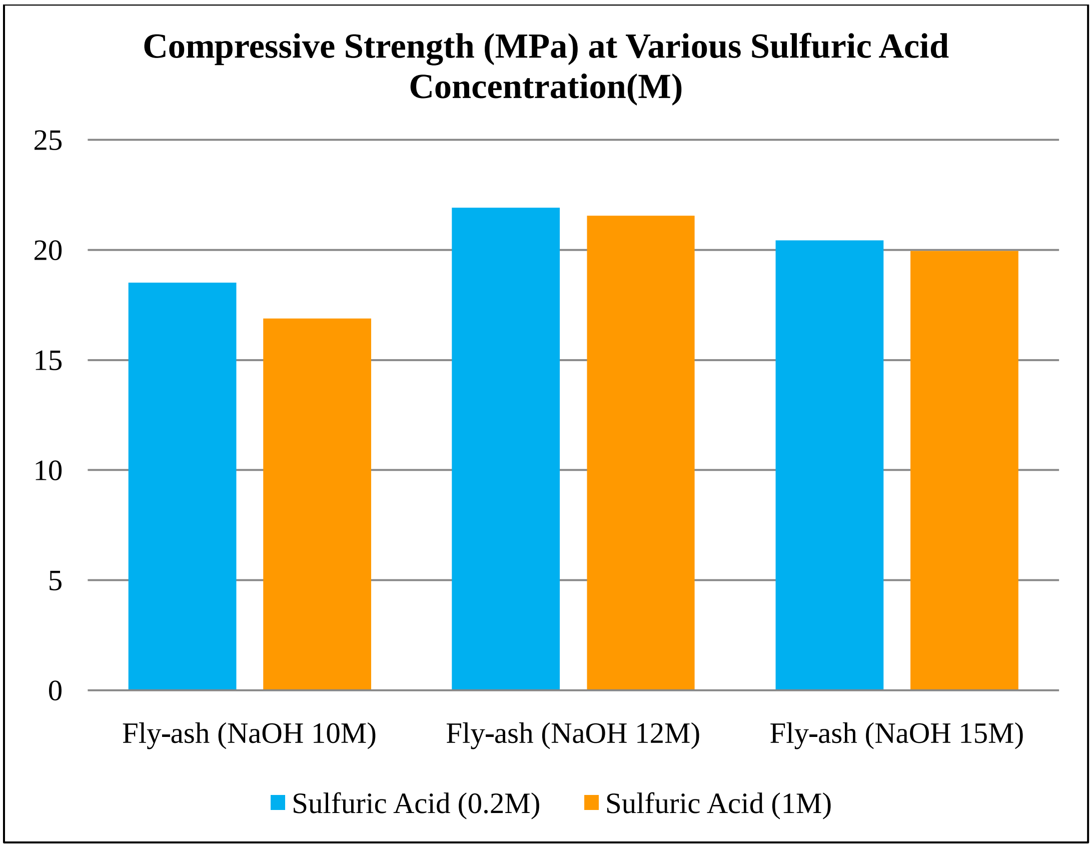


Figure 20: Compressive Strength (MPa) of Fly-Ash Based Geopolymer Cement (2) at Various Sulfuric Acid Concentrations (M)

The graph above shows the compressive strength of Fly-ash based Geopolymer cement (Formulation 2) at various Sulfuric acid there are 0.2 M. and 1 M. After immerse the samples in sulfuric acid, Fly-Ash based Geopolymer cement with 10M, 12M and 15M of NaOH results a high compressive strength than formulation 1 (Table 16) and 12M of NaOH results the highest compressive strength, but loss in strength initially and the samples used 10 M. and 15 M. of NaOH also loss in strength. In additional, **Appendix C** shows the physical characteristics of Fly-ash based Geopolymer cement (Formulation 2) after immerse in sulfuric acid at 0.2 M and 1 M.

Table 16: Compressive Strength (MPa) Results for Fly-Ash Based Geopolymer Cement (Formulation 2) at Various Sulfuric Acids (M)

Cement Types	Sulfuric Acid (0.2M)	Sulfuric Acid (1M)
Fly-ash (NaOH 10M)	18.52	16.88
Fly-ash (NaOH 12M)	21.92	21.56
Fly-ash (NaOH 15M)	20.44	19.96

4.3 DATA ANALYSIS AND DISCUSSION

The discussion part of this project will be divided into 4 parts there are Cement slurry formulation, Concentration of NaOH, Effect of sulfuric acid solution to cements and Curing time. In this section, we will analyze the findings and come up with a proper explanation on the reasons behind the results.

- **Cement Slurry Formulation**

For Class G cement (Base case), we prepared the cement slurry and testing cement slurry according to American Petroleum Institute API-RP-10B. Based on 44% water to cement ratio, the amount of cement will be 792 g. and for water should be 349 g. Normally, Class G cement results a high compressive strength and oil and gas industries always using this type for cementing, but Class G cement is the one of major greenhouse gases producer, so it is important to find the new cement that can reduce the CO_2 and have better quality than Portland cement. The results of compressive strength are 13.2 MPa (1 day), 15.44 MPa (3 day) and 16.41 MPa (5 day). From the results, 5 days curing time cements result the optimum compressive strength.

Geopolymer cement is one of the best environmentally friendly materials to replace the Portland cement. This project divided into 2 formulations for Fly-ash based Geopolymer cement to develop and introduce as alternative cement which has a high compressive strength and less effect from sulfuric acid. First formulation for Fly-ash based Geopolymer cement also using the 44% water to cement ratio and using NaOH, Na_2SiO_3 and water as liquid. 1:2.5 proportions are the ratio of sodium hydroxide (NaOH) solution to sodium silicate (Na_2SiO_3) and use water 200 g. The results of compressive strength in this formulation indicate lower compressive strength than base case. However, the second formulation results higher compressive strength than formulation1 and base case. This formulation also used the Fly ash 349 g. same as previous formulation but this experiment using only liquid NaOH.

From this part, It is determined that the formulation 2 for Fly-ash based Geopolymer cement results a high compressive strength than the base case and water is one material that affect to the compressive strength of Fly-ash based Geopolymer cement.

- **Curing Time**

Based on the experiments conducted, it is found that the compressive strength increases with the curing time. Longer curing time improved the polymerization process that occurs in the Geopolymer cement. For this project, we use a various curing time there are 1 day, 3days and 5 days. Curing time of 5 days resulted in optimum compressive strength. Thus, it can be concluded that a curing time is directly proportional to compressive strength.

- **Sodium Hydroxide (NaoH) Solution**

This Project design to use the various concentration of sodium hydroxide (NaOH) solution in Fly-ash based Geopolymer cement slurry there are 10M, 12M and 15M. From the results part for formulation 1 Fly-Ash based Geopolymer Cement with 10M, 12M and 15M of NaOH results the optimum compressive strength are 1.52 MPa, 2.16 MPa and 2 MPa respectively and 12M of NaOH results the highest compressive strength. This formulation indicates a lower compressive strength than the base case because this formulation of cement slurry is mixing with the water 200 g. However, formulation 2 Fly-Ash based Geopolymer Cement with 10M, 12M and 15M of NaOH results a higher compressive strength than the previous formulation and base case. From the results part, 12M of NaOH results the highest compressive strength.

From this part, It is determined that concentration of NaOH solution affects the compressive strength of the Fly-ash based Geopolymer cement. From formulation 1 and 2 indicate that the 12M of NaOH results the highest compressive strength and

10M of NaOH results the lowest compressive strength. Moreover, formulation 2 for Fly-ash based Geopolymer cement can introduced as alternative cement which has a higher compressive strength than base case and 12M of NaOH is the best materials to use in the preparing and testing cement slurry.

- **Effect of Sulfuric Acid Solution to Cements**

The experiments indicated the optimum compressive strength at various curing time and then repeat the experiment again and immerse the samples in Sulfuric acid solution at various concentrations there are 0.2M and 1M. For Class G cement, after we immersed the samples in H_2SO_4 (24 hours) and then remove the cement cubes from sulfuric acid and measure the compressive strength. The results show the Sulfuric acid solution affects to loss compressive strength and H_2SO_4 Concentration at 1 M. reduces a greater level of compressive strength with respect to 0.2 M.

Fly-ash based Geopolymer Cement (formulation 1 and 2) in sulfuric acid indicated the H_2SO_4 solution affects to loss compressive strength and H_2SO_4 Concentration at 1 M. reduces a greater level of compressive strength with respect to 0.2 M same as the base case. For Fly-ash based Geopolymer Cement (formulation 1) in sulfuric acid, cement slurry mixed with 12M of NaOH results a compressive strength value higher than 10M and 15M. From the results part, this formula results a low compressive strength and if the samples immerse in sulfuric that made the results of compressive strength is very low because of acid destroy the Geopolymerization process. In additional, Fly-ash based Geopolymer Cement (formulation 2) in sulfuric acid, cement slurry mixed with 12M of NaOH results a compressive strength value higher than 10M and 15M same as the previous formula but this formula indicates a high compressive strength than base case before and after immersed in sulfuric acid solutions.

This part can conclude that the increasing of H_2SO_4 concentration considerably affects the compressive strength of Portland Cement and Geopolymer Cement. Formulation 2 for Fly-ash based Geopolymer cement can introduced as alternative cement which has a higher compressive strength than base case after immersed in H_2SO_4 Solutions.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

6.1 Relevancy to the Objectives

In conclusion, the ultimate objective of this project is to find out the efficiency of Fly-ash based Geopolymer cement for well cementing. This project aims to prove the benefits of using Fly-ash Geopolymer cement. Based on the experiment and the results, it can be concluded that formulation 2 for Fly-ash based Geopolymer cement that using liquid NaOH only results a high compressive strength than the base case. Water is a one factor that affect to the compressive strength of Fly-ash based Geopolymer cement in formulation 1 for Fly-ash based Geopolymer cement. In additional, this experiment found that the compressive strength increases with the curing time. Thus, a curing time is directly proportional to compressive strength. Moreover, the concentration of NaOH solution is a one factor that affects to the compressive strength of the Fly-ash based Geopolymer cement. From formulation 1 and 2 indicate that the 12M of NaOH results the highest compressive strength and 10M of NaOH results the lowest compressive strength. Formulation 2 for Fly-ash based Geopolymer cement can introduced as alternative cement which has a higher compressive strength than base case (Class G cement) and 12M of NaOH is the best materials to use in the preparing and testing cement slurry. In additional, after immersed the sample in H_2SO_4 solutions then we can conclude that the increasing of H_2SO_4 concentration considerably affects the compressive strength of Portland cement and Geopolymer Cement. Based on the outcome of this experiment, it can be said that the objectives of this paper are achieved successfully.

6.2 Suggested Future Work for Expansion and Continuation

There are a lot of factor still to be considered for Fly-ash based Geopolymer cement for oil well cement. The cement curing setting should be done in curing chamber that imitates oil well environment to see how Fly-ash based Geopolymer cement performs in it and if curing at temperature room should curing in the bottle that can maintain the same temperature. Field Emission Scanning Electron Microscopy (FESEM) is the machines that will support this experiment to scan the effect of acid that erode to cement. This project designed to immerse in sulfuric acid only 24 hours, thus it should be extended the time to observe the effect of acid to cement on compressive strength and physical characteristics.

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APPENDICES

Appendix A: Physical Characteristics of Class G Cement After Immerse in Sulfuric Acid at 0.2 M and 1 M.

Figure 21: Physical Characteristics of Class G Cement After Immerse in Sulfuric Acid at 0.2 M.

Figure 22: Physical Characteristics of Class G Cement After Immerse in Sulfuric Acid at 1 M.

Appendix B: Physical Characteristics of Fly-Ash Based Geopolymer Cement (Formulation 1) After Immerse in Sulfuric Acid at 0.2 M and 1 M.

Figure 23: Physical Characteristics of Fly-ash based Geopolymer Cement with 12 M NaOH (Formulation 1) After Immerse in Sulfuric Acid at 0.2 M.

Figure 24: Physical Characteristics of Fly-ash based Geopolymer Cement with 12 M NaOH (Formulation 1), After Immerse in Sulfuric Acid at 1 M.

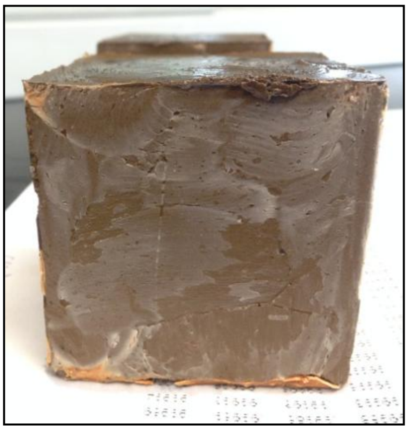

Figure 25: Physical Characteristics of Fly-ash based Geopolymer Cement with 10 M NaOH (Formulation 1) After Immerse in Sulfuric Acid at 0.2 M.

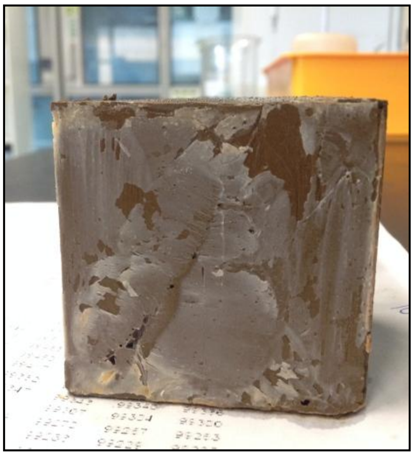

Figure 26: Physical Characteristics of Fly-ash based Geopolymer Cement with 10 M NaOH (Formulation 1) After Immerse in Sulfuric Acid at 1 M.

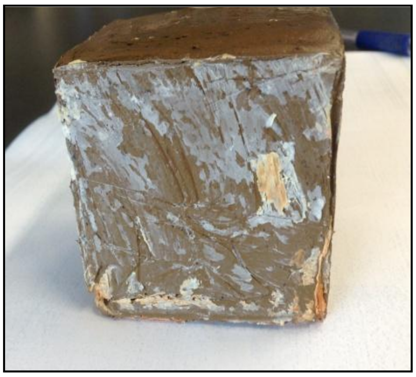

Figure 27: Physical Characteristics of Fly-ash based Geopolymer Cement with 15 M NaOH (Formulation 1) After Immerse in Sulfuric Acid at 0.2 M.

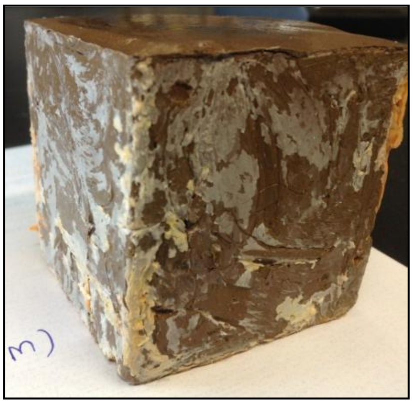

Figure 28: Physical Characteristics of Fly-ash based Geopolymer Cement with 15 M NaOH (Formulation 1) After Immerse in Sulfuric Acid at 1 M.

Appendix C: Physical Characteristics of Fly-Ash Based Geopolymer Cement (Formulation 2) After Immerse in Sulfuric Acid at 0.2 M and 1 M.

Figure 29: Physical Characteristics of Fly-ash based Geopolymer Cement with 12 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 0.2 M.

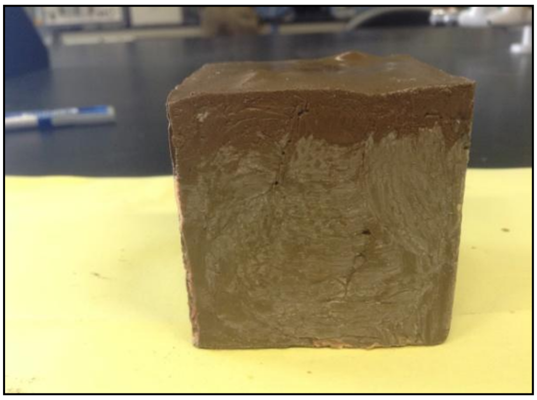

Figure 30: Physical Characteristics of Fly-ash based Geopolymer Cement with 12 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 1 M.

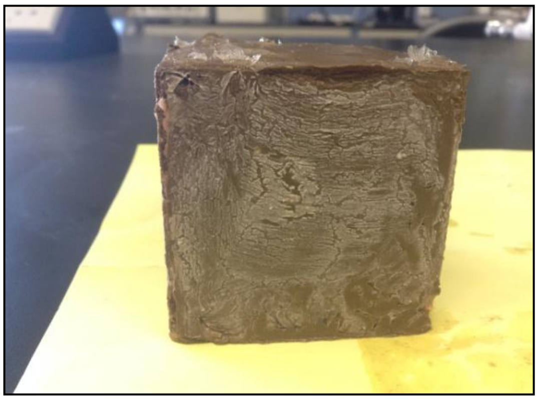

Figure 31: Physical Characteristics of Fly-ash based Geopolymer Cement with 10 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 0.2 M.

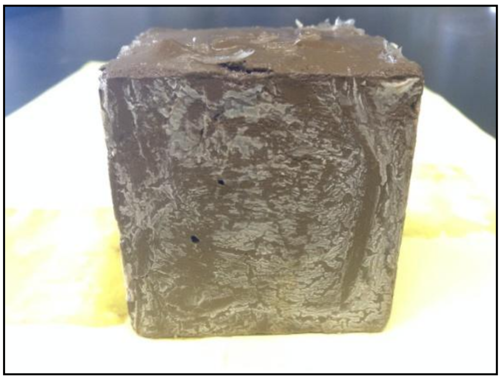

Figure 32: Physical Characteristics of Fly-ash based Geopolymer Cement with 10 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 1 M.

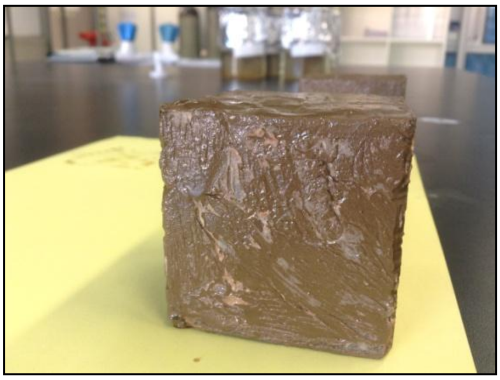

Figure 33: Physical Characteristics of Fly-ash based Geopolymer Cement with 15 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 0.2 M.

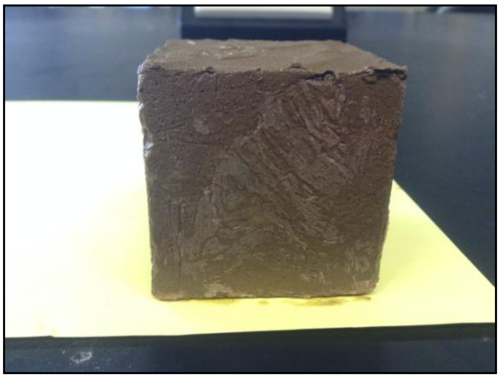

Figure 34: Physical Characteristics of Fly-ash based Geopolymer Cement with 15 M NaOH (Formulation 2) After Immerse in Sulfuric Acid at 1 M.