POTENTIAL OF WEATHERED LAWIN TUFF FOR GENERATING FLY ASH CEMENT FOR WELL CEMENTING

by

Amirul Afiq bin Yaakob

11715

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Petroleum Engineering)

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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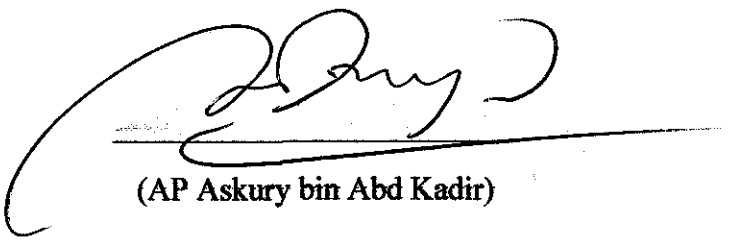

(AP Askury bin Abd Kadir)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

~~JULY 2010~~

JAN 2011

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.

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ABSTRACT

This paper is mean to analyze the potential of weathered Lawin tuff in generating fly ash cement especially for well cementing. Lawin tuff is a pyroclastic rock by compacted volcanic ash obtained from Grik, Perak, Malaysia. Basically, fly ash used as a replacement for some of the Portland cement content of concrete because of its pozzolanic properties. Pozzolanic materials are typically high in SiO2 and Al2O3, low in CaO with little or no reactivity when immersed in water. However, with water and Ca(OH)2, fly ashes generally react to form a calcium silicate hydrate. The pozzolanic and cementitious properties of fly ash making it a useful cement replacement material for producing high performance cement. In this study, sample of weathered volcanic tuff was taken from Lawin and analyses in term of its physical and chemical properties and also performance when blend with Type G cement. From the soil properties, the weathered volcanic ash can be classified as silt fine grained with intermediate plasticity. The micrograph structure from SEM analysis shown the ash particulates have different sizes and shapes. Proven with XRF analysis which shown the weathered volcanic ash have high SiO2 and Al2O3 content and low in CaO content. Due to the low content of CO2, the compressive strength of the volcanic ash cement lower than Type G cement, but higher for long term strength. Other quality tests conducted such as fluid loss, thickening time and free water content in order to meet API standard for oil well cementing.

ACKNOWLEDGEMENT

Apart from the efforts of me, the success of this project depends largely on the encouragement and guidelines of many others. I take this opportunity to express my gratitude to the people who have been instrumental in the successful completion of this project.

I would like to show my greatest appreciation to my supervisor, AP Askury bin Abd Kadir. I can't say thank you enough for his tremendous support and help. I feel motivated and encouraged every time I attend his meeting. Without his encouragement and guidance this project would not have materialized.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Use of **fly ash** cement (blended cement) has gained momentum in almost all the countries, playing a significant role in advance concrete technology to ensure longer durability compared to ordinary Portland cement. Investigations into fly ash have been undertaken worldwide and all research proves that fly ash can be used with absolute confidence in manufacturing of cement and it can dramatically improve the durability of concrete in all environments without any adverse effect. Fly ash enhances properties of Portland cement in almost every application and is used worldwide as a partial replacement or extender for cement in concrete. Needless to mention proper use fly ash will drastically reduce the production cost of cement without compromising the quality. There are three (3) classes of fly ash used in Portland cement which are Type N (tuffs and volcanic ashes), Type F (Fly ash with pozzolanic properties) and Type C (fly ash with pozzolanic and cementitious properties).

The fly ash used in this study is the natural fly ash from Lawin tuff, Grik, Perak. **Tuff** is a type of rock which is formed from compacted volcanic ash and fragments of material associated with volcanic eruptions. There are a number of different types of tuff, with the rock being classified on the basis of what it contains, how large the particles embedded in the rock are, and how it formed.

This study is the part of a study of the material properties of weathered volcanic ash and the performance of the volcanic ash in Type G cement especially in well cementing. For the mineralogy properties and quantitative analysis of fly ash, laboratory experiment conducted using **X-ray Fluorescence (XRF)** and **Scanning Electron Microscope (SEM).** After mixing the fly ash with Type G cement, we will conduct some cement test quality such as compressive strength, setting times, free water content and fluid loss test in order to achieve the API standard requirement of well cementing.

1.2 Problem Statement

Currently, most of the fly ash Portland cement is made by industrial fly ash which is generated by combustion of coal. This byproduct fly ash maybe has the similar properties and components with natural fly ash (volcanic ash). Hence, there is some possibility that the volcanic ash from Lawin tuff can be used as the cement replacement materials in producing high performance cement. According to the American Coal Ash Association [1], fly ash production in 1992 totaled 44 metric tons, of which only 7 metric tons were used in concrete. The use of fly ash in the concrete industry continues to grow. On 2006, over 15 million metric tons of fly ash was added to Portland cement concrete. (*See Appendix 3, I4 and 5 for worldwide cement production*). According to the Malaysian statistic department, a study conducted in 2001, cement industry in Malaysia alone produce clinker up to 16 Million tons per year and ordinary cement about 21 Million tons per year. Plus, there is no Malaysian cement company produce Portland cement from natural fly ash especially volcanic ash from Lawin tuff.

1.3 Significant of Project

Therefore, it is significant and beneficial to come out with fly ash cement production from volcanic ash in line in the market and moreover we have the raw material for cement replacement material extracted from the country itself which is volcanic ash from Lawin tuff. It will give advantages and benefits to our government and cement company because of high demand from oil and gas industry locally and abroad. Plus, the national oil and gas company also can execute their project with low cost since the cement materials produced locally.

1.4 Objectives

- To study the potential of using Lawin tuffs to produce fly ash cement for well cementing.
- To investigate and analyze the mineralogy, morphology and element composition of natural fly ash from Lawin tuff.
- To study the suitability of the volcanic ash cement in well cementing processes in term of best composition and quality performance.

1.5 Scope of Study

The main scope of the study is to investigate the potential of Type G cement by mixing volcanic ash from Lawin tuff. There are 3 stages of the study. First is the research and investigation on chemical and physical properties of volcanic ash from Lawin tuff. Second stage will focus on laboratory tests on slurry proportion of Type G cement and volcanic ash, and cement tests such as compressive strength, fluid loss free water content and thickening time. Lastly is the results analysis and discussion on the performance of the volcanic ash cement.

1.6 The Relevancy of Project

Portland cement (Type G), which is primarily a construction material, is used extensively in oil and gas wells. To provide products that perform satisfactorily the high temperatures and pressures encountered in many well-cementing operations, the cement manufacturers market special oil-well types of Portland cement in addition to the regular construction types of cement. Based on current situation, Lawin tuff is still not widely used in cement manufacturing in Malaysia. So, this project is hoped to experimentally find the other substitute of Portland fly ash cement from Lawin tuff for the importance in oil and gas industry. Plus, with my background as a Petroleum Engineering student in Universiti Teknologi PETRONAS (UTP), it is relevance for me to do study and research in this interesting topic.

1.7 Feasibility of the Project within the Scope and Time frame

This project will be feasible in UTP because there are different equipments to test the rheology of cement properties such as viscosity, density, thickening time, compressive strength. This project was conducted for 2 semesters. The first semester is focusing on research study and information gathering while the second semester focuses on lab experiments and data evaluation.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 – Weathering Process of Volcanic Tuff

Volcanic tuff is a pyroclastic, consolidated rock composed of compacted and cemented volcanic ash from volcanic eruptions million years ago. The rock is soft and porous. Texture and chemical/mineralogical composition are viable, and the grain size of the ash is below 4 mm. The color of tuff is depends on the weathering process and composition. Lawin tuff have experienced weathering process which existing as a type of soil. Soil development, in the chemical sense, is roughly synonymous with weathering. Weathering reactions generally due to the effects of water, O2 and CO2, that create soil solids and the soil solution.

The particle surfaces and soil solutions created by weathering tend to be more similar chemically than the composition of the parent minerals. Weathering of igneous and metamorphic rocks changes these dense solids into unconsolidated particles whose surfaces and newly formed particles offer differ markedly from the chemical composition and structure of the parent minerals. The changes during weathering of sedimentary rocks are less striking. *Appendix 6* shows the composition of common soil parent materials. The crystal structures and ion valences in rock minerals are stable at the conditions under which the rocks formed. The physical conditions of erosion, freezing, and thawing, glaciations, heating and cooling, and root growth at the earth's surface break rocks apart, which exposes more surface for chemical weathering. A bigger change in the rock minerals, however, results from the new chemical conditions: exposure to water, oxygen, carbon dioxide, and organic compounds. For sedimentary rocks, weathering is due to change in those chemical conditions.

Appendix 7 represents an idealized course of weathering in a soil profile. The basicity and acidity are emphasized because pH is an easily measured indicator of the state of weathering. The secondary minerals formed in soil from weathering products tend to be small in size and poorly crystallized to amorphous. Weathering continues after the formation of secondary minerals because the secondary minerals are stable only between certain concentration limits of soluble silica, alkali and alkaline earth

cations, and H^+ in the soil solution. As these solutes are leached away, the concentration changes make the initial secondary minerals (smectites, calcite, qypsum, etc) unstable. As weathering progresses, these intermediate minerals weather further to still more stable chemical states.

2.2 – Lawin tuff [15]

The volcanic fragmental were deposited contemporaneously and in close association with the detrital strata of the Baling Formation. They are considered to represent a period of explosive acid volcanism and ensuing marine deposition of the erupted material. It is evident that this activity coincided with the time of change from the shallow-water shelf deposition characteristic of the lower part of the Baling sequence to that of the deeper-water geosynclinals conditions of the upper part of the succession. It has not been established whether the volcanic activity was continuous of if it was interrupted by intermittent relatively quiescent period.

The tuffs form a thick, though laterally discontinuous unit, which can be traced into the areas covered by adjacent topographical sheets. Although their occurrence is certain only in Upper Perak, possible equivalents have been recorded to the northwest in Kedah and also to the south in Perak.

These rocks, in addition to recognizable volcanic fragments and what is almost certainly volcanic dust, contain variable quantities of detrital material produced by normal erosional processes. Fragments of scoriaceous rhyolite resembling flow material have been noted but in such lava flows have been recognized with certainty in the map area. The effects of regional metamorphism are evident throughout in varying degrees, and where most severe a subschistose to schistose texture is apparent. The groundmass of the tuffs normally shows some foliation around the larger crystal fragments.

Mineral and chemical analyses indicate that tuffs to be of rhyolitic to rhyodacitic composition. Although several lithological variations occurs the tuffs in general are grey to green, speckled, bedded rocks composed of grains and crystal fragments of quartz, potassic feldspar, perthitic feldspar, and plagioclase feldspar, up to 5 mms in size, set in a fine-grained or cryptocrystalline matrix of quartz, mica, and chlorite. It is probable that a considerable amount of volcanic dust was present as an original constituent, being in form of fine siliceous matter and iron oxides. No other

evidence of the possible presence of lava flows have been seen within the map area. However, an occurrence of metamorphosed rock which strongly resembles a rhyolite has been recorded near Kuala Temengor. The occurrence in the Sungai Perak just south of Kuala Lebey, described as a basic volcanic rock by J.B Scrivenor (1915), is considered to be a serpentinized basic intrusive.

Table 1 gives the chemical compositions of three specimens of tuff. Specimens 1 and 2 were obtained from a road exposure at milestone 3 on the Grik to Kuala Rui road and the third was collected from the Sungai Nak Sah three quarters of a mile south of Bukit Nak Sah.

Constituents	Specimen 1 (%)	Specimen 2 (%)	Specimen 3 (%)
SiO2	66.80	79.50	68.20
Al2O3	16.10	9.60	12.90
Fe2O3	1.89	0.96	0.92
FeO	1.82	1.35	4.01
TiO2	0.14	0.33	0.39
MnO2	trace	trace	0.19
P2O2	0.05	0.06	0.10
MgO	1.65	0.73	2.02
CaO	0.22	trace	4.10
Na2O	0.21	0.14	2.29
K2O	6.59	4.17	3.37
CO2	0.07	0.07	0.29
H2O-105degC	0.78	0.18	0.24
H2O+105degC	3.57	1.92	1.31
Totals	99.89	99.01	100.33

Table 1 – Chemical Analyses of Tuffs from the Grik Area (*Analyst: P. C. Leong*)

Specimen 1 is an example of a potassium-rich tuff containing abundant potassic feldspar, and can be classed as rhyolitic. Specimen 2 is a tuffaceous sandy shale containing abundant detrital quartz. It was obtained from a band interbedded with the pure tuff of specimen 1. Specimen 3 is a tuff characterized by higher soda and lime, and lower potash contents than found in specimen 1. These differences are a reflection of the relatively greater proportion of plagioclase feldspar. The tuff of specimen 3 can therefore be classed as being of rhyodacitic composition.

2.3 Oilwell (Type G) Cements

Oil well cements are used for cementing work in the drilling of oil wells where they are subject to high temperatures and pressures. They usually consist of Portland or pozzolanic cement with special organic retarders to prevent the cement from setting too quickly. Generally, oil well cements must be slow setting and resistant to high temperatures and pressures. The *American Petroleum Institute* [4] classification of cement types, specifications for materials, and test procedures are almost universally employed. Most oilwell cements are based on relatively coarsely ground sulfate-resisting Portland cement clinker. A range of admixtures is employed to give the properties required for specific locations in a well. In addition to gypsum as a set regulator, retarders such as sodium lignosulfonate or gluconic acid are needed at depths of more than about 2000m. For cementing where temperatures in excess of about 110degC occur, silica is added to prevent the formation of coarse crystals of αC2SH, which results in an increase in permeability and strength reduction.

2.4 Pozzolanic Reactions

Pozzolanic materials are typically high in SiO2 and Al2O3, low in CaO, with little or no reactivity when immersed in water. However, with water and Ca(OH)2, fly ashes generally react to form a calcium silicate hydrate [26]. Fly ash, along with consolidated volcanic ash, and silica fume, are pozzolanic mineral admixtures with important applications in the production of concrete. Each of these mineral admixtures is comprised of glassy phase and lesser amounts of crystalline phases.

Pietersen [25] states that the glassy phase is the reactive phase in fly ash, and that its dissolution rate increases with pH above 9 in environments such as the pore solution of concrete. In addition, *Bijen and Pietersen* [27] indicate other factors influencing the reactivity of fly ash are: alkalinity of the pore solution due to K+ and Na+ ions from the ash or the cement; temperature influence on the pore water hydroxide ion concentration; and an increase in alkalinity with a decrease in water/cementitious materials ratio.

Beneficial effects of fly ash in concrete include increased workability, or reduction in water requirements for a similar workability [28]. This is often attributed to what is termed the "ball bearing" effect of the spherical fly ash particles, though it

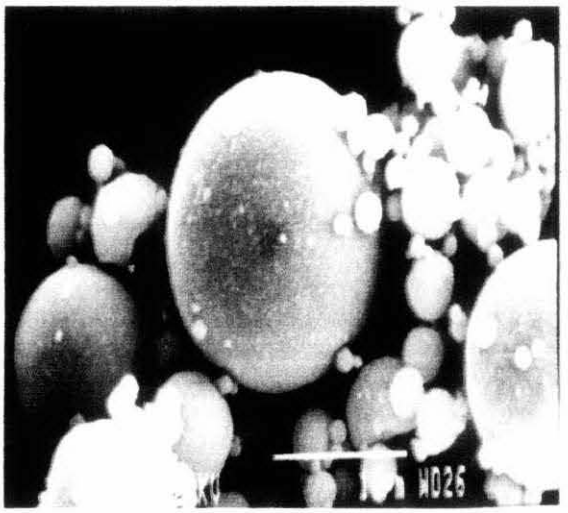
has also been attributed in part to a dispersion of the cement floe structure. *Bijen and Pietersen* [27] attribute mineral admixture benefits not only to their chemical reactivity, but also to physical and physiochemical effects such as improved dispersion of cement particles; nucleation sites for hydration products; acceleration of the cement dissolution; and, due to their fine particle size, a filler effect. The replacement of cement by fly ash reduces the heat of hydration and temperature rise reducing the possibility of cracking due to thermal stresses. Increased durability of fly ash concretes exposed to sulfate waters, sea water, and acids is achieved through a reduction in permeability, a decrease in volume fraction of calcium hydroxide, and an increase in volume fraction of calcium silicate hydrates.

2.5 Experimental Theory

2.5.1 Scanning Electron Micrograph (SEM) [9]

The objective of using SEM is to know the physical characterization of volcanic ash. For SEM analysis, results or SEM images from volcanic ash are compared with the SEM image of byproduct fly ash. Usually, byproduct fly ash particles consist of solid spheres and some hollow cenospeheres. The particle sizes of fly ash usually vary from less than 1 μm to more than 100 μm.

Figure 1 show sub-angular and spherical particles with relatively smooth grains consisting of quartz, while **Figure 2** shows clusters of iron particles formed due to partial decomposition of pyrite and with dark quartz inclusions. The heat-treated fly ash (**Figure 3 & 4**) shows a decrease in particle size as compared to fly ash sample.



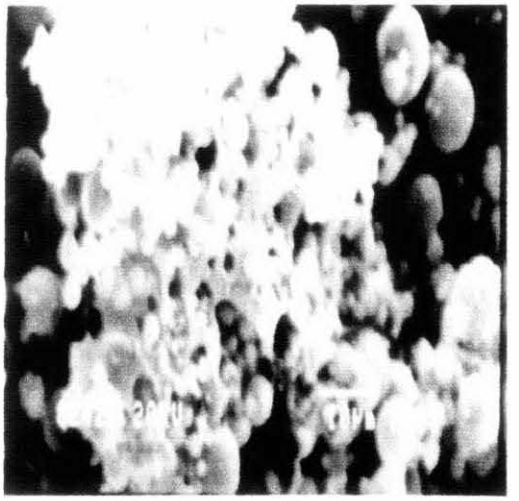
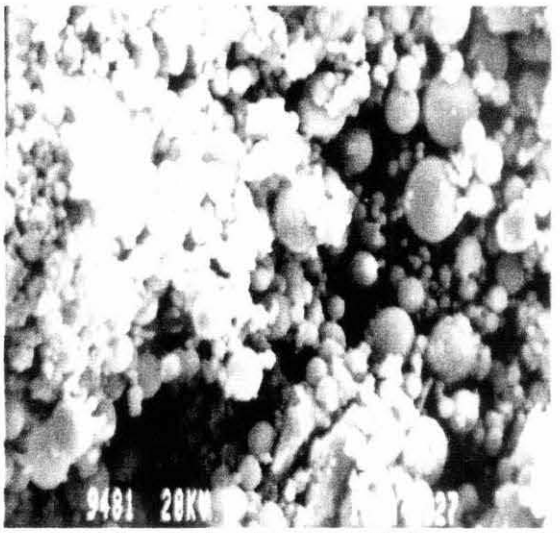


Figure 1 & 2 – SEM micrograph of fly ash [9]



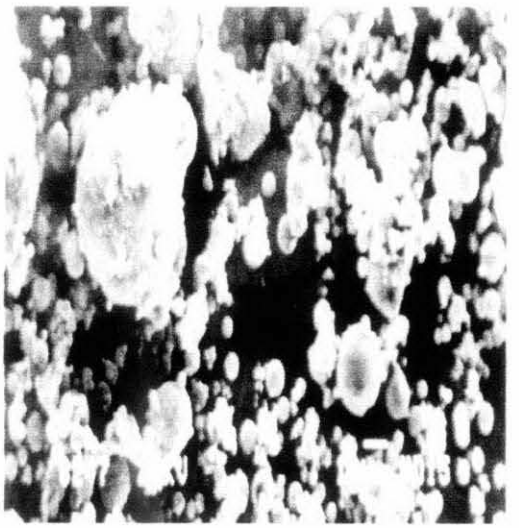


Figure 3 & 4 – SEM micrograph of heat-treated fly ash at 105°C [9]

2.5.2 X-Ray Fluorescence (XRF)

XRF is used to determine the chemical analysis and composition of the volcanic ash. The analysis of major and trace elements in geological materials such as Si, Al, and Fe by XRF is made possible by the behavior of atoms when they interact with X-radiation. XRF is particularly well-suited for investigations that involve bulk chemical analysis of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment. XRF is limited to analysis of relatively large samples, typically >1gram. The materials also should be prepared in powder form and effectively homogenized, and also compositionally similar.

2.5.3 Soil Properties

- **Moisture content [8]**

Moisture content of soil is required as a guide to classification of natural soils and as a control criterion in re-compacted soils and is measured on samples used for most field and laboratory test. The oven-drying method is the definitive procedure used in standard laboratory practice.

Moisture Content, W = $\frac{(m_2-m_3)}{(m_3-m_1)}$ X 100% **Equation 1**

Where;

m_1= mass of container (g)

m_2= mass of container and wet soil (g)

m_3= mass of container and dry soil (g)

- **Specific Gravity [8]**

Specific gravity is important to be used in the calculation of fly ash cement slurries and slurry density. Small pyknometer method is used for soils consisting of clay silt and sand-sized particles whereas the large pyknometer method is suitable for soils containing particles up to medium gravel size.

Particle Density/Specific Gravity, $\rho_s = \frac{(m_2-m_1)}{(m_4-m_1)-(m_3-m_2)}$ Mg/m^3

Equation 2

Where;

m_1= mass of pyknometer + cap assembly (g)

m_2= mass of pyknometer + cap + soil (g)

m_3= mass of pyknometer + cap + soil + water (g)

m_4= mass of pyknometer + cap + water (g)

- **Plastic Limit [8]**

  Plastic limit value can be determined by calculate the average moisture content (*using Equation 1*) of 20g samples which have been mould and rolled into thread shape between fingers. It is used together with the liquid limit to determine the plasticity index which when plotted against the liquid limit on the plasticity chart provides the classification of the soil sample.

  Plastic Index, I_p= LL-PL **Equation 3**

  Where;

  LL = Liquid Limit

  PL = Plastic Limit

- **Liquid Limit [8]**

  Liquid limit can be determine by take the reading/penetration of cone penetrometer and calculate the moisture content of the samples used. Then, plot the relationship between the moisture content and cone penetration with the percentage moisture content as abscissa and the cone penetration as ordinates, both on linear scales. From the linear graph, read off the moisture content at 20mm cone penetration and report as liquid limit (LL) of soil.

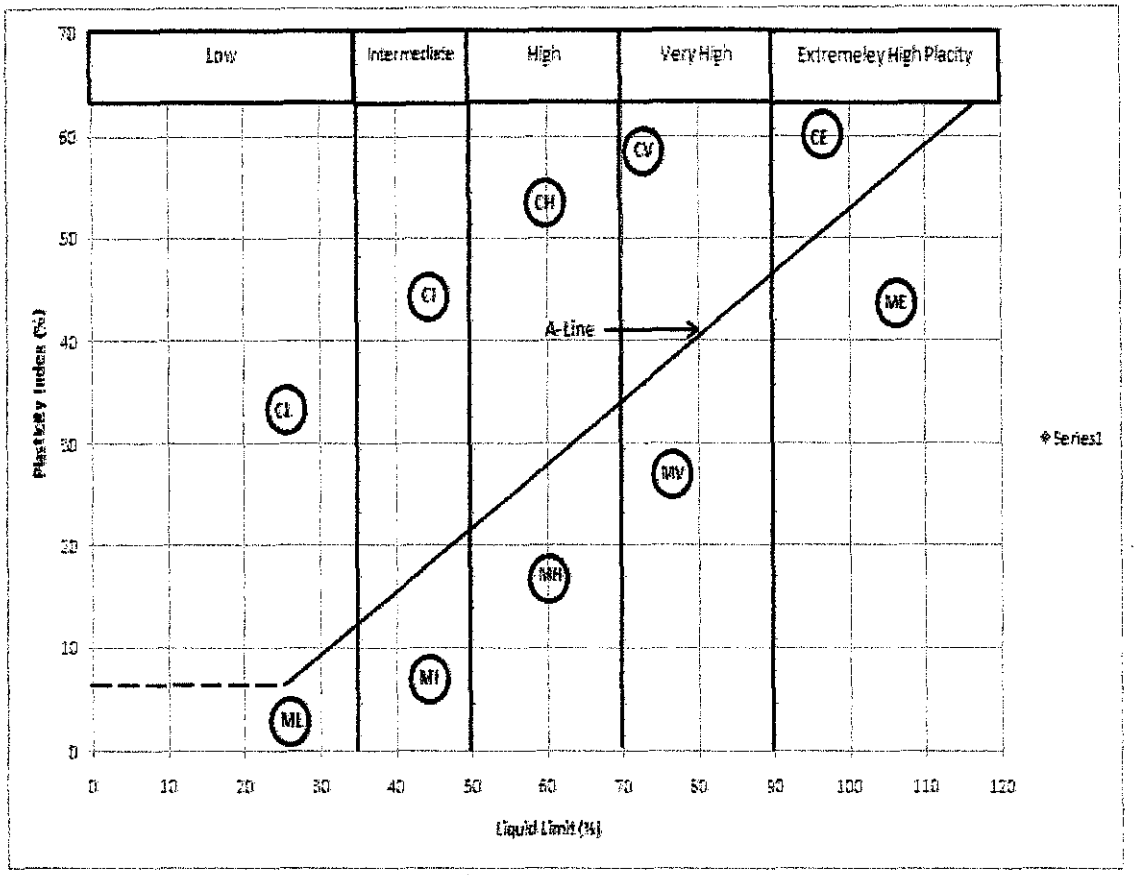


Figure 5 – Plasticity Chart for the Classification of Fine Soils [8]

	Primary Letter	Secondary Letter
Coarse-grained soils	G = Gravel S = Sand	W = Well graded P = Poorly graded Pu = Uniform Pg = Gap graded
Fine-grained soils	F= Fines (Undifferentiated) M = Silt C = Clay	L = Low plasticity I = Intermediate plasticity H = High plasticity V = Very high plasticity E = Extremely plasticity
Organic soils	Pt = Peat	O = Organic

Table 2 - Sub-group symbols in the British Soil Classification System [8]

2.6 Cement Test

2.6.1 Fluid loss test [5]

Fluid loss is the measurement of the water loss of the cement expressed in volume per unit time under reservoir temperature and pressure. The fluid loss for neat cement is directly proportional to water cement ratio. API Fluid loss is double the filtration volume obtained if blowout is not obtained. The fluid loss test in laboratory involves a static condition where slurry will be placed in a standard filter cell. The water loss through a 325-mesh screen is measured as a function of time. The cement slurry will be in static form and dehydration of slurries will usually result in decreasing fluid loss behavior with time.

$$Calculated\ API\ Fluid\ Loss : 2x\ Qt\frac{5.477}{\sqrt{t}} \qquad \textbf{Equation 4}$$

Where;

Qt is the volume of filtrate collected at the time of blowout, ml

t is the time of blowout, expressed in minutes

**Blowout – The time when nitrogen blows through in less than 30mins of testing*

Fluid loss control is particularly important when squeeze cementing across permeable formations. The slurry fluid loss must be tailored to the formation type and the permeability (*Young, 1967*). The generally accepted API fluid loss rates are listed below.

- Extremely Low Permeability Formation: 200mL/30min
- Low Permeability Formation: 100 to 200mL/30min
- High Permeability Formation (>100mD): 35 to 100mL.30min

When squeezing fractured limestone or dolomite formations, the situation is different from that for sandstone, because the permeability consists of interconnected voids or fracture systems. All cement particles can enter these channels and, as the slurry slowly dehydrates, it will travel

relatively long distances into the formation. To confine the cement within a close range around the wellbore, the dehydration process must occur quickly. Cement systems with high fluid loss rates (300 to 800mL/30min) are used to allow a fast cake build up. In high pressure squeezing, when overcoming the formation fracture pressure, the slurry is pumped into the induced fractures, and dehydrates against the fracture walls. If the formation permeability is sufficiently high, a medium to high fluid loss slurry (200 to 500mL/30min) will usually permit caking and subsequent diversion of slurry to smaller cracks.

2.6.2 Compressive strength test [4] [5]

Compressive strength is the capacity of compressive pressure that the cement can withstand at maximum. API RP-10B includes two methods to measure the strength development of cements. One is destructive test using 2 inch cubes cured in moulds at simulated downhole conditions. The other uses a special device known as the Ultrasonic Cement Analyzer (UCA). In this research, UCA is used as the device to know the compressive strength of volcanic ash cement. With this instrument, a sample of cement is held in pressure cell and subjected to insitu ultrasonic pulse velocity measurement. In general, the predictions of strength development when using the UCA, when compared to destructive test are found to be conservative. In other words, the strengths predicted by UCA tend to be lower than from the cube method at the same curing conditions.

Properly designed cement slurry will set after it has been placed in its appropriate location within the well. Cement strength is the strength the set cement has obtain, which can refer to compressive strength or sometimes tensile strength. When cement has developed 500psi (3447 kPa), compressive strength in 24 hours, and the strength is usually deemed sufficient to hold pipe or casing and continue for operations. For lead slurry operations, minimum strength required is normally around the range of 250-300psi (lower density of cement), while for tail slurry, around 500psi as tail slurry has higher density.

2.6.3 Thickening time test [6]

Thickening time often called "pumping time" is the time cement slurry remains sufficiently fluids to be pumpable under downhole temperature and pressure. The thickening time must be long enough to allow the slurry to be mixed and placed without risk of premature setting. Desired thickening times are based on the estimated job time to pump the fluids, plus a safety factor. Excessive thickening time should be avoided to eliminate lengthy WOC (waiting of cement) times.

Thickening time can be measured by using consistometer. This device allows agitation of the cement slurry under simulated well conditions of temperature and pressure, while measuring the consistency of the slurry. In a shallow well, the slurry can be designed for a fairly short pumping time (e.g. two hours). Accelerators are commonly used. However, a hesitation squeeze job may require a pumping time as long as six hours. Therefore, one must add sufficient retarder to assure slurry placement, and reversing out of the excess.

2.6.4 Free water test [4]

Free fluid or free water is the liquid (water and dissolved chemicals) that separates from the bulk of the cement slurry under static conditions. The amount of free fluids depends on several variables including the composition of the cement slurry, the temperature, the mixing and conditioning history, etc.

Free fluid is an indication of the stability of the cement slurry. Cement slurries with high levels of free fluid (normally ±2% of the slurry volume) often tend to segregate or settle out under static and/or dynamic conditions. In the API operating free water test, the slurry is heated to BHCT (or BHSQT for squeeze operations) in a pressurized consistometer in accordance with the appropriate schedule, cooled to 194°F and then transferred into a 250mL graduated glass cylinder. If the free fluid test is going to be conducted above room temperatures, the graduate glass cylinder is placed in a pre-heated curing chamber or water bath for the duration of the test. The cylinder is sealed to prevent loss of fluid through evaporation, and then allowed to

remain quiescent, on a vibration free surface for the two hour duration of the test.

2.7 General Properties Requirements for Slurry [*ANSI/API Recommended Practice 10B-2*]

a. Minimum & Maximum Density

For conventional onsite requirement, the density of the cement slurry has to be a least:

+0.5 - 1.0ppg > drilling fluid density + 0.5ppg > spacer density Lower than the Equivalent Circulating Density (ECD) to the formation

b. Maximum Permeability and Porosity

According to [*McElfresh, 1981*], the porosity exceeding 35-40% induce cement elongated cracks during perforation stages. For the permeability, it should not exceed 1mD to provide a barrier for fluid intrusion to contact with the casing from formation.

c. Maximum fluid loss of the slurry *(classified based on the different casing sections)*

Surface	≤ 500cc/30min	Intermediate	≤ 250cc/30min
Production	≤ 100cc/30min		

d. Minimum Thickening time

The minimum thickening time is the job time plus safety factor (normally 30 minutes to 60 hours). The thickening time consists of mixing time, pumping displacement time, time for plug to rupture and safety factor.

e. **Minimum compressive strength**

The minimum compressive strength based on API Class G requirements in 2.1MPa (8 hours) at temperature 38 degC and atmospheric pressure, while 10.3MPa at temperature 60 degC and atmospheric pressure.

f. **Maximum free water**

The maximum free water for API Class G requirements is about 5.8mL.

CHAPTER 3

METHODOLOGY

3.1 Methodology Flow Chart

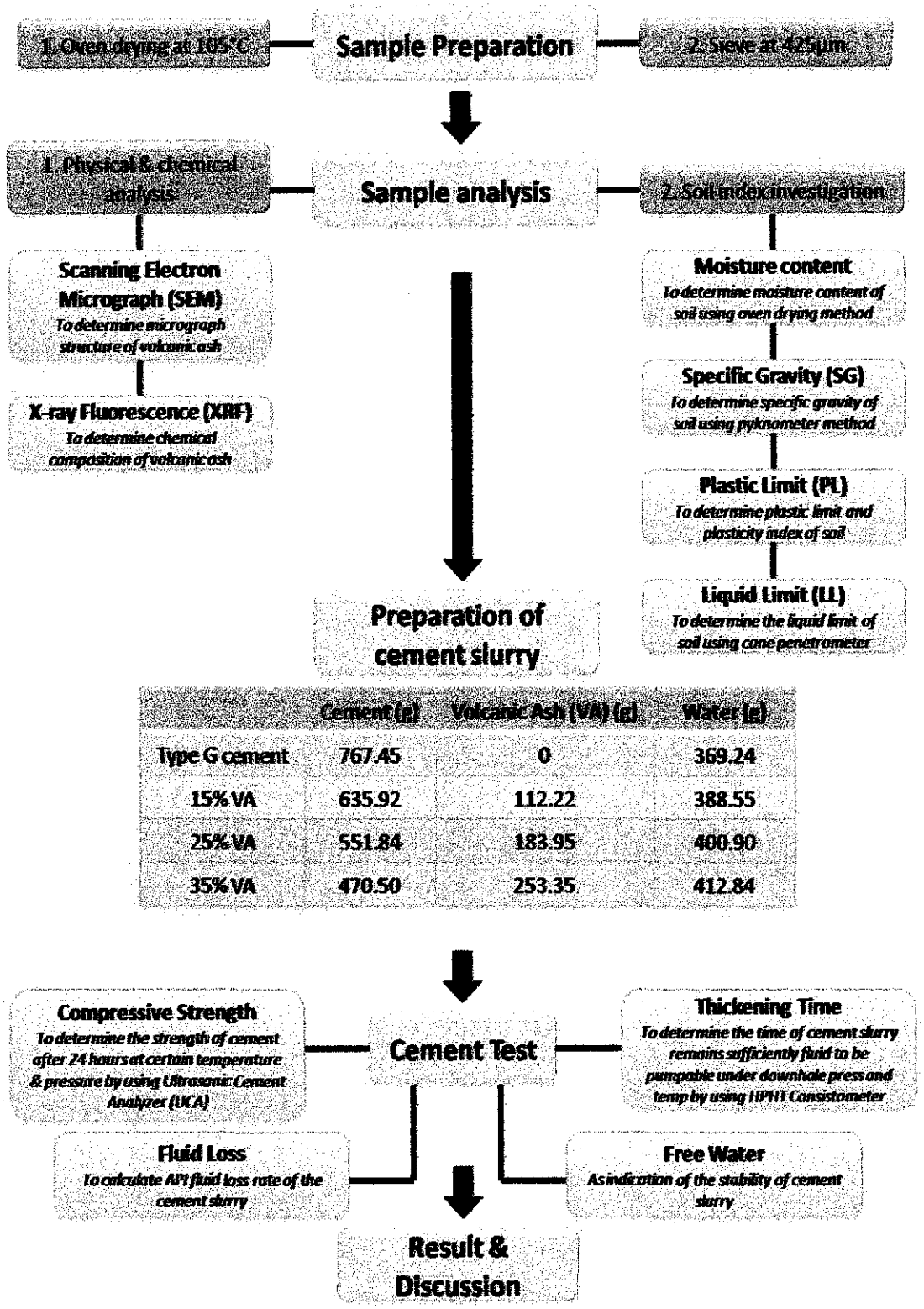


Figure 6 – Project workflow chart

3.2 Description of project activities

Introduction

Prior to achieve the objectives of the study, researches and literature reviews have been done based on the previous researches or works. Although most of the past researches and studies more toward byproduct fly ash from the combustion of coal and biomass fly ash, studies from various sources such as journals, textbook references, and previous research help me to understand the properties of the fly ash and its current application. So, all results and studies from previous researchers can be the guidance to produce fly ash cement from Lawin volcanic ash. There are some evaluations and experiment need to be carried out such as **Scanning Electron Microscope (SEM) and X-ray Fluorescence (XRF)** analysis of the volcanic ash, laboratory experiments on cement testing quality and comparison between weathered Lawin volcanic ash cement and neat Type G cement.

1. **Sample collection and preparation**

   First of all, the sample was collected around Lawin tuff in Grik, Perak. The volcanic ash sample was collected from different places in order to get variety samples since we still do not know the properties of the samples. The samples might be in soil phase. For SEM and XRF analysis, the samples were analyzed in powder phase. So, some of the volcanic ash sample will be grinding to small particles as much as possible. Before that, the volcanic ash will be heat-treated at temperature 105°C for 24 hours in order to dry the moisture content. Then the dried volcanic ash was crushed into smaller particles and was sieved at 45μm siever.

2. **SEM and XRF analysis of fly ash samples**

   For SEM analysis, we can know the morphology and micrograph of the samples. At this stage, only two (2) samples being analyzed due to some limitations. Sample 1 is as-received weathered volcanic ash and Sample 2 is heat-treated weathered volcanic ash. Both samples are use to know the

distribution, surface phase, grain sizes and shapes of the particles in the samples. Then, compare the results with the byproduct fly ash.

For XRF analysis, Sample 1 and Sample 2 are used to know the elements and chemical composition of the samples. All of this analysis important in order to know the properties of the natural fly ash and in order to compare it with byproduct fly ash, so that we can determine either it is suitable or not for mixing in Portland cement.

3. Soil Properties investigation [8]

Sample/Material used in this research is from weathered volcanic ash which can be classified as soil. So it is important to know the properties of the soil.

i. Determination of Moisture Content (Oven-Drying Method)

The objective is to determine the moisture content in soil using the oven-drying method. Water is present in most naturally occurring soil. The amount of water, expressed as a proportion by mass of the dry solid particles, known as the moisture content, has a profound effect on soil behavior. In this context a soil is dry when no further water can be removed at temperature not exceeding 110°C. (*See Appendix 8 for lab procedure determination of moisture content.*)

ii. Determination of Specific Gravity/Particle Density

The objective is to determine the value of particle density/specific gravity of soils by using the large pyknometer method (Figure 7). It is important to know the specific gravity of the weathered volcanic ash because it useful for the determination of slurry proportion and slurry density later. (*See Appendix 9 for lab procedure determination of specific gravity.*)

iii. Determination of Plastic Limit

The objective is to determine the plastic limit and plasticity index of soil. The plastic limit is the empirically established moisture content

at which a soil becomes too dry to be plastic. It is used together with the liquid limit to determine the plasticity index which when plotted against the liquid limit on the plasticity chart provides a means of classifying cohesive soil. (*See Appendix 10 for lab procedure determination of plastic limit.*)

iv. Determination of the Liquid Limit

The objective is to determine the liquid limit of soil using cone penetrometer (**Figure 7**). The liquid limit is the empirically established moisture content at which a soil passes from the liquid state to the plastic state. (*See Appendix 11 for lab procedure determination of liquid limit.*)

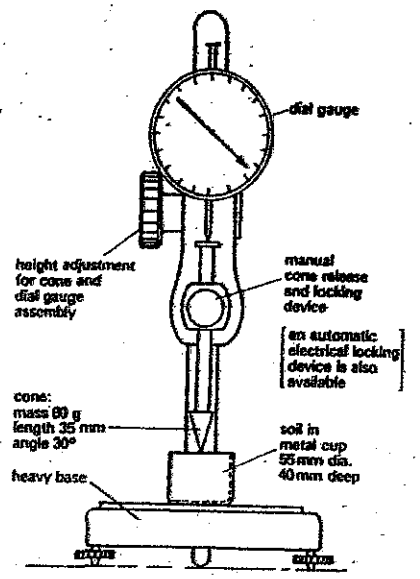


Figure 7 – Cone Penetrometer

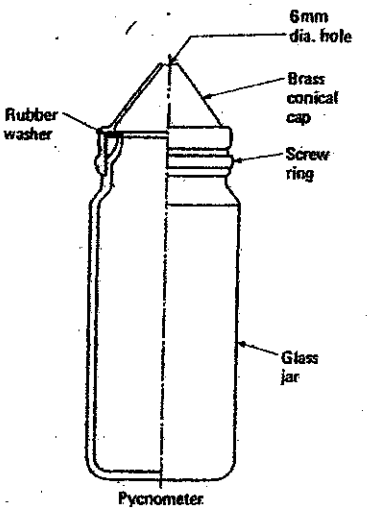


Figure 8 - Pyknometer

4. Mixing of samples with Portland cement

In this stage, some cement slurries will be prepared by mixing Portland cement type G with volcanic ash with different proportions. The water content might be maintained at water ratio 0.55 or at slurry density 15.8ppg for all volcanic ash proportions. The cement slurries will be prepared by

using constant speed cement mixer. Additive or retarder might be added into the cement slurry upon requirements of certain test.

5. Sample testing

To produce fly ash cement that satisfies with API standards for well cementing, the produced cement will have to go through several qualities testing including compressive strength, fluid loss, free water content, and thickening time. The results comparison with neat Type G cement will determine the performance of the volcanic ash.

- Fluid loss test [3]

  In the high pressure and high temperature fluid loss test, slurry is prepared and immediately placed in the preheating atmospheric pressure consistometer and stirred for 20 minutes. The slurry is then poured into the preheated high pressure filter press and maintained at the final temperature of the schedule of the duration test. Due to lack of expertise for handling the machine, LPLT filter press is used in this experiment. Cement slurries were tested at the ambient temperature and pressure first. Then, cement slurries were tested at 100psi differential pressure. The cumulated water in 30 minutes is the fluid loss of the cement. (*See Appendix 12 for lab procedure fluid loss test.*)

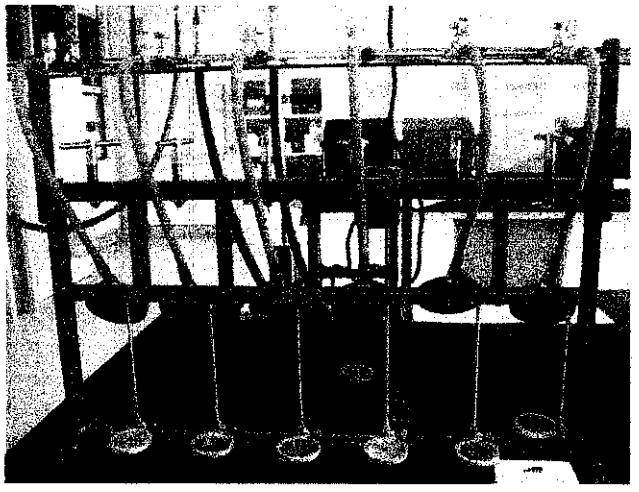
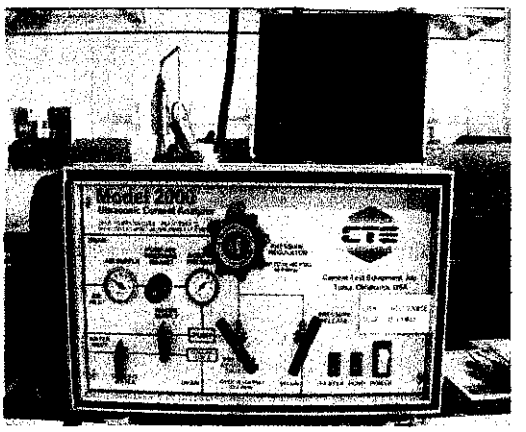


Figure 9 – LPLT Filter Press

- Compressive strength measurement [3]

  Compressive strength is the capacity of compressive pressure that the cement can withstand at maximum. In this experiment, Ultrasonic Cement Analyzer (UCA) is used in order to know the compressive strength of the cement samples. All of the cement samples were tested at the pressure 3000psi and temperature 300°F for 24hours. (*See Appendix 13 for lab procedure of compressive strength test.*)



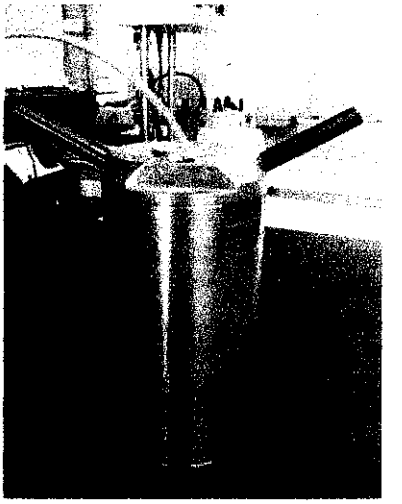


Figure 10 – Ultrasonic Cement Analyzer (UCA) **Figure 11** – UCA test cell

- Thickening time test [3]

  In the thickening time test, prepared slurry is immediately poured into a consistometer container and the slurry is being stirred, the temperature and pressure is increased until 250°F and 3000psi. Stirring is continued until the slurry reaches a consistency 80-100Bc. Retarder R-21LS is used to add length of thickening time. (*See Appendix 14 for lab procedure of thickening time test.*)

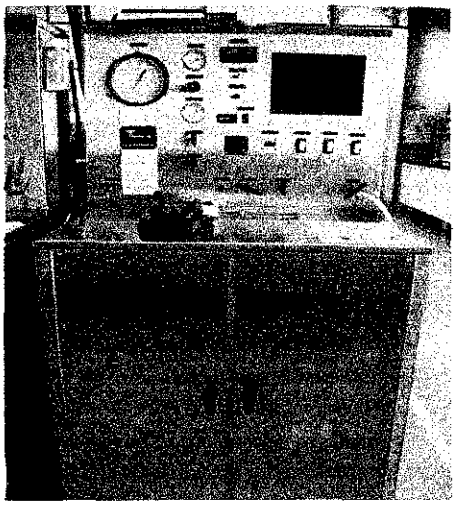


Figure 12 – HPHT Consistometer

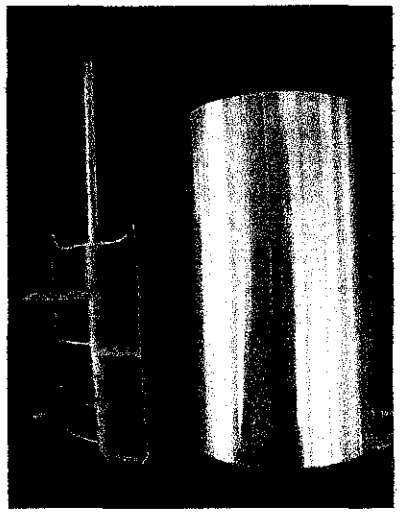


Figure 13 – HPHT Consistometer Test Cell

- Free water test [3]

  Prepared slurry is immediately place in the atmospheric pressure consistometer and stirred for 20 minutes. The slurry is then remixed for an additional 35 seconds and followed by pouring it into a 250 ml graduated cylinder. The mouth of the cylinder is sealed and then is placed on a vibration free surface and allowed to stand undisturbed for 2 hours. The volume of water remove from the top of the slurry is recorded as the amount of free water content.

6. Result and data analyzing

After conducted all experiments and quality controls, the results will be tabulated in tables or graph in order to analyze trend of the results. This include the plotting the graph of setting time, compressive strength, fluid loss and free water content.

7. Discussion

Discussion on the analyzed data is to be made after data reviewing. Should anything of the results goes wrong or unsuccessful, the data from the quality control will be reviewed again.

3.3 Consumables and Equipments required

The consumable materials which are required for this project are Class G Oil well cement, fresh water, light grease, retarder, and fluid loss additive. The consumables are used only in the cement slurry and specimen preparation. Below are the quantities that were required.

Table 3 - Type of Consumables and Quantities

Types of Consumable	Quantity (Approximate)
Class G Oil Well Cement	10-15 kg
Fresh Water*	4-7 liters
Light Grease	5-10 usages for Compartments
Retarder (R-21LS)	8-10mL
Fluid Loss additive	8-10mL

**Only used for purpose of cementing not including flush/wash*

The laboratory equipments listed below are used for cement slurry preparation, cement curing stages and also for laboratory testing methods. Below are the equipment and the primary functions:

Table 4 - Main Equipments for Laboratory Preparation and Testing

Main Equipment(s)	Functions
Scanning Electron Micrograph (SEM)	To analyze microstructure of the sample.
X-Ray Fluorescence (XRF)	To analyze element composition of the sample.
Oven	To dry the volcanic ash.
Pyknometer	To know the liquid limit of the soil.
Cone Penetrometer	To know the plastic limit of the soil.
Model 7000 Constant Speed Mixer	Mixing of Base slurry
SOLTEQ® Compressive Strength Tester V2.03 BETA	Determination of compressive strength
OFITE Filtration Loss	Determination of fluid loss volume
SOLTEQ® Pressurized Consistometer	Determination of thickening time

3.4 Gantt chart

Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Briefing & update on student progress																
Project work commences																
XRF, XRD & SEM analysis																
Soil index analysis																
Compressive strenght test																
Fluid loss test																
Thickening time test																
Submission of progress report 16 March 2011																
PRE-EDX combined with seminar/ Poster Exhibition/ Submission of Final Report 4 April 2011																
EDX 11 April 2011																
Final Oral Presentation 20 April 2011																
Delivery of Final Report to External Examiner / Marking by External Examiner 20-27 APRIL 2011																
Submission of hardbound copies 04 MAY 2011																

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 SEM Result and Analysis

For SEM analysis, two samples have been analyzed at different magnification. Sample 1 is weathered volcanic ash and Sample 2 is heat-treated volcanic ash. Below are the images/results from SEM for both samples.

Sample 1	Sample 2

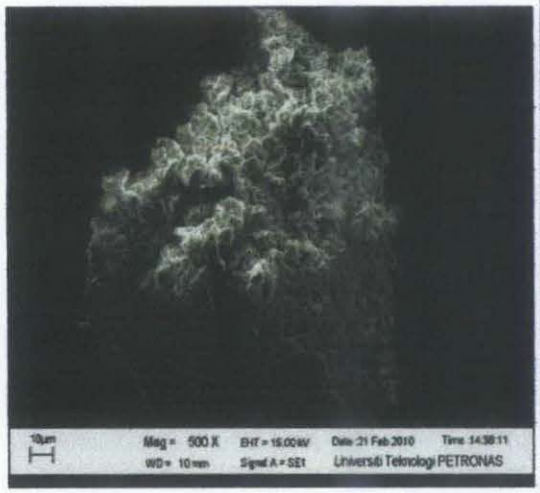
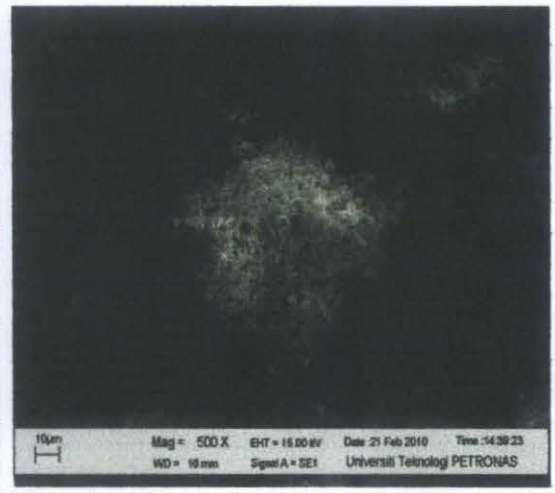

	

Figure 14 - Magnification: 500X	**Figure 15** - Magnification: 500X

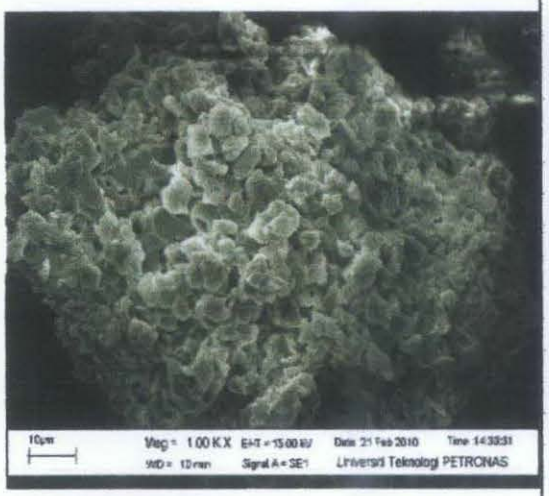
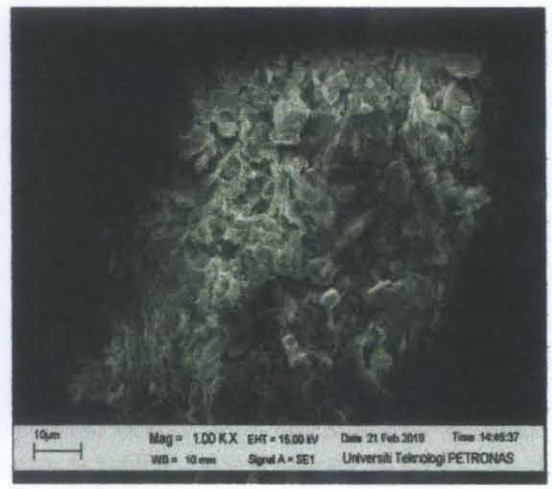

	

Figure 16 - Magnification: 1000X	**Figure 17** - Magnification: 1000X

Figure 18 – Magnification: 3000X

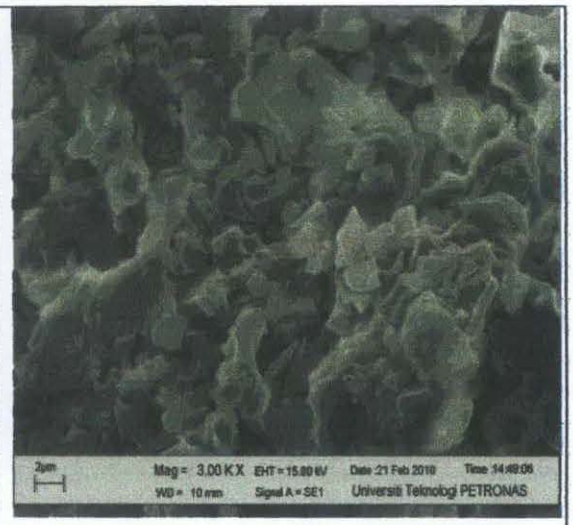


Figure 19 – Magnification: 3000X

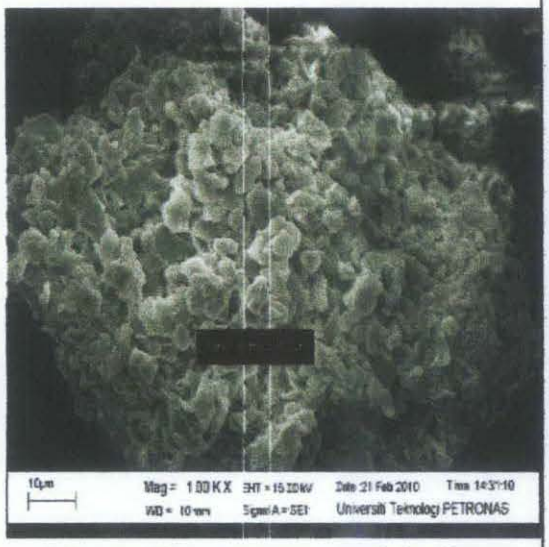


Figure 20 – Average particle size

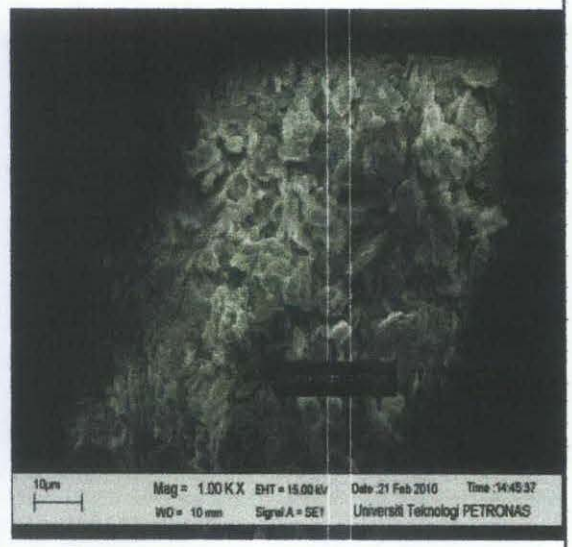


Figure 21 – Average particle size

Based on all micrograph images above, particulates of volcanic ash are even-granular and less than 10μm, have different shapes and sizes which is conformity with its particulate size analysis. From the SEM analysis also, indicates that the ash has a loose structure and a lot of small holes among the particulates which can be conclude that the ash can be crush into smaller size.

Similar results were obtained from the investigation conducted with heat-treated volcanic ash. The images of Sample 2 show a small decrease in particle size as compared to Sample 1. Figure 19 shows that the average particles size for Sample 1 is around 5.582μm and Figure 20 shows the average particles size for Sample 2 is around 4.689μm. There are only small changes because the volcanic ash only heat at temperature 105°C and not sintered at high temperature.

Particles characterization should be can be done by SEM and also EDX. By EDX, type of particles of volcanic ash can be pointed and analyzed. But due to some gas supply problems, the EDX cannot works for the characterization.

However, the investigation reveals that the micrograph or particles structure of volcanic ash are different with the most fly ash particles micrograph (Figure 1 & 2). So, it can be conclude that the characteristics of volcanic ash cement should be different with the characteristics of fly ash cement due to the different particles shape which contribute to the workability, permeability and viscosity of the cement.

4.2 XRF Results and Analysis

O	Al	Si	K	Fe	F	Al2O3
-1000.0KCps	12.3 KCps	57.1 KCps	19.3 KCps	26.0 KCps	-1000.0 KCps	**12.3 KCps**
50	**10.8**	**35.1**	**2.97**	**0.605**	**5.340**	**20.4**

Table 5 – XRF result from lab

Constituents	Specimen 1 (%)	Specimen 2 (%)	Reference (P.C. Leong)
SiO2	72.59	72.73	79.5
Al2O3	20.4	23.3	9.60
Fe2O3	0.86	0.65	0.96
FeO	0.78	0.59	1.35
K2O	3.58	3.23	4.17
MgO	1.63	0.31	0.71
CaO	Trace	Trace	0.22
Total	99.84	100.81	

Table 6 – Calculated chemical composition of weathered Lawin's volcanic ash

For chemical analysis by XRF, two samples: as-received weathered volcanic ash and heat treated volcanic ash, have been analyzed. The results are stated in the Table 5 and Table 6. Table 5 is the result from the XRF lab. It is indicate the weight percentage of each elements existed in the volcanic ash. It was shown that the weathered volcanic ash from Lawin tuff has low silica content which is 35.1%.

From the result, it was calculated that the weathered Lawin tuff has lower SiO2 content but high Al2O3 content compared to the analysis done by P.C Leong. The calculated chemical compositions are calculated based on the weight percent of the element, molecular weight and also the molar reaction of the elements. It can be said that the weathered volcanic ash is tuffaceous sandy shale containing abundant detrital quartz. It was obtained from a band interbedded with the pure volcanic tuff.

As the conclusion of XRF analysis, it is concluded that weathered volcanic ash from Lawin tuff have high content of SiO2 and Al2O3, but low content of CO2. Due to the low content of CO2 in the volcanic ash also, we can know that the reaction of the volcanic ash cement will become slower compare to the neat cement.

4.3 Soil Properties Results and Analysis

4.3.1 Moisture Content

After dried in oven at 105°C for a period of 24 hours, the moisture content of the volcanic ash samples were determined. Based on the Table 7, the **average moisture content of weathered volcanic ash is about 25.38%.** It is means that about 25.38% water is present in the weathered volcanic ash. This actual moisture content value might be more than this value since the moisture content test not carried out slightly after the sample collection. So the moisture content might be dry naturally before the test. Moisture content of the volcanic ash might be effect the density and viscosity of the cement slurry, so this 25.38% of moisture content should be dried before we blend the volcanic ash with cement.

Container No:		**1**	**2**	**3**	**Average**
Mass of wet soil + container (m2)	**(g)**	**45.5**	**47.3**	**46.4**	

Mass of dry soil + container (m3)	**(g)**	**40.1**	**41.5**	**40.9**	
Mass of container (m1)	**(g)**	**18.9**	**18.9**	**18.9**	
Mass of moisture (m2-m3)	**(g)**	**5.4**	**5.8**	**5.5**	
Mass of dry soil (m3-m2)	**(g)**	**21.2**	**22.6**	**22**	
Moisture content, W = (m2-m3) x 100% (m3-m1)	**(%)**	**25.47**	**25.66**	**25**	**25.38**

Table 7 – Moisture content determination of VA soil

4.3.2 Specific Gravity

Specific gravity is the ratio of the density of a substance to the density of a reference substance such as water. By using small pyknometer with water as the reference substance, after 24 hours, the measured specific gravity (SG) is 5.03 Mg/m³. This SG value is used for the calculation of volcanic ash cement slurry later. It will determine the value of cement, volcanic ash and water required to make the cement slurry at a slurry density. Without knowing this SG value, we cannot know the slurry density, hence we should use different water ratio and get different slurry density of the cement.

Mass of jar + gas jar + plate + soil + water (m3)	**(g)**	**1798.6**
Mass of jar + gas jar + plate + soil (m2)	**(g)**	**935.35**
Mass of jar + gas jar + plate + water (m4)	**(g)**	**1478.4**
Mass of jar + gas jar + plate (m1)	**(g)**	**535.6**
Mass of soil (m2-m1)	**(g)**	**399.75**
Mass of water in full jarr (m4-m1)	**(g)**	**942.8**
Mass of water used (m3-m2)	**(g)**	**863.25**
Volume of soil particles (m4-m1)-(m3-m2)	**ml**	**79.55**
Particle density/Specific Gravity, ρ $\rho = \frac{m2-m1}{(m4-m1)-(m3-m2)}$	**Mg/m³**	**5.03**

Table 8 – Specific Gravity determination of VA soil

4.3.3 Plastic Limit

The plastic limit of a soil is the moisture content, expressed as a percentage of the mass of the oven-dried soil, at the boundary between the plastic and semi-solid states. The threads of soil reach its plastic limit when it begins to crumble when rolled to a diameter of 3mm. From the experiment, the average moisture content of soil threads is 36.36%. So this is the value of plastic limit of the soil. The actual value might be different since the test not carried out after the samples taken from the tuff. From this value, plasticity index can be calculated after get the value of liquid limit.

Container No.		1	2	3	4	Average
Mass of wet soil + container (m2)	g	26.67	25.5	25.25	26.24	
Mass of dry soil + container (m3)	g	25	23.7	23.5	24.8	
Mass of container (m1)	g	20.42	18.68	18.7	20.87	
Mass of moisture (m2-m3)	g	1.67	1.8	1.75	1.44	
Mass of dry soil (m3-m1)	g	4.58	5.02	4.8	3.93	
Moisture Content/Plastic Limit $W = \frac{m2-m3}{m3-m1} \times 100\%$	%	36.46	35.86	36.46	36.64	36.36

Table 9 – Plastic limit determination of VA soil

4.3.4 Liquid Limit

The liquid limit of a soil is the moisture content, expressed as a percentage of the mass of the oven-dried soil, at the boundary between the liquid and plastic states. The moisture content at this boundary is arbitrarily defined as the liquid limit and is the moisture content at a consistency as determined by means of the standard liquid limit apparatus. The value of liquid limit is determined by the plot of the relationship between the moisture content and cone penetration with the percentage moisture contents as abscissa and the cone penetrations as ordinates. From the linear graph, the value of liquid limit at 20mm cone penetration is 40.1%.

Test No.		1			2			3			4		
Dial gauge reading	mm	16.5	16.7	16.3	19.3	19.9	19.6	22.7	22.1	22.4	25.9	25.6	26
Average penetration	mm	16.5			19.6			22.4			25.83		
Container No.		LL1			LL2			LL3			LL4		
Mass of wet soil + Container	g	50.96			52.69			52.45			48.05		
Mass of dry soil + Container	g	44.2			43.2			41.7			36.5		
Mass of container	g	20.5			19.1			18.6			18.5		
Mass of moisture	g	6.76			9.49			10.75			11.55		
Mass of dry soil	g	23.7			24.1			23.1			18		
Moisture content	%	28.52			39.38			46.5			64.17		

Table 10 – Liquid limit determination of VA soil

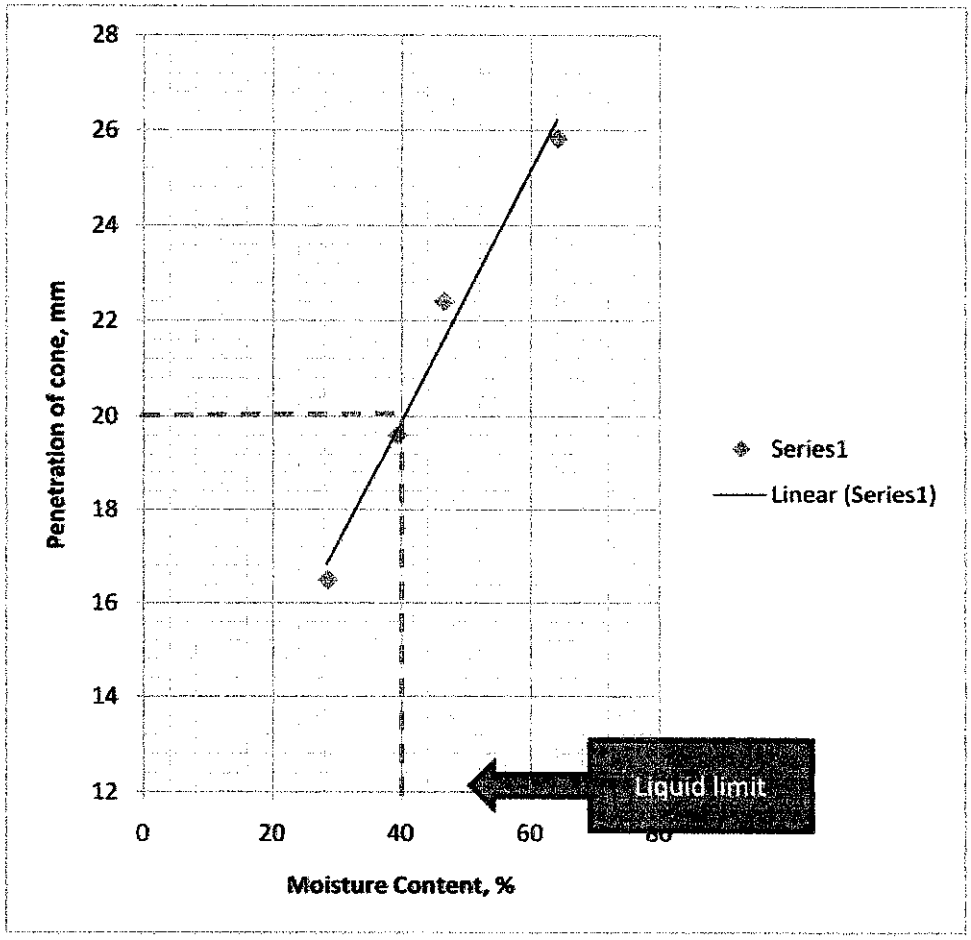


Figure 22 – Liquid limit determination

So, from the plastic limit test, the **plastic limit value is 36.36%**. The **liquid limit value is 40.1%**. From these values, Plasticity Index can be calculated in order to obtain the classification of soil.

Plastic Limit, PL = 36.36%

Liquid Limit, LL = 40.1%

Plasticity Index, Ip = LL-PL = 40.1-36.36 = **3.74**

From this Ip value, soil sample classification is determined by read it using plasticity chart (**Figure 23**). At plasticity index of 3.74, concluded that the soil is **silt fine-grained soils with intermediate plasticity.**

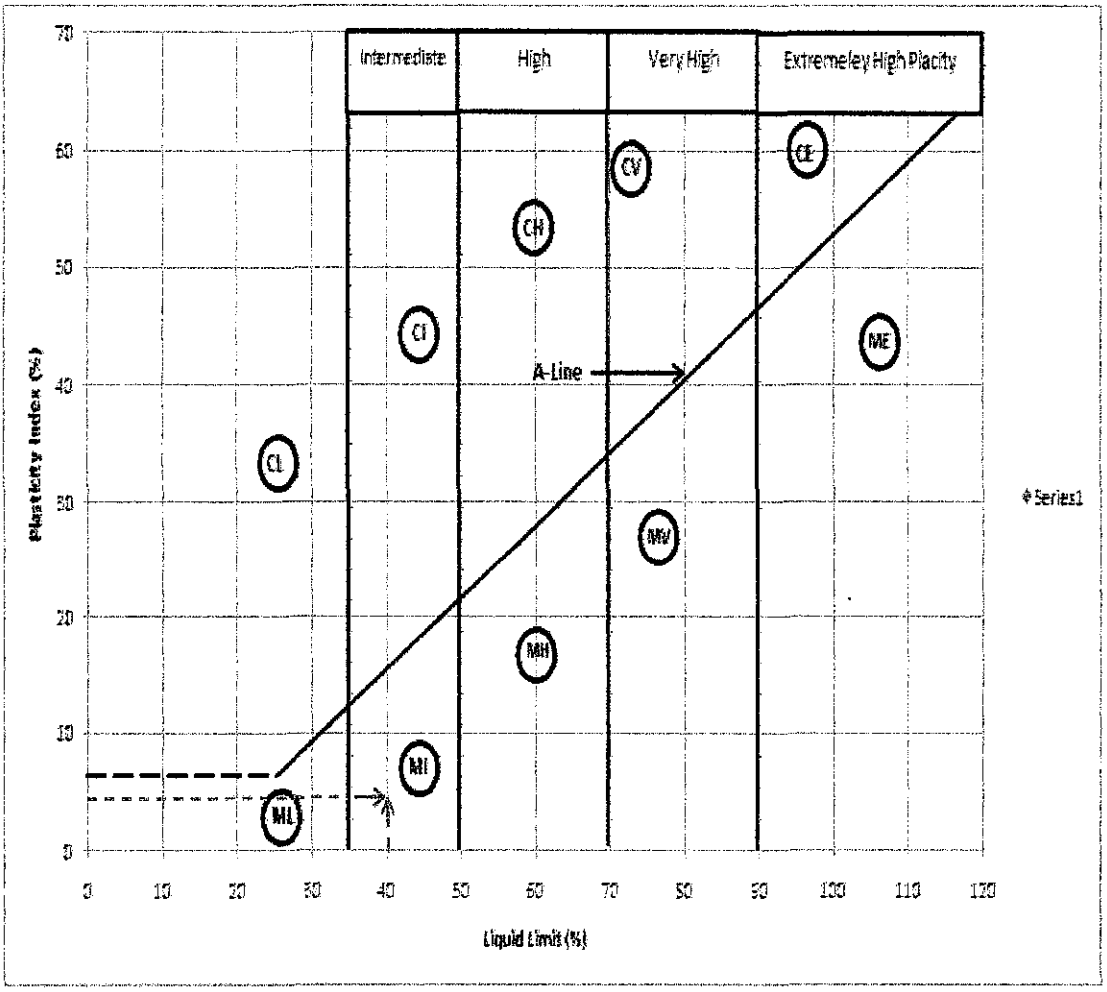


Figure 23 – Plasticity chart for the classification of fine soil

4.4 Cement Test Results and Analysis

4.4.1 Cement Slurry Proportion

For cement slurry, at first, two types of cement slurry were created. First type of the cement slurry is the cement slurry with water ratio 0.55 (**Table 11**). The percentage of volcanic ash added mixed with cement is based on the 1:1 ratio calculation. Second type is the cement slurry with same slurry density which is 15.8ppg (**Table 12**). The cement slurry proportion was calculated by using a calculation spreadsheet. In this spreadsheet, specific gravity of samples is important in order to calculate the amount of each sample. For each types of cement slurry, different percentage of volcanic ash will be added or mixed with cement.

	water	cement	VA
15%	330	510	90
25%	330	450	150
35%	330	390	210

Table 11 – Slurry proportion with water ratio 0.55

	water	cement	VA
15%	388.55	635.92	112.22
25%	400.9	551.84	183.95
35%	412.84	470.5	253.35

Table 12 – Slurry proportion with slurry density 15.8ppg

Different percentage of volcanic ash will resulted different viscosity of cement slurry. After mixed all the slurry proportions, obtained that more volcanic ash percentage, more viscous the cement slurry. Here, some analysis should be done before go further with cement tests. For example, for thickening time test, the 35% volcanic ash replacement will make the slurry more viscous and difficult to pump into the well, hence the thickening time will fast. So, retarder can be added later into the cement slurry to increase the thickening time.

4.4.2 Compressive Strength Test

Results of the compressive strength by using Ultrasonic Cement Analyzer (UCA) for different volcanic ash percentage are shown in **Table 13** and **Table 14.** Neat Type G cement also tested in order to make comparison with the performance of the volcanic ash cement. For lead slurry operation, the required minimum compressive strength required to hold the casing is usually around 250psi-300psi, while for tail slurry which generally has higher density than lead slurry, requires minimum compressive strength of 500psi in the time of 24 hours. The compressive strength test using UCA is tested at pressure 3000psi and temperature 300°F for 24 hours.

At 8 hours period, for both cement slurry proportion, 15% volcanic ash content has the higher strength followed by 25% and 35% volcanic ash. 15% VA has a very fast rate of reaction during hydration because of the small amount of volcanic ash explains why it has higher strength compared to others at earlier stage. At 12 hours period also, 15% VA still has the highest strength, followed by 25% VA and 35% VA.

After 24 hours, it can be observed from the results that the compressive strength of 35% VA is higher than 25% VA and 15%. The 15% VA retrograded when reach certain period. This retrogression is due to high temperature (above 250°F) and can be solved by adding silica into the cement slurry. At early of the test, the compressive strength of all cement samples are 0psi. The strength only started to increase after almost two hours of the test. This is due to the long reaction the cement with the volcanic ash. The more volcanic ash percentage, the cement reaction with volcanic ash to reach maximum compressive strength will be longer.

From the overall results and the maximum compressive strength for all cement samples, the compressive strength of cement with 35% VA has higher strength than 25% and 15%. The 15% VA has higher strength than others only at early of reaction. But, the Type G cement (neat cement) still has higher compressive strength than others. So, it can be concluded that volcanic ash reduce the compressive strength of cement but, more volcanic ash, higher the compressive strength.

Generally, neat cement which are produced at 15 - 17 ppg exhibit higher compressive strength because it is basically a compacted unit of cement with less than 2% of gas bubbles. The compressive strength reduces with density because, as the density is decreased, indicates the cement contains more water per volume of cubes.

	8 hours	12 hours	24 hours	Max.
Gcement	1600	2000	2040	2100
15%	1100	1200	950	1200
25%	950	1070	1220	1220
35%	650	1150	1630	1700

Table 13 – Compressive strength for slurry proportion 1 (Table 11)

	8 hours	12 hours	24 hours	Max.
G cement	1600	2000	2040	2100
15%	1270	1400	1150	1400
25%	1050	1330	1470	1470
35%	750	1250	1700	1700

Table 14 – Compressive strength for slurry proportion 2 (Table 12)

(*See Appendix 15 -18 for UCA results*)

	50 psi @ hr:min	500psi @ hr:min	Max. Strength @ hr:min
G cement	1:50	2:40	2040psi @ 16:00
15% VA	1:55	3:00	1400psi @ 14:00
25% VA	2:00	4:00	>1470psi @ >24:00
35% VA	2:10	5:50	>1650psi @ > 24:00

Table 15 – Gel strength, minimum strength and maximum strength of cement

*Based on slurry proportion 2 (*Appendix 15-18*)

Table 15 shows the gel strength, minimum strength and maximum strength of the cements based on the slurry proportion 2. The gel strength of the cement is reached when the strength of the cement is 50psi. So from the result, indicates that 35% volcanic ash cement takes more time to reach its gel strength. On the other hand, 500psi of strength is the minimum strength that the cement required before other cement or drilling job can be continued. So

the time taken to reach 500psi strength is the time of Wait of Cement (WOC). For the maximum strength, it shows that 15% volcanic ash cement not suitable to be used since the strength will retrograde, compared to 25% and 35% VA, the strength keep build up more than 24 hours.

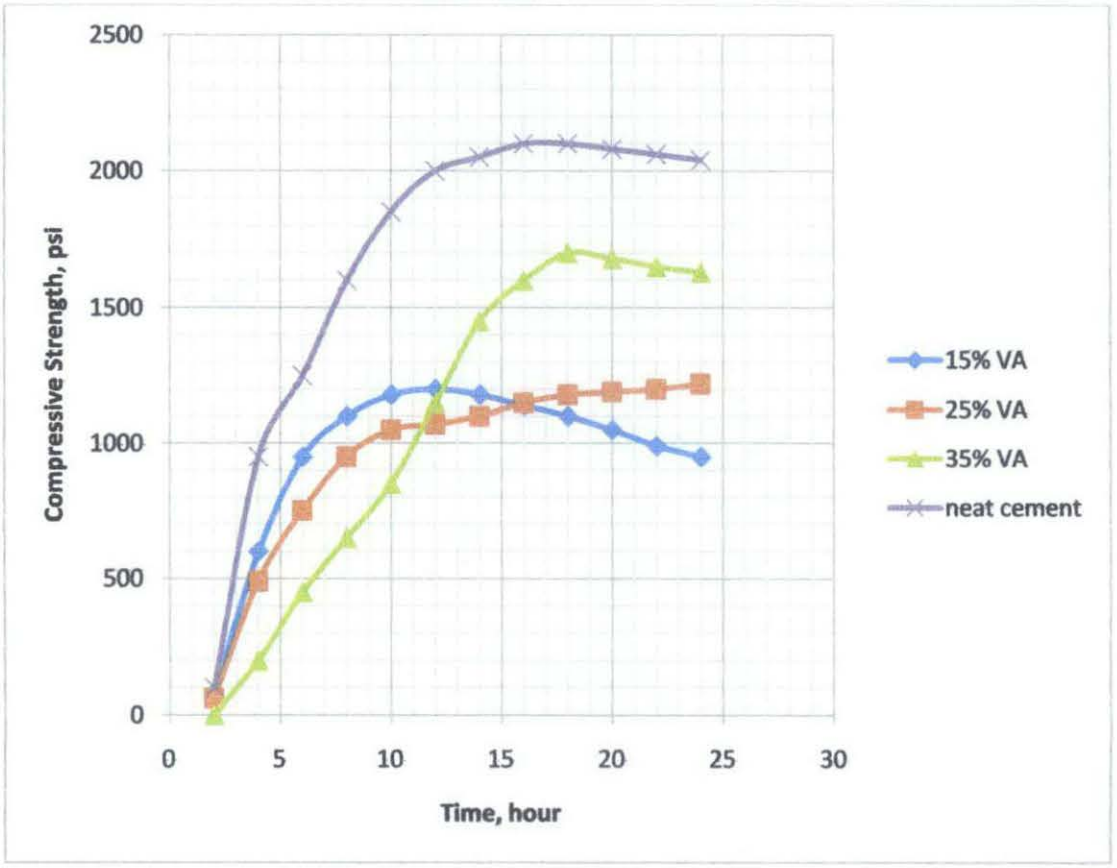


Figure 24 - Compressive strength for slurry proportion 1 (Table 11)

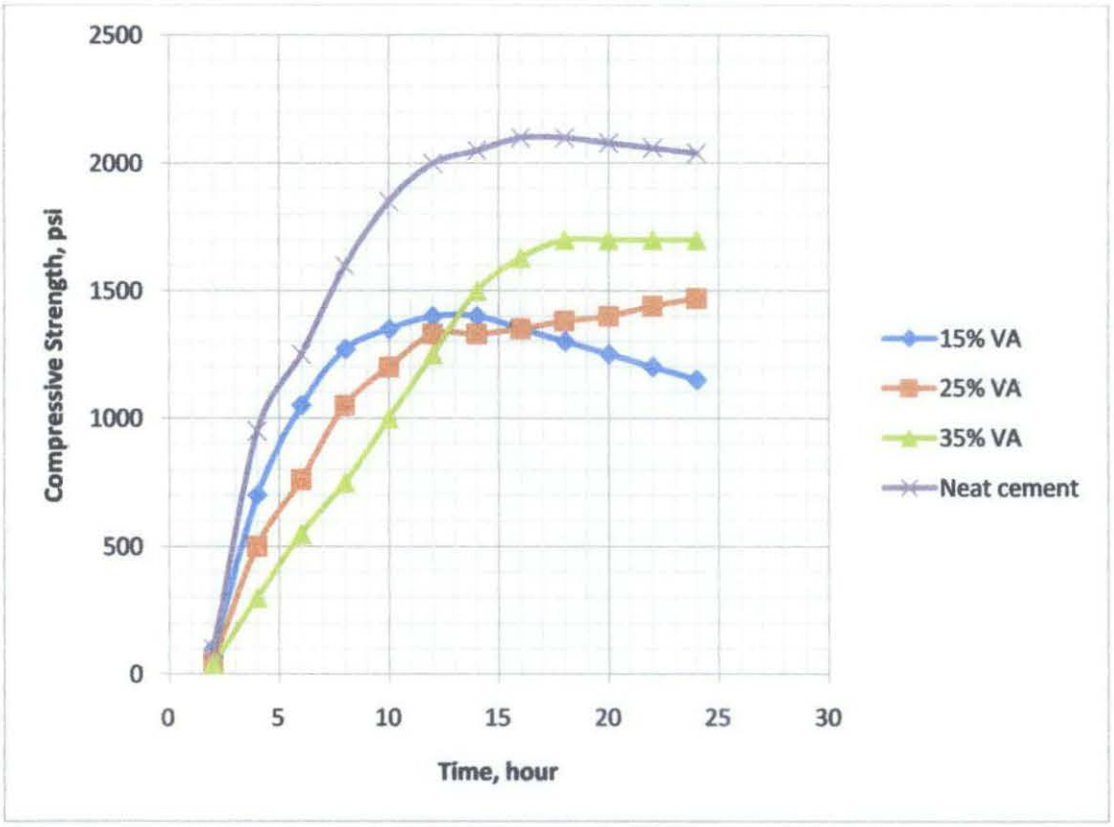


Figure 25 - Compressive strength for slurry proportion 2 (Table 12)

For next cement test, only proportion no.2 (Table 12) is used due to limitations of volcanic ash samples and also limitations of lab equipments. Since the trend of the result of compressive strength test between both proportions are not much different, so it is acceptable for using only 1 type of proportion for the next cement test.

4.4.3 Fluid lost test

Higher fluid loss indicates insufficient slurry strength and volume when it is pumped into the well which may require costly secondary cementing. The fluid may also escape to the formation which may in turn cause water wet coal to expand and cause sloughing. The OFITE LPLT is preferred over the HPHT Filtration loss equipment or the stirred fluid loss tester because no fluid loss materials were added in the slurry and no pressure would be required to sufficiently drain out the free water in the slurry. The stirred loss fluid tester is only used for reservoir temperature above 200°F.

Table 16 shows the amount of fluid loss of the cement with different volcanic ash percentage at ambient temperature and pressure. It was found that 15% VA cement released less water as compared to 25% VA and 35% VA. It proves that, during the cement reaction and with the existing of water, fine particles of the volcanic ash will react with the excess calcium oxide and calcium hydroxide produce during early of reaction to form additional cementitious material which filled the existing voids and thus will reduce the number of voids, and will reduce the permeability of the cement.

Time (min)	G cement	15% VA	25% VA	35% VA
0.25	0.8	0.4	0.8	0.7
0.5	1.0	0.9	1.7	1.1
1	1.8	1.0	2.1	1.5
2	2.5	1.5	2.6	2.1
5	3.6	2.4	3.3	3.5
10	5.4	3.1	4.2	4.5
15	6.3	3.5	4.5	4.9
20	6.8	3.7	4.7	5.1
25	7.1	4.0	4.9	5.3
30	7.2	4.3	5.0	5.4
API Fluid Loss (double of filtrate volume)	14.4	8.6	10.0	10.8

Table 16 – Fluid loss test at ambient temperature and pressure

However, results on fluid loss test at 100psi differential pressures with different percentage of volcanic ash are different. When test at 100psi, the nitrogen blows through at less than 30min of test duration. The volume collected and time taken are recorded at which the blowout occur. ISO Fluid Loss is calculated and expressed as milliliters per 30min. For test that run the entire 30min without "blowing out", the value of collected filtrate volume was doubled and reported as the fluid loss value. For the test that "blow out" in less than 30min test interval, ISO Fluid Loss is calculated by using **Equation 5** (*Nelson E, SLB*).

Calculated ISO Fluid Loss = $Ft\frac{5.477}{\sqrt{t}}$ **Equation 5**

Where;

Vt is the volume of filtrate collected expressed in milliliters

t is the time of the blowout, expressed in minutes.

Table 17 shows the results for fluid loss test at 100psi differential pressure. The ISO fluid loss rate calculated by using Equation 4 and these values shall be reported as Calculated ISO Fluid Loss. From the results, the Calculated ISO Fluid Loss of cement with 15% VA is higher compared to cement with 25% VA and 35% VA. This is due to the amount of volcanic ash which makes the slurry become more viscous and muddy. The Calculated ISO Fluid Loss rate is depends on the application of the cement at field. It can be adjusted by added fluid loss additive into the cement slurry. So actually it does not matter how much the fluid loss of the volcanic ash cement, but it should be adjusted by adding fluid loss additive in order to suit the well condition and type of cementing job.

	Volume (ml)	**Time taken (min)**	**Calculated ISO fluid loss rate (ml/30min)**
Type G **cement**	83.3	0.46	672.68
15% VA	84	1.10	438.66
25% VA	85	1.45	386.61
35% VA	85.5	2.01	330.30

Table 17 – Fluid loss test at 100psi differential pressure

4.4.4 Thickening time test

Thickening time is a measurement of time during which a cement slurry remains in a fluid state and is capable of being pumped, plus a safety factor. For instance, a thickening time of 1.5 hours, let say if we are to pump 100bbls, means our pumping rate will be 1.1 bbl of cement per minute. At

field/laboratory practices, the slurry must be tested within 5 minutes of mixing.

Table 18 shows the results of the thickening time of the cement tested at 3000psi and 250°F. 0.1% of retarder R-21LS is added to the cement in order to increase the thickening time of volcanic ash cement. With the difference content of volcanic ash, cement with 35% volcanic ash has higher pumping time compared to 15% VA and 25% VA. The amount of volcanic ash in the cement composition has an influence on the setting time of the cement and the amount of retarder added also helped to delay the thickening time. Although the 35% VA cement has higher viscosity compared to others (consistency of the cement at early of test was higher), but it takes more time to reach 80Bc. It is meaning that, the more volcanic ash percentage, more the pumping time (thickening time). However, as the consistency reached 60Bc, it will only take few minutes to reach maximum of 80-100Bc as that is the when slurry is deemed unpumpable during API thickening time test.

	Initial Bc	Time@20Bc (hr)	Time@40Bc (hr)	Time@60Bc (hr)	Time@80Bc (hr)
G cement	10.3	0.58	1.06	1.15	1.28
15%	15.7	1.22	2.1	2.12	2.14
25%	17.5	2.2	2.45	2.49	2.53
35%	22.1	0	3.23	3.35	3.37

Table 18 – Thickening time of samples + retarder

4.4.5 Free water test

The results of free water between Type G cement and volcanic ash cement with different percentage when added with the fluid loss additive are shown in **Table 19**. Generally, with different percentage of volcanic ash, volcanic ash cement has less free water than Type G cement. This is because the volcanic ash in the cement consumes some water during its reaction and makes the cement to set with less free water. This is also because the volcanic ash is little bit muddy and due to the classification of the volcanic soil.

	0% additive (ml)	1% additive (ml)
Type G cement	1.4	0.7
15% VA	0.5	0.2
25% VA	0.47	0.18
35% VA	0.46	0.15

Table 19 – Free water analysis

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 – Conclusion

From the literature review research and laboratory experiments performed, it can be concluding that;

I. Volcanic ash from Lawin tuff has potential to be used as the replacement material in cement for well cementing. From the laboratory experiments, volcanic ash cements have high enough compressive strength, suitable fluid loss rate for certain cementing works and long enough thickening time. However, in term of economical and availability of volcanic ash sources, it is not economical to use volcanic ash since it is difficult to get the volcanic ash.

II. Byproduct fly ash cement is better than volcanic ash cement when compare the mineralogy and composition properties. By using fly ash, there are much advantages compared to volcanic ash such as high compressive strength, low permeability and easier to pump. However, volcanic ash still can be used with cement, depends on it composition and properties. Further research need to be done on how to enhance the characteristics of volcanic ash chemically.

III. Volcanic ash cement is suitable to be used in well cementing process, depends on the types of cementing works. By looking at the compressive strength, fluid loss rate and thickening time tested, there are some enhancement and adjustment need to be done such as addition of retarders, additives or else, in order to suit with the well condition and type of cementing works.

However, further testing need to be done on adding and mixing with additives to the cement, mixing with different proportions, different pressure and temperature, and few others to exactly verify the justification.

5.2 Recommendation

These are some of the recommendations to further enhance the volcanic ash cement properties in future work:

I. Volcanic ash maybe can be heat-treated with more high temperature in order to enhance the characteristics of the ash when added with cement. When expose to high temperature, the ash become finer, hence reduce the permeability of the cement.

II. Foaming stabilizers (surfactant) to be used when testing the cement with addition of fluid loss additive.

III. Evaluate the performance of the cement by doing more experiments with different proportion, different slurry densities and also by using any other additive in order to enhance the characteristics of the cement.

IV. The volcanic ash cement should be tested with more different percentage of volcanic ash until 50% in order to precisely analyze what is the best composition of the cement and what the maximum quantity of the volcanic ash can be added into the cement.

REFERENCES

1. American Coal Ash Association, Inc., 1913 I Street N.W., 6th Floor, Washington, D.C. 2006.
2. Khandaker M. Anwar Hossain, 2002. *Chloride induced corrosion of reinforcement in volcanic ash and pumice based blended concrete,* Department of Civil Engineerin, Ryerson University.
3. Shahrin Shahruddin, Ariffin Smasuri, Ahmad Suhaimi, Abu Samah Nasir and Zainuddin Ahmad. *Possibility Studies of Using Local Cement in Oil and Gas Wells Cementing Operations in Malaysia,* Cement Research Group, Petroleum Engineering Department.
4. ANSI/API Recommended Practice 10B-2, First Edition, July 2005
5. The Chevron Texaco and BP Cement Manual
6. Eric B. Nelson, 1990, Well Cementing, Schlumberger Educational Services, Texas
7. *"BJ Bulletin Products Ver 1.0"* – BJ Services Sdn Bhd, on Cementing, Simulation, Remedial, and Equipments Product and Services, April 2001
8. Laboratory Procedure, Soil Index Determination, Universiti Teknologi PETRONAS
9. Samson Oluwaseyi Bada, June 2008. *Evaluation and treatment of coal f ly ash for adsorption application,* University of the Witwatersramd, Johannesburg, South Africa.
10. G.C. Bye, 1999. *Portland Cement, Second Edition,* Thomas Telford Limited.
11. V.M. Malhotra, 1993. *Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Volume II,* American Concrete Institute.
12. V.M. Malhotra, 2004. *Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete,* American Concrete Institute.
13. S.N. Ghosh, 2002. *Advances in Cement Technology: Chemistry, Manufacture and Testing, Second Edition,* Tech Books International.
14. M.H. Zhang, V.M. Malhotra, 2000. *Laboratory-produced high-volume fly ash blended cements compressive strength and resistance to the chloride-ion penetration of concrete,* Cement and Concrete Research.

15. P.C Leong, Analysis of Grik, Geological Setting of Perak, 1990

16. April 2002, *Process and Quality Control by X-ray Analysis*, Industrial Minerals.

17. *Quantitative Analysis of Geological Samples: Combined XRD and XRF analysis*, Bruker Advanced X-ray Solutions.

18. P. Kumar Mehta, *High Performance, High Volume Fly Ash Concrete for Sustainable Development*, University of California, Berkeley, USA.

19. J.J Beaudoin and R.F Feldman, *Partial Replacement of Cement by Fly Ash in Autoclaved Products – Theory and Practice*, National Research Council Canada.

20. Paul E. Stutzman, May 1995. *Compositional Analysis of Beneficiated Fly Ashes*, NISTIR, Gaithhersburg.

21. United States Patent, 5,346,550, 1994, *Low Temperature Well Cementing Compositions and Methods.*

22. Hinrich L. Bohn, Brian Lester McNeal, George A O'Connon, Soil Chemistry, John Wiley and Sons, 2001.

23. ACI Committee 211, 1998, *Guide for Selecting Proportions for High Strength Concrete with Portland cement and Fly Ash.*

24. N. Shafiq, M.F Naruddin and I. Kamaruddin, 2007. *Comparison of Engineering and Durability Properties of Fly Ash Blended Cement Concrete Made in Malaysia and UK*, Institute of Minerals, Materials and Mining.

25. Pietersen, H.S., "Reactivity of Fly Ash and Slag in Cement", Thesis, Deflt University of Technology, Deflt, the Netherlands, 1993.

26. Taylor, H.F.W., Cement Chemistry, Academic Press, San Diego, CA, 475 pp, 1990.

27. Bijen, J. And H. Pietersen, "Mineral Admixtures: Reactions, Micro-Structure and Macro-Properties," in M.W. Grutzek and S.L.Sarkar, Eds., Advances in cement and concrete, Proc. Eng. Found.Conf., 1994.

28. Helmuth, R., "Fly Ash in Cement and Concrete, Portland Cement Association, 1987.

APPENDICES

Appendix 1

Ground granulated iron blast-furnace slags—ASTM C 989 (AASHTO M 302)

- Grade 80
  - Slags with a low activity index
- Grade 100
  - Slags with a moderate activity index
- Grade 120
  - Slags with a high activity index

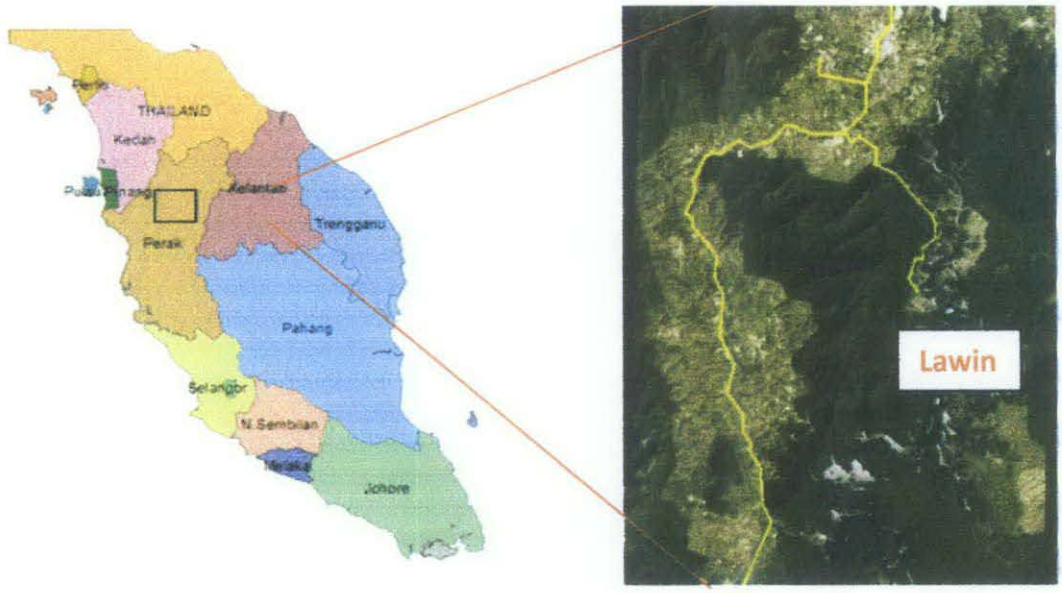
Fly ash and natural pozzolans—ASTM C 618 (AASHTO M 295)

- Class N
  - Raw or calcined natural pozzolans including:
    Diatomaceous earths
    Opaline cherts and shales
    Tuffs and volcanic ashes or pumicites
    Calcined clays, including metakaolin, and shales
- Class F
  - Fly ash with pozzolanic properties
- Class C
  - Fly ash with pozzolanic and cementitious properties

Silica fume—ASTM C 1240

Specifications and classes of Supplementary Cementitious Materials

Appendix 2



Location of the tuff

Appendix 3

Regional and world cement production to year 2010* (million tones)

	1995	2000	2005	2010	% of Total 1995	% of Total 2010
European Union	168.1	187.9	194.1	189.3	12.1	9.4
Other parts of Europe	65.8	80.0	90.2	94.7	4.7	4.9
Former Soviet Union	58.1	80.3	110.1	128.2	4.2	6.6
North America	92.9	94.9	94.8	94.7	6.6	4.9
Central and South America	89.4	106.6	127.4	145.0	6.4	7.5
Africa	64.8	74.3	80.7	85.5	4.6	4.4
Middle East	63.5	75.6	76.9	73.4	4.6	3.8
East Asia	623.4	732.7	798.8	844.3	44.6	43.4
S/SE Asia	161.2	219.1	255.0	279.2	11.6	14.4
Oceania	8.0	10.6	11.1	11.8	0.6	0.6
World Totals	1396.1	1662.1	1839.1	1946.1	100.0	100.0

*From: World Cement Annual Review, World Cement, Vol. 28, No. 7, July 1997, p.p 3-60.

Appendix 4

Coal Ash Production and Utilization, 2004*

Country	Production (million tonnes)	Utilization in Concrete
China	>600	>15
India	>110	15%
U.S.A.	>60	10%
Russia	60	5
Germany	30	12
U.K.	10	10

*The above data include fly ash, bottom ash, and slag. For every 100 tonnes of fly ash, there are approximately 25 tonnes of bottom ash and boiler slag.

Appendix 5

Worldwide production (million of tones)

	Cement	Fly Ash	Others*
Current Production	1600	900	20
Anticipated Year 2020	3000	2000	>100

*Silica fume, slag, natural pozzolans, metakoalin.

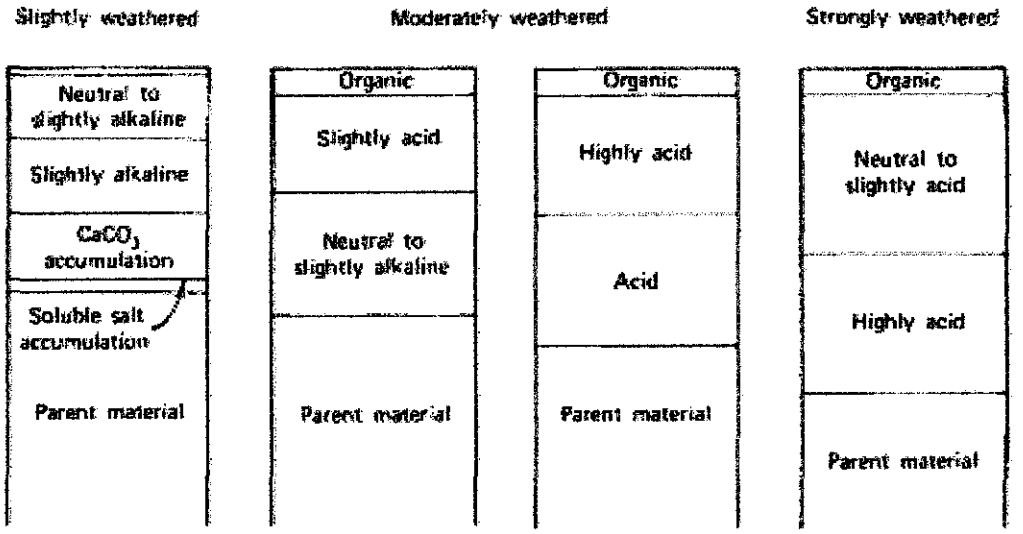
Appendix 6

Compound	Granodiorite[a] (Granitic) (%)	Basalt[a] (%)	Shale[b] (%)	Sandstone[b] (%)	Limestone[b] (%)
SiO_2	65.1	49.3	58.1	78.3	5.2
K_2O	2.4	1.2	4.3	1.4	0.04
TiO_2	0.5	2.6	0.6	0.2	0.06
Al_2O_3	15.8	14.1	15.4	4.8	0.8
Fe_2O_3	1.6	3.4	4.0	1.1	0.5
FeO	2.7	9.9	2.4	0.3	..
MgO	2.2	6.4	2.4	1.2	7.9
CaO	4.7	9.7	3.1	5.5	42.6
Na_2O	3.8	2.9	1.3	0.4	0.05
H_2O	1.1	..	5.0	1.6	0.8
P_2O_5	0.1	0.5	0.17	0.08	0.04
SO_3	..	..	0.6	0.07	0.05
CO_2	..	..	2.6	5.0	41.5
Total	100	100	100	100	100

[a]From G. W. Tyrell. 1950. *The Principles of Petrology*. Dutton, New York.
[b]From F. J. Pettijohn. 1957. *Sedimentary Rocks*. 2d ed. Harper & Row, New York.

Average composition of several parent material rocks [22]

Appendix 7



Schematic progression of basic and acidic zones through soils during soil development. This sequence also represents soil profiles from arid to humid to humid tropical regions. [22]

Appendix 8 – Moisture Content Determination (Lab Procedure)

1. Clean and dry the moisture content tin and weight it to the nearest 0.01g (m1). Take a sample of at least 30g of soil, crumble and place loosely in container, and replace the lid. Then weight the container and contents to the nearest 0.01g (m2).
2. Remove the lid, and place the container with its lid and contents in oven and dry at 105 degC to 110 degC for a period of 24 hours. Do not replace the lid while the sample is in the oven.
3. After drying, remove the container and contents from the oven and place the whole in the desiccators to cool.
4. Replace the lid and then weight the container and content to the nearest 0.01g (m3)
5. Calculate the moisture content of soil specimen.

Appendix 9 – Determination of particle density or specific gravity (Lab Procedure)

1. Take a sample of soil of about 1.5kg and sieve the sample. Break down the coarse particles retrained on a 20mm test sieve to less than that size.

2. Divide the sample into 2 specimens, each weighting 400g by riffling.
3. Put these specimens into the oven for drying at 105 degC and the store the specimens in air tights container until required.
4. Clean and dry the pyknometer and weigh the whole assembly to the nearest 0,5g (m1)
5. Remove the screw top and transfer the first specimens from its sealed container directly into the jar.
6. Weigh the jar and its content and the screw top assembly to the nearest 0.5g (m2)
7. Add water at a temperature of within the average room temperature during the test to about half of fill of the jar. Stir the mixture thoroughly with the glass rod to remove air trapped in the soil.
8. Fit the screw cap assembly and tighten it so that the reference marks coincide. Fill the pyknometer with water.
9. Agitate by shaking the pyknometer. Allow air to escape and froth to disperse. Leave the pyknometer standing for at least 24h at room temperature.
10. Top up the pyknometer with water so the water surface is flush with the hole in the conical cap.
11. Dry the pyknometer on the outside and weigh the whole to the nearest 0.5g (m3)
12. Empty the pyknometer, wash it thoroughly and fill it completely with water at room temperature.
13. Dry the pyknometer on the outside and weigh to the nearest 0.5g (m4), then calculate the particle density.

Appendix 10 – Determination of Plastic Limit (Lab Procedure)

1. Take a sample of the soil of sufficient size to give a test specimen weighing at least 20g which passes the 425 μm test sieve and place it on the glass plate.
2. Allow the soil to dry partially on the plate until it becomes plastic enough to be shaped into the ball.
3. Mould the ball of soil between the fingers and roll it between the palms of the hand until the heat of the hand has dried the soil for slight cracks appear on

the surface. Divide these samples into two sub-samples of about 10g each. Divide each sub-sample into four more samples.

4. Mould the soil in fingers and use enough pressure to reduce the diameter of the thread to about 3mm.
5. Gather together the portions of crumbled soil thread and transfer them to a suitable container and replace the lid immediately.
6. Calculate the moisture content of the samples using oven drying method and express the value as the plastic limit value.

Appendix 11 – Determination of Liquid Limit (Lab Procedure)

1. Take a sample of the soil sufficient size to give a test specimen weighing at least 300g which passes the 425 μm test sieve and place it on the glass plate.
2. Add some water and mix the paste for at least 10 minutes using the two spatulas.
3. Push a portion of the mixed soil into the cup with spatula taking care not to trap air.
4. Use cone penetrometer and get the reading of the cone penetration.
5. Calculate the moisture content of each specimen.

Appendix 12 – Fluid Loss test procedure

1. The OFITE LPLT Filtration Tester is used for measurement of fluid loss for testing under 1000psia and 200F°. (Stirred fluid loss tester used for cement slurry with fluid loss additives only)
2. Two o-rings are placed in between the filter to prevent leakage of cement which will plug the filter mesh (325x60) which allows flow of clean water during the test.
3. The filter mesh should be washed thoroughly, with a filter paper placed on top of it, which forms the bottom seal. The bottom seal is then fitted into the vessel body.
4. Nitrogen gas supply is opened to allow flow of gas to the top cap of the cup.

5. 450 ml of slurry is poured into the vessel with finger holding the bottom exit to prevent water from escaping before timer apparatus is set up. The top cap is sealed with an o-ring and tightened.
6. A cylindrical tube is placed below the water outlet, and finger is released. Stop watch is used to time the volume of clear water accumulated for every minute for the first 5 minutes. Then readings are taken every 5 minutes until 30 minutes elapsed.
7. API Fluid Loss is calculated based on equation and recorded.

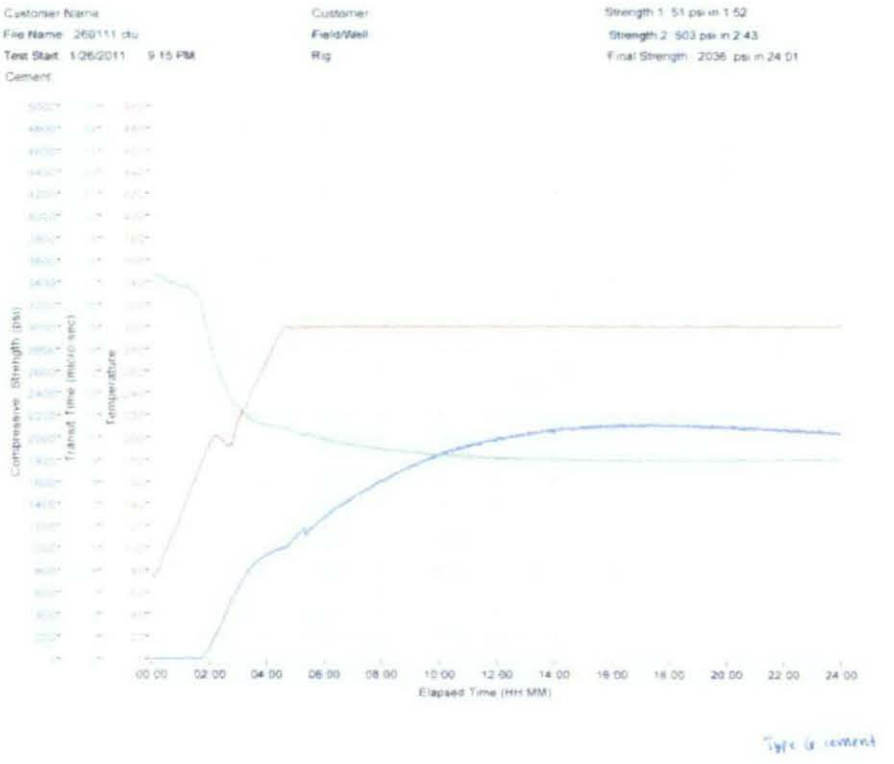
Appendix 13 - Compressive strength test procedure

1. The OFITE Compressive Strength Tester is turned on.
2. The cement cube specimen is placed in the lower platen of the hydraulic cylinder. The upper platen is adjusted to ensure that it touches the specimen. The upper platen is adjusted by loosening the locking nuts above the platen, and then the two lower nuts are turned to fit the cement specimen. The surfaces of the two platens are ensured to be parallel.
3. Safety shield is closed before beginning the test. The Compressive Strength Tester Software in the PC is opened. The "Options" from the "Edit" menu is selected. In "Data File Directory", the folder for the data to be saved is chosen.
4. The height (in inches) is input into the main screen in the "Cube Height" field. The file data is selected from the "Edit File". Relevant information is filled in and "OK" is clicked. The loading rate of "4000PSI/min" is selected for this experiment.
5. "Pump On" button is clicked to start test. Then, "Run Test" is clicked and is hold to begin test while observing the specimen.
6. When the specimen fails (crushed), the "Run Test" button is released to stop the test and pump. The maximum load (compressive strength) is shown in the "Max Load (PSI)" field. Step 1-7 is repeated for 2 more specimens for each density.
7. The results obtained for every 3 samples are taken as average and recorded.

Appendix 14 - Thickening time test

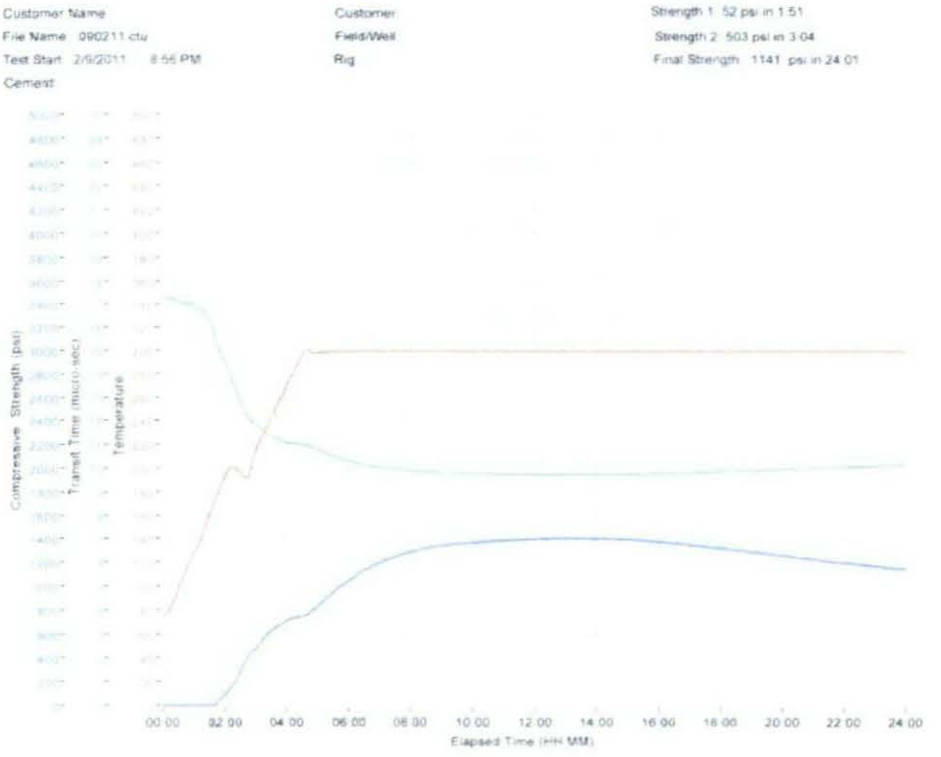
1. The POWER is turned to ON position on the Pressurized Consistometer.
2. The temperature ramp and soak parameters are programmed at the curing chamber to be 100°F for first 15minutes, and the soaked to 150°F for another 15minutes and soaked until the Bc unit reaches 100Bc.
3. The inner portion of slurry cup including the blade of the rotator and suction ring is slightly greased and assembled (as original position).
4. The head screw is then locked at a specified height which is parallel to the Potentiometer Mechanism's level for the ball valve when fitted and slurry cup is placed in an upside down position on the slurry cup stand.
5. The cap and the rings are reopened, and pour the slurry into the cup in an upside down position. The slurry needs to be overflowed and the cup is locked at the bottom with a nut. The slurry cup is placed into the pressure vessel and locked.
6. The thermocouple is inserted but not tightened. AIR SUPPLY valve is opened to transfer oil from the oil vessel to the pressure vessel. When oil run out the top, the thermocouple is tighten with a spanner.
7. The HEATER and TIMER are turned ON at the touch screen. Pressure is adjusted to 750psi until the desired consistency of 30Bc, 70Bc, and 100Bc is reached.
8. Once done, the alarm will be alerted and COOLING WATER valve is opened, while the TIMER and HEATER are turned to off position. AIR TO CYLINDER and PRESSURE RELEASE valve are opened to release pressure and allow backflow.
9. Cement slurry can be disposed from cup when temperature drops below 120°F.

Appendix 15 – Compressive strength for Type G cement



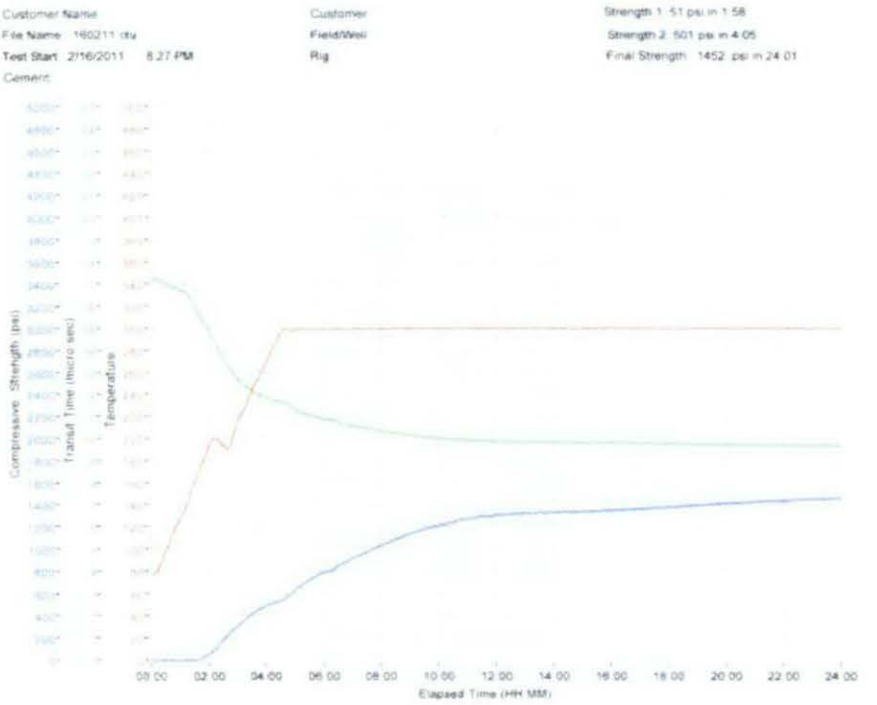
Type G cement

Appendix 16 – Compressive strength for 15% volcanic ash cement

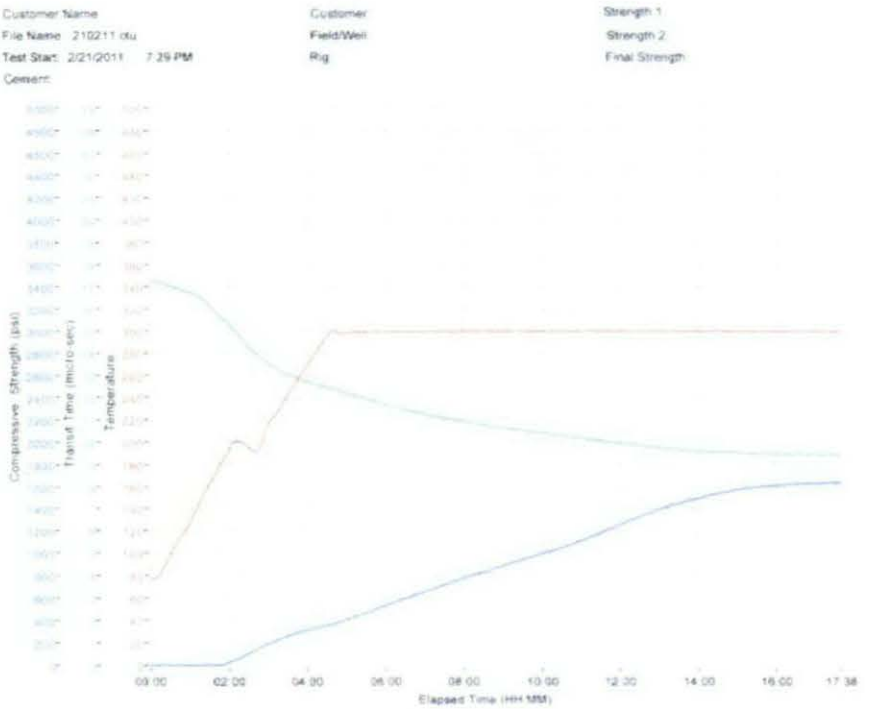


15% VA

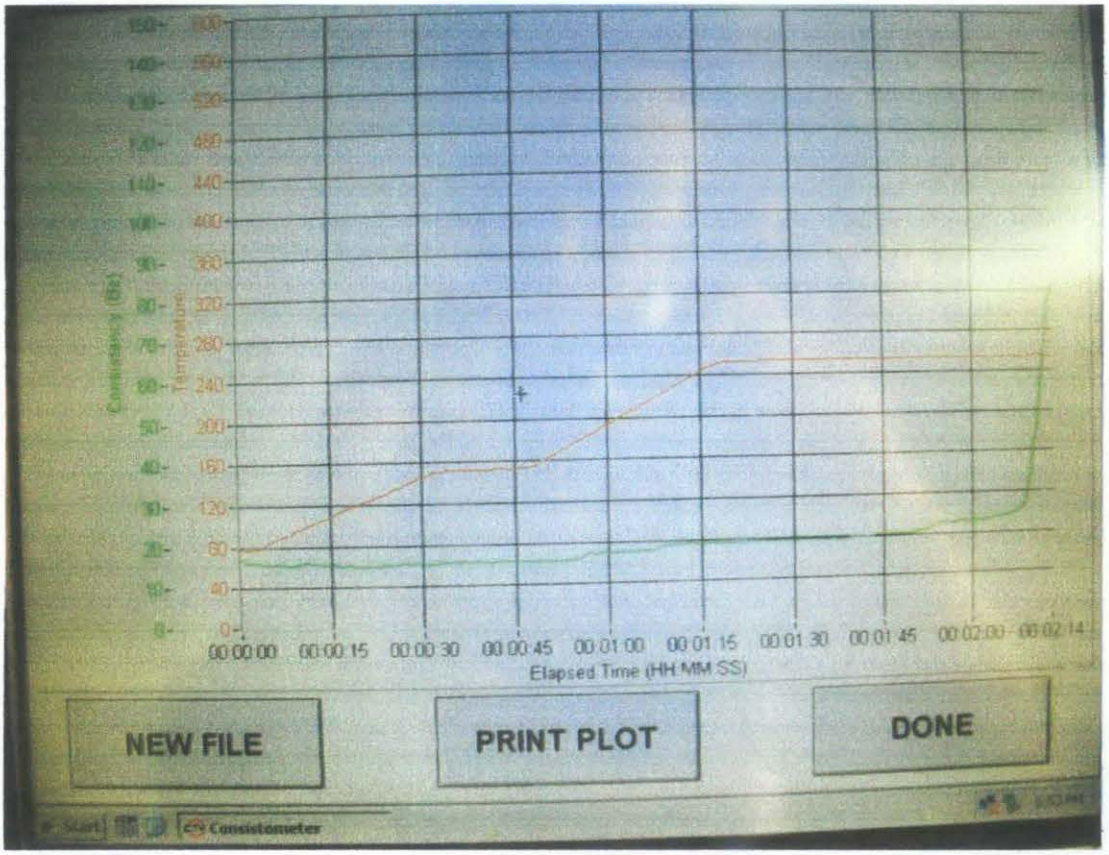
Appendix 17 – Compressive Strength for 25% volcanic ash cement



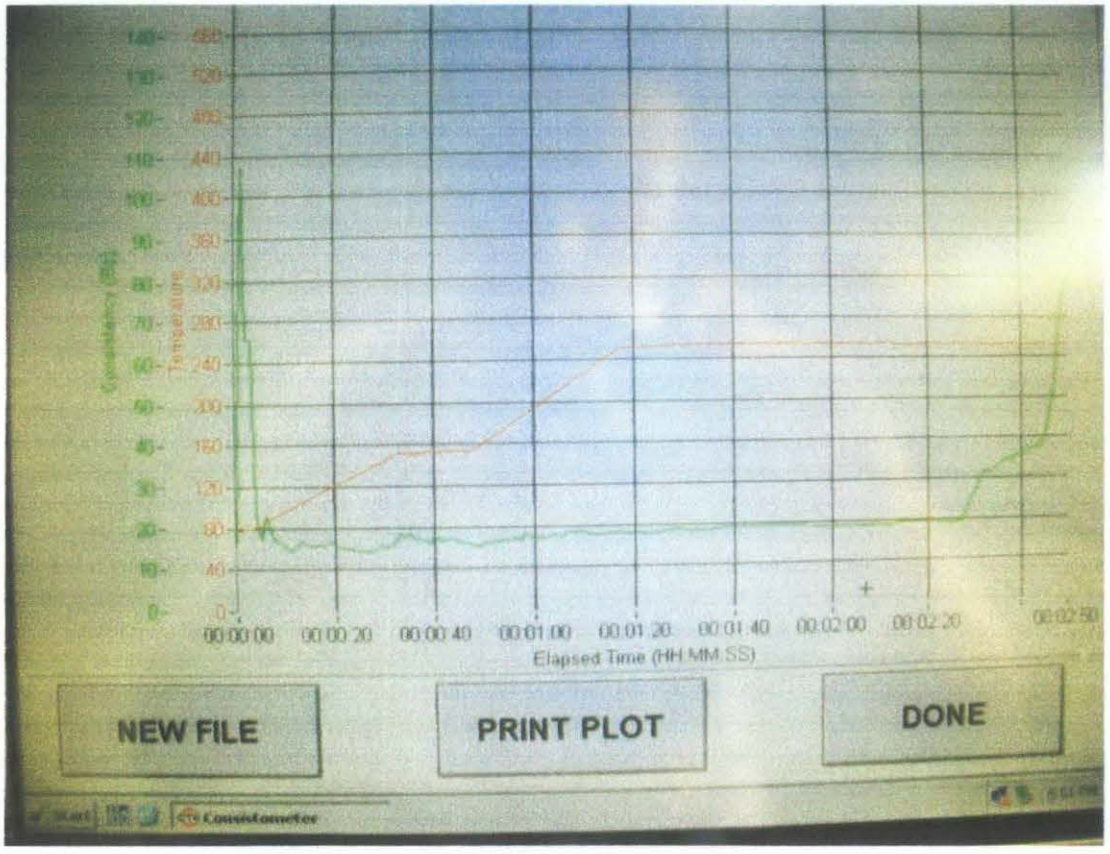
Appendix 18 – Compressive strength for 35% volcanic ash cement



Appendix 19 – Thickening time for 15% volcanic ash cement



Appendix 20 - Thickening time for 25% volcanic ash cement



Appendix 21 - Thickening time for 35% volcanic ash cement