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The Potential Of Lawin Tuff For Generating A Portland Fly Ash Cement To Be Used In Oil Well Cementing

by

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CERTIFICATION OF ORIGINARITY

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 here have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

The current Portland Fly Ash cement is widely used in both construction and oil well cementing process. This paper will focus on cement for oil well cementing process only. Volcanic tuff, which is consolidated volcanic ash largely made up of silicon dioxide and calcium oxide, can be used as a substitute for Portland cement, or as a supplement to it. The materials which make up fly ash are pozzolanic, meaning that they can be used to bind or cement materials together. It will increase the long term compressive strength, reduce fluid loss, good resistance to sulphate attack , less CO2 emission ,less permeable and more environmental friendly compare to coal fly ash.

This project is about doing research using tuff in Lawin, Perak to generate Portland Flyash cement. Lawin Tuff is a type of volcanic rock consisting of consolidated volcanic ash ejected from vents during a volcanic eruption. The current fly ash use in Portland cement is from industrial burning of coal and it contains heavy metals and radioactive mineral. Thus, this project is hoped to use natural fly ash from tuff to generate Portland Fly Ash cement that can be used in oil well cementing. Several tests are carried out to determine the best proportion of tuff used to mix with Portland cement and generate best results.

Chapter 1: Introduction

1.1 Background Study

Natural pozzolans generally contain pyroclastic rocks. These rocks generally contain carbonate, clay and zeolite group minerals as filling/binding materials. Zeolitization is the transformation of the glassy structure in natural pozzolan to zeolite-group minerals with external effects. Zeolites can lose their water contents with the effect of heat. In other words, with the help of their channel shaped and largely spaced framed mineral structures they can easily take and release water ions .These ions do not take part in the cage structure. One more important aspect is that zeolites can release alkali atoms and take in calcium and magnesium ions .Therefore, when pyroclastics rich in zeolite minerals are mixed with slaked lime and water, they can form stable silicate minerals. [6.Ahmet Cavdar, Sukru Yetgin, 2005]

Portland flyash cement contains up to 30 % fly ash. Fly ash is a waste product generated by thermal power stations. Fly ash is a burnt and powdery derivative of inorganic mineral matter that generates during the combustion of pulverized coal in the thermal power plant. The burnt ash of the coal contains mostly silica, alumina calcium and iron as the major chemical constituents. Depending on the burning temperature of coal, the mineral phases in crystalline to non crystalline structures such as quartz, mullite, hematite, magnetite, Westite. Metallic iron, orthoclase and fused silicates usually occur in the burnt coal ash. Silica and alumina account for about 75 to 95 % in the ash.The technology of replacing Portland cement with fly ash offers numerous benefits such as increased strength, durability and resistance to chemical attacks.

Tuff is a type of rock consisting of consolidated volcanic ash ejected from vents during a volcanic eruption. The products of a volcanic eruption are (a) volcanic gases, (b) magmas, and (c) steam from water heated by the magma. Where all three interact violently, especially where there is an abundance of water, the magma is blown apart. If the resulting pieces of ejecta are small enough, the material is called volcanic ash, consisting of sand-sized or smaller particules. These particles are small, slaggy piece of lava that have been tossed into the air by outbursts of steam and other gases and have become vesicular by the expansion of the gases within them while they were still plastic.

Tuffs may be grouped as vitric, crystal, or lithic when they are composed principally of glass, crystal chips, or the debris of pre-existing rocks, respectively. In extensive deposits, tuff may vary greatly not only in texture but also in chemical and mineralogical composition. There has probably been no geological period entirely free from volcanic eruptions; tuffs therefore range in age from Precambrian to Recent. Most of the older ones have lost all original textures and are thoroughly recrystallized; many old basaltic tuffs are represented by green chlorite and hornblende schists and many rhyolitic tuffs by sericite schists.

Hydration is the result of a chemical reaction that occurs between water and the chemical compounds present in portland cement. Portland cement is predominately composed of two calcium silicates which account for 70 percent to 80 percent of the cement. The two calcium silicates are dicalcium silicate (C_2S) and tricalcium silicate (C_3S).The other compounds present in portland cement are tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and gypsum. For the sake of simplicity this discussion focuses only on the reaction between the calcium silicates and water.The reaction of dicalcium silicate and tricalcium silicate with water (abbreviated as"H") produces calcium silicate hydrate (C-S-H) and calcium hydroxide (CH), as illustrated in the following chemical equations.

$2\ C_2S + 9H$(water) $C_3S_2H_8 + CH$

$2\ C_3S + 11H$(water) $C_3S_2H_8 + 3CH$

C-S-H is a poorly crystalline material with a variable composition that forms extremely small particles less then 1.0 υm in size. C-S-H is the main cementitious compound, or glue, that gives concrete its inherent strength. The structure of C-S-H becomes much more stable and resistant to subsequent environmental changes upon prolonged moist curing or curing at elevated temperatures. Calcium hydroxide, on the other hand, is a well-crystallized material with a fixed composition. CH contributes somewhat to concrete's inherent strength because it will form large crystals inside voids, thereby reducing porosity. However, CH is a soluble compound, meaning it will move throughout the pore system in the presence of water, making it extremely vulnerable to chemical attack.

1.2 Problem statement:

According to the Environmental Protection Agency (EPA), industry fly ash contains heavy metals, including nickel, vanadium, arsenic, beryllium, cadmium, barium, chromium, copper, molybdenum, zinc, lead, selenium and radium. Additionally, traces of radioactive materials are present in fly ash. Given the large quantities of fly ash that are produced, a tremendous amount of radioactive waste is generated. This radioactivity is due to the elements in the decay chain of uranium and thorium, the radium is of great concern as 226Ra decays to form radon (222Rn) which has a half-life of days and is able to form mobile daughter radioisotopes.

The cement industry, as of 2007, produced 5% of the total greenhouse gases in the atmosphere, particularly carbon dioxide. The cement industry, particularly cement kilns, also emit hazardous air pollutants. The burning of hazardous waste in kilns is a major problem for air quality.

Alternative cements provide an excellent technical option to OPC at a much lower cost and have the potential to make a significant contribution to the oil and gas industry.

1.3 Significant of the Project:

This project is done by doing research to use Lawin Tuff as substitute for Portland Fly ash cement in oil well cementing process. For the current time, there is no economic value for using tuff in Lawin. The study of the rock (tuff) characteristic and the new cement formed is important for both geological field and oil and gas cementing industry. The current Portland Fly Ash cement is made from industrial fly ash and since tuff is from from volcanic ash, most probably tuff can replace fly ash and exhibit same characteristic in mix cement.

The meaningful use of volcanic tuff can not only transform it into a natural resource to produce low-cost cementing materials but also can help to decrease environmental hazards (created due to the deposition of volcanic materials on the land), leading to sustainable development. The development of less expensive and environmentally friendly (the use of volcanic tuff as a cement replacement can lower greenhouse gas emissions associated with the production of cement as well as provide a safe way for the removal of such debris) volcanic tuff-based concrete with acceptable strength and durability characteristics can be extremely helpful in the development and rehabilitation of volcanic disaster areas around the world.

1.4 Objectives

1. To study on the possibility of using Lawin Tuff as substitute for Portland Fly Ash Cement.
2. To study the rheological behavior and suitability of Portland Fly Ash cement with Lawin Tuff to be used in oil well cementing that meet API Standard.
3. To determine and analyze the density based on various tuff-cement rations, thickening time, fluid loss, compressive strength, permeability, porosity for Portland cement
4. To determine the correct and best composition of the tuff in Portland Fly Ash.

1.5 Scope of Study

The scope of study mainly investigates rheological behavior of cement from the mixing of Lawin Tuff into Portland cement. The study will be divided into two stages, the first stage aims to research and understand chemical and physical properties of Lawin Tuff and rheological behavior of Portland Fly Ash Cement. Second stage will focus on experimental researches on Portland cement mixture with Lawin Tuff and determine if it meet API standard for oil well cementing process. There are 8 classes of API specified cement (Class A to Class H), where in Malaysia, most common used is Class G produced by Pan Malaysian Cement (PMC) in Pasir Gudang. Result collected from experiments will be analyzed and discussed.

1.6 The Relevancy of the Project

Portland Cement was used in the energy services industry to isolate the oil-containing region of the earth from down-hole water, a process modernly referred to a zonal isolation. The technique of oil well cementing was soon developed .After the primary hole is drilled, a steel casing, through which the oil will later flow, is placed inside. The current Portland fly ash cement is used widely in construction and well cementing. This project is hoped to find other substitute for Portland Fly Ash cement which is important especially in oil and gas to cement the well. The Lawin Tuff and fly ash are a type of pozzolan and has cementitious properties.

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 research will be carried out for 2 semesters and first semester is focus on research study and information gathering. Second semester will focus on lab experiment and analyse the different testing. Comparison will be made between Portland fly ash cement and mixture of Portland cement with tuff. With my initiative and enthusiasm in completing the research project, i believe that 2 semesters are enough to carry out this project.

CHAPTER 2

THEORY & LITERATURE REVIEW

2.1 Theory

a. Laboratory density and volume calculation for base slurry

A slurry of approximately 600ml shall be sufficient to perform most laboratory test procedures while not overfilling the mixing container. For the purpose of these calculations, assume that relative density is equal to density expressed in grams per milliliters (g/ml)

$$Volume\ of\ slurry(ml),\ \ V_s = V_c + V_w + V_a \ \ldots\ldots\ldots\ldots\ (2.1)$$

$$Mass\ of\ slurry\ (grams),\ m_s = m_c + m_w + m_a \ \ldots\ldots\ldots\ldots\ (2.2)$$

$$Density\ of\ slurry\ \left(\frac{grams}{ml}\right),\ \rho_s = \frac{m_s}{V_s} \ \ \ldots\ldots\ldots\ldots\ (2.3)$$

Where,

V_c is the cement volume, in mililiters

V_w is the water volume, in mililiters

V_a is the additive volume, in mililiters

m_c is the slurry mass, in grams

m_w is the water mass, in grams

m_a is the additive mass, in grams

Conversion factor:

$$ppg\ \left(\frac{lbm}{gal}\right)\ x\ 1.198264E+02\ = kg/m^3 \ \ldots\ldots\ldots\ldots\ (2.4)$$

$$\frac{kg}{m^3}\ x\frac{1000g}{1kg}\ x\frac{1m^3}{1000\ell}\ x\frac{1\ell}{1000m\ell} = \frac{g}{m\ell} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.5)$$

Thickening time – Amount of time necessary for the slurry to reach a consistency of 100 poises at different well temperature, depth and pressure.

Compressive strength – Force perunit interval cross-sectional area in psi necessary to crush the cement speciment.

Fluid loss test– The measurement of the water loss from the cement expressed in 30 minutes of time.

c) Chemical composition of Portland Cement:

a) Tricalcium Silicate (50%)
b) Dicalcium Silicate (25%)
c) Tricalcium Aluminate (10%)
d) Tetracalcium Aluminoferrite (10%)
e) Gypsum (5%)

2.2 Literature Review

Formation of Lawin Tuff

The Baling formation of eastern Kedah and northern-most Perak, Peninsular Malaysia has long been proposed for group rank. This proposal is adopted here although it is still not possible to formalize fully this rock unit. The Baling group extends across the international frontier into Thailand (as the Bannang Sata group) where it evidently attains its maximum development, at least in terms of areal extent, but it has not yet been studied in detail in that country.The Baling consists of arenite and carbonate of the Papalut quartzite below, and black siliceous argillite, with minor calcareous rocks, of the Kroh formation, above. A thick sequence of rhyolitic pyroclastic rocks (the Grik tuff) occurs around the passage between two foregoing formations in the Grik area of Perak.

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 ni 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.

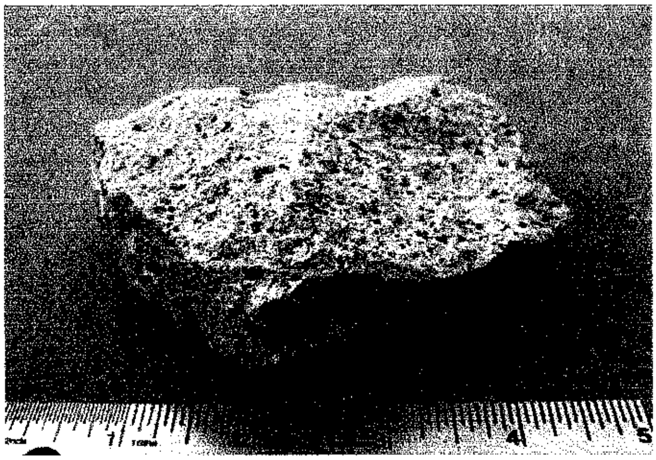


Figure 1:Rhyolite Tuff (Welded)

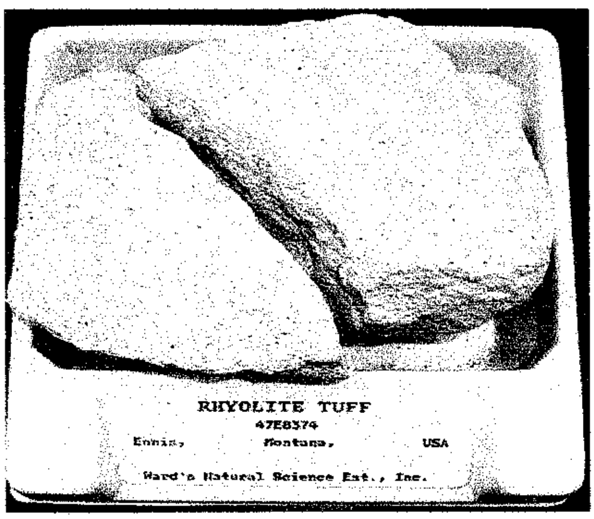


Figure 2:Rhyolite Tuff(Unwelded)

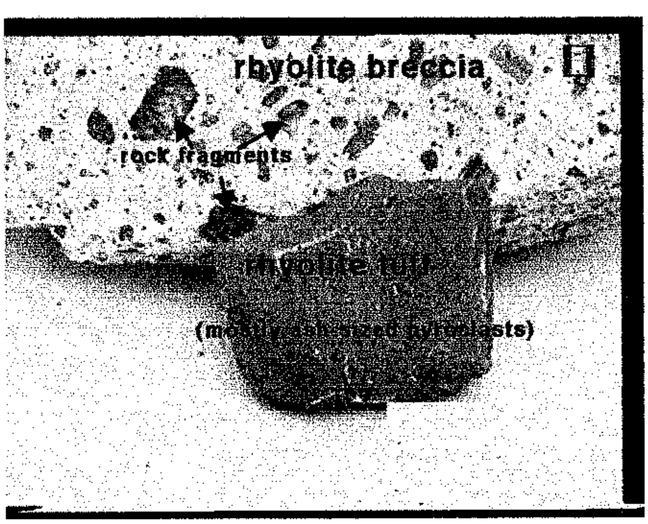


Figure 3:Rock fragments in tuff

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(By previous researchers)*

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.

The search for alternative binders or cement replacement materials has continued in the last three decades and from the economical, technological and ecological points of view, cement replacement materials play an undisputed role in the construction industry and also oil and gas cementing operation. Comprehensive research has been carried out in the past on the use of fly ash (FA), pulverized-fuel ash (PFA), blast furnace slag (BFS), rice husk ash, silica fume (SF), etc., as cement replacement materials. Suitability of using volcanic ash (VA) as a cement replacement material in concrete production has been done by Hossain, Khandaker MA, Lachemi, Mohamad. The performance of volcanic ash concrete (VAC) mixtures was evaluated by conducting comprehensive series of tests on fresh and hardened properties.

Regular testing is therefore required if volcanic ash is to be used as a pozzolana and this has been a constraint to its commercial exploitation. However, volcanic ash or volcanic tuff have recently been, successfully used as a pozzolana in many countries including the US, Germany, Japan, Italy, Kenya and Indonesia, with pilot plants tested in Tanzania and Rwanda. For example, 200,000 tonnes of volcanic pozzolana were used in the construction of the Glen Canyon dam in the US, completed in 1964. [15.]

2.2.1 Pozzolans

A pozzolan is broadly defined as an amorphous or glassy silicate or aluminosilicate material that reacts with calcium hydroxide formed during the hydration of Portland cement in concrete to create additional cementitious material in the form of calcium silicate and calcium silicoaluminate hydrates.

To function properly, pozzolans must be amorphous or glassy and generally finer than 325 mesh (45 microns) in particle size. Finer particle sizes generally have greater reactivity, meaning they more quickly convert to supplementary cementitious material, helping in early strength development as measured by standardized tests.

Pozzolans can continue to react in concrete for many years, further strengthening the concrete and making it harder and more durable during its service life. Pozzolans also serve to densify and reduce the permeability of concrete, which helps to make it more resistant to deterioration and swelling associated with various exposure conditions.

Figure 4: Pozzolans

At the basis of the Pozzolanic reaction stands a simple acid-base reaction between calcium hydroxide, also known as Portlandite, or ($Ca(OH)_2$), and silicic acid (H_4SiO_4, or $Si(OH)_4$). For simplifying, this reaction can be schematically represented as following:

$$Ca(OH)_2 + H_4SiO_4 \longrightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\ H_2O \longrightarrow CaH_2SiO_4 \cdot 2\ H_2O$$

or summarized in abbreviated notation of cement chemists:

$$CH + SH \longrightarrow CSH$$

The product of a general formula ($CaH_2SiO_4 \cdot 2\ H_2O$) formed is a calcium silicate hydrate, also abbreviated as CSH in cement chemist words. The ratio Ca/Si, or C/S, and the number of water molecules can vary also the above mentioned stoichiometry may differ slightly.

2.2.2 Materials Investigation

Chemical and physical properties of VA and finely ground VP are compared with those of PC in following table. Chemical analysis indicated that VA and VP have very similar compositions and are principally composed of silica (about 60%) while the main components of PC are calcium oxide (maximum 65%). Both VA and VP have compounds like calcium oxide, alumina and iron oxide (total about 31%).

Chemical compounds	VA (%)	VP (%)	PC (%)
Chemical composition			
Calcium oxide (CaO)	6.10	4.44	60–67
Silica (SiO_2)	59.32	60.82	17–25
Alumina ($Al2O_3$)	17.54	16.71	3–8
Iron oxide (Fe_2O_3)	7.06	7.04	0.5–6.0
Sulphur trioxide (SO_3)	0.71	0.14	1–3
Magnesia (MgO)	2.55	1.94	0.1–4.0
Sodium oxide (Na_2O)	3.80	5.42	0.5–1.3
Potassium oxeide (K_2O)	2.03	2.25	0.5–1.3
Loss on ignition	1.03	1.52	1.22
Physical properties			
Fineness, m^2/kg	242	285	320
Compressive strength of 50 mm cubes, MPa			
7-day			26
28-day			32
Specific gravity			3.15
Unit mass, kg/m^3			3150
Bulk density, kg/m^3	2450[a]	1870[a]	–

Figure 5: Material Investigation

Note: VA: Volcanic Ash

VP: Volcanic Pumice

PC: Portland cement

Figure 2: Chemical compounds of Volcanic Ash, Volcanic Pumice and Portland Cement

VA has the potential to be used as additives to Portland cement for the manufacture of blended cements like other pozzolanic materials such as fly ash. Several tests were conducted to study the suitability of VP as pozzolanic materials.

The pozzolanic activity of VP was tested according to the Italian Standards where the samples were mixed with cement and water and kept for 1–2 weeks. The total alkalinity (OH^-) and lime concentration (CaO) is then measured. The material is considered pozzolanically active if the level of concentration falls below the lime solubility isotherm. The results indicate that all VP samples fall below the lime solubility isotherm and are therefore pozzolanically active. Being pozzolanically active, VP have cementitious characteristic and can economically be used as a cement additive to manufacture blended cement. [5.Hossain, K. M. A,2005]

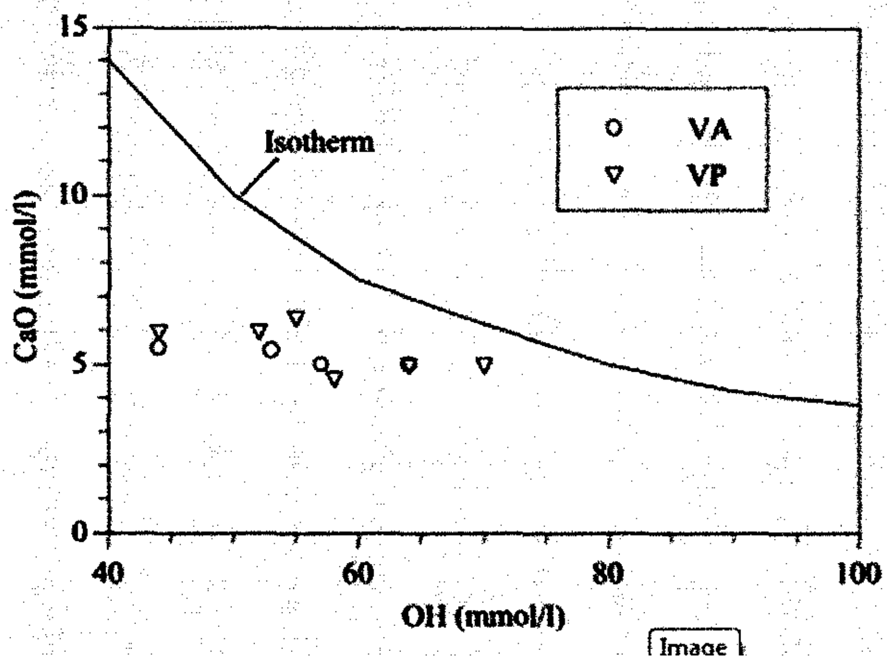


Figure 6 : Pozzolanic activity test of VA Source: [5].Hossain, K. M. A,2005]

2.2.2 Processing of Volcanic Ash and Tuff

Once the deposits have been excavated most volcanic ashes will require only minor processing before use as a pozzolana. Many ashes are only loosely cemented and can easily be excavated by hand, although others may need mechanical or pneumatic equipment.

Some lithic tuffs may require blasting with explosives. The ash may require drying, and in dry sunny climates this can simply be achieved by spreading the ash in a thin layer on a specially prepared drying floor, similar to those commonly used to dry crops. Alternatively, in wet climates, and for large quantities, inclined rotary driers are normally used.

If the ash is cemented it will need to be crushed before entering the dryer. Some volcanic ashes will already be in a very fine, loose powdered form and may not require crushing or grinding. Other ashes may be of sufficient fineness but be cemented together. These will require milling or crushing. Coarse ashes and lithic tuffs will need to be ground in a ball mill or similar. [15.]

2.2.3 Green Cement

The idea of green cement is (that) we use waste materials that have similar properties, like when you think about why there are so many buildings in Rome that are still around. Cement as we use it now was only invented the 1700s, I think 1750. But how did the Romans build the Pantheon? It is more than 2,000 years old! They are built from volcanic ash mainly. Even volcanic ash has cement-like properties. In Malaysia, (there's) not that much. So that's why this business is not so easy in Malaysia. But in other countries, (like) Indonesia, China (and) India, there is a huge volume of unutilised volcanic ash available. That, theoretically could be used to build buildings. [19. Greenlandplanet,2010]

Microscopic analysis shows that the volcanic ash improved the density of the concrete and does not see any sign of damaging expansion or low compressive .If ash is to be used in making cement, it must have uniform quality, and there needs to be enough of it to make it commercially viable. Concrete to be used outside must be dense enough to prevent water or salt from seeping in and causing frost damage or corrosion of reinforcement rods.[17. Kathrine Schmeichel, 2010]

Coal ash has the same characteristics as volcanic ash. We can use it as additive in cement. There are differences in strength of the resulting cement product, the cost of production, among others. Handling pozzolan or volcanic ash is easier than handling coal ash because of its chemical composition. We do not like its (coal ash) effect on our water supply. There will be more problems with coal ash. [18.website, 2010]

2.2.4 Conclusion from previous study

1. The addition of volcanic ash (VA) up to 40% was beneficial in improving the workability of volcanic ash concrete (VAC). The slump values of VACs ranged between 50 and 115 mm and showed satisfactory workability with no segregation or excessive bleeding, especially within 50% VA replacement. [5.Hossain, K. M. A,2005]

2. Compressive strength of VACs reduced sharply when VA content increased beyond 40%. VACs having a 28-day compressive strength in excess of 15 MPa can be achieved by using up to 40% VA. [5.Hossain, K. M. A,2005]

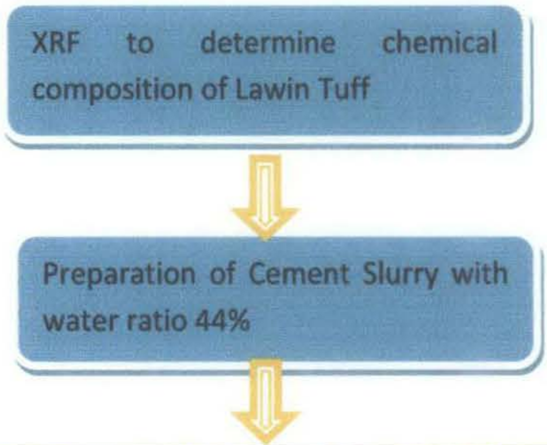
3. Compressive Strengths of natural pozzolans are directly proportional with the increase in SiO_2 ratio and inversely proportionally to Al_2O_3 and Fe_2O_3 ratios. Again it is seen that increase in the MgO and K_2O ratios decrease the pozzolanic activity. [6.Ahmet Cavdar, Sukru Yetgin, 2005]

CHAPTER 3

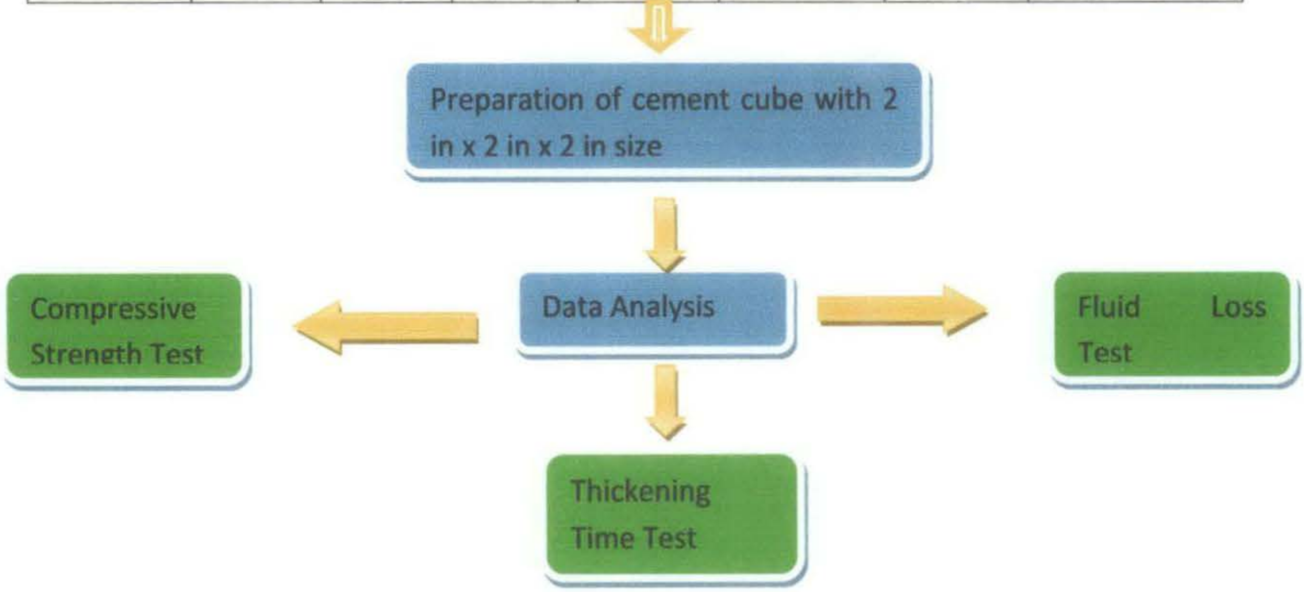
METHODOLOGY / PROJECT WORK

3. Methodology

3.1 Methodology Flow-Chart



Percentage of Cement	Mass of Cement, mc(g)	Mass of ash, ma(g)	Mass of Water, mw(g)	Volume of cement, Vc(ml)	Volume of ash,Va(ml)	Volume of water,Vw	Density,Ps lb/gl
0%	600.000	0.000	264.000	231.286	0.000	317.637	13.136
10%	540.000	47.308	258.415	208.158	23.129	310.918	13.017
20%	480.000	94.615	252.831	185.029	46.257	304.199	12.896
30%	420.000	141.923	247.246	161.901	69.386	297.479	12.771
40%	360.000	189.231	241.662	138.772	92.515	290.760	12.643



3.2 Project Activities

3.2.1 Introduction to Project activities

In order to achieve the objective of this project, research and study has been carried out prior to the submission of report. The Society of Petroleum Engineers (SPE) Technical Papers, textbook references, Petroleum Society and journals from different sources have been studied to acknowledge the past and current applications of volcanic tuff in cement. Besides, the results of the previous researchers have been analyzed to better aid in carrying out the project.

Some of the planned for the cement evaluations are as follows:

A. Literature Review
B. Chemial composition of the Lawin tuff will be analyzed using with **X-ray fluorescence (XRF).**
C. Laboratory Experiments (Class G Portland cement and volcanic tuff cement)
   i. *Cement slurry preparation (curing stage)*
   ii. *Compressive strength test*
   iii. *Fluid loss test*
   iv. *Thickening time test*
D. Comparisons and Analysis of laboratory results

3.2.2 Consumables and Equipments

The consumable materials which are required for this project are class G Oil well cement, fine volcanic ash (lawin tuff) fresh water and light grease. Below are the quantities required.

Types of Consumable	Quantity
Class G Oil Well Cement	15-20 kg
Lawin Tuff	10 kg
Light Grease	200ml to be apply on some compartments
Water	20 Liter

Table 2: Types and quantity of consumable

Equipments	Functions
Model 7000 Constant Speed Mixer	Mixing of cement slurry
SOLTEQ Curing Chamber	Curing of cement slurry under reservoir condition
SOLTEQ Compressive Strength Tester	Measurement of Compressive Strength
OFITE Filtration Loss	Determination of fluid loss volume
SOLTEQ Pressurized Consistometer	Determination of thickening time
Mortar Grinder	Grinding of rocks into fine powders.
Sieve (63 micrometer)	To sieve the fine powder of rocks

Table3 : Types of Equipment used in laboratory and their functions

3.2.3 Sample Collection and Grinding

Lawin Tuff was collected at Grik, Perak. Approximately 10-13 kg of fresh volcanic tuff was collected from Lawin. The tuff is in big pieces and easily fractured. The tuff was then brought back to UTP for further analysis

After that, raw materials are homogenized by crushing, grinding and blending using Mortar Grinder. The fine powder of tuff were then sieved in block 14 using 63 μM sieve (minimum size of sieve available in lab) so that all the raw material passes a 63 μM . It is recommended to sieve using 45 μM. This is because the fineness of tuff will greatly affect the properties of cement. From the following classification of ash, we can conclude that our grade of grinded Lawin Tuff is coarse due to equipment limitation.

Grade	Definition
fine	minimum 75% passing 45 micron sieve
medium	minimum 65% passing 45 micron sieve
coarse	minimum 55% passing 45 micron sieve

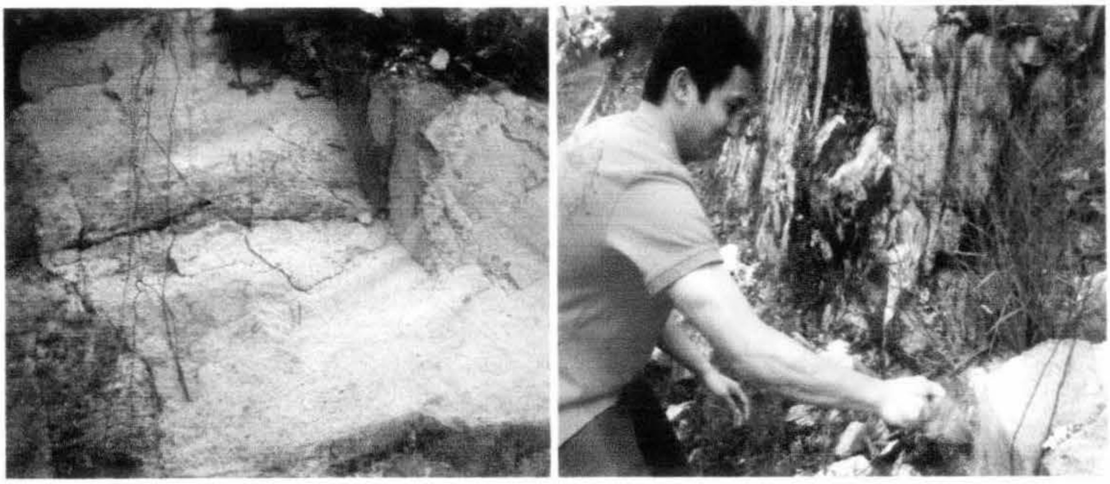


Figure 7 : Collection of tuff sample in Lawin.

Figure 8: Lawin Tuff that has been grind into powder form

Figure 9 : Lawin Tuff with less than 63 μM size.

3.2.4 XRF Analysis.

Chemical composition of the Lawin tuff will be analyzed using with **X-ray fluorescence (XRF)** (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology.

3.2.5 Preparation of Cement Slurry

The absolute density of the pozzolan (tuff) and Portland type G cement are required to perform the calculation of tuff and cement needed for different mixing ratio. When used with Portland cement in oil well cementing, the amount of pozzolan is based on the absolute replacement of a portion of the Portland cement by an equivalent absolute volume of ash. These are designated by a ratio of percentages such as (35:65). The first number refers to pozzolan and the second number refers to Portland cement.

The volume of a sack of cement is 3.62gal and if a 35:65 blend is wanted, then the pozzolan represents 1.27 gallons(35% of 3.62 gal) and the Portland cement represents 2.35(65% of 3.62 gal) The absolute volume of pozzolan (1.27) and the absolute volume of Portland Cement are then used to calculate the pounds of each material from the absolute density values of pozzolan and Portland Cement. Absolute density for Portland cement is 26lbm.gal and tuff is 20.5 lbm/gal. The mass of pozzolan is 26 lbm(1.27 x 20.5 lbm/gal) and mass of cement is 61.1(2.35 x 26 lbm/gal)

The following table give the calculation of 1 sack of cement for different mixing ratio.

Percentage of Ash	Volume of Ash,gal	Volume of Cement,gal	Mass of Ash,lbm	Mass of Cement, lbm	Mass of Ash, kg	Mass of Cement, kg
0%	0	3.62	0	0	0	0
10%	0.362	3.258	7.421	84.708	3.36609139	38.42270172
20%	0.724	2.896	14.842	75.296	6.73218278	34.15351264
30%	1.086	2.534	22.263	65.884	10.09827417	29.88432356
40%	1.448	2.172	29.684	56.472	13.46436556	25.61513448

Table 4 : Calculation for 1 sack of cement

Absolute Volume of cement, U.S.Gal	Absolute Density Cement lbm/gal	Absolute Density Ash lbm/gal
3.62	26	20.5

Table 5: Absolute Density of Lawin tuff and Portland Type G cement

Percentage of Cement	Mass of Cement, mc(g)	Mass of ash, ma(g)	Mass of Water, mw(g)	Volume of cement, Vc(ml)	Volume of ash,Va(ml)	Volume of water,Vw	Density,Ps lb/gl
0%	600.000	0.000	264.000	231.286	0.000	317.637	13.136
10%	540.000	47.308	258.415	208.158	23.129	310.918	13.017
20%	480.000	94.615	252.831	185.029	46.257	304.199	12.896
30%	420.000	141.923	247.246	161.901	69.386	297.479	12.771
40%	360.000	189.231	241.662	138.772	92.515	290.760	12.643

Table 6: Calculation for cement slurry

The laboratory works involves only use of the Class G cement . Equations used to obtain the density variations with different cement-water mixture.

$$\rho_s = \frac{m_c + m_w + m_{ash}}{\left(\frac{m_c}{\rho_c}\right) + \left(\frac{m_w}{\rho_w}\right) + \left(\frac{m_{ash}}{\rho_{ash}}\right)}$$

Where, Water density, 1 g/ml

Class G cement density, : or 2.594186 gm/ml

Lawin tuff density, : 2.045416 gm/ml

Procedures:

1. The amount of cement, ash and water are first calculated and determined.
2. Class G cement, ash and water are weighted using the electronic balance.
3. Pour the water into the mixer before starting the mixer.
4. The power is turn to ON and the START button is pushed to start the motor and elapsed time to finish mixing is 50 seconds. Remember to choose "MIX 1" button to rotate at low speed (4000rpm). Cement is slowly added into the mixer followed by ash .
5. Closed the mixer with the cover and observe the elapsed time. When the time reaches 35 seconds, press the "MIX 2" button to start mixing at high speed (12000rpm)
6. Start any testing immediately after mixing of cement slurry.

3.3 Testing Methods

3.3.1 Compressive Strength Test

Cement Slurry will set after it has been places in between casing walls in the well. Cement Strength is the strength the set cement has obtained. Compressive Strength is the force per unit cross sectional area that need to crush the cement specimen. In oil cementing, there are generally 2 types of cementing. One is lead slurry and the minimum compressive strength required to hold the casing is around 250-300psi while for tail slurry it requires higher density and larger minimum compressive strength of 500 psi for 24 hours. 3 samples (cement cube) for each ash percentage variation will be tested. When cement has developed 500 psi compressive strength in 24 hours, the strength is usually sufficient to hold the pipe or casing in the well.

Cement cubes will be tested for its compressibility with two different methods which are:

i. Compression Machine 2000K, ELE ADR:2000 (Destructive)
ii. OFITE Compressive Strength Tester Vr 2.03 Beta (Destructive)

Testing Procedure for OFITE Compressive Strength Tester

1. The OFITE compressive Strength Tester is turned on.
2. The cement cube specimen is platen of the hydraulic cylinder. The upper plate is lower down to ensure it touches the cement cube.

3. Safety shield is closed before beginning the test. The Compressive Strength Tester Software in the computer is opened. Select “Options” from the “edit” menu.
4. The height of the specimen is input into the main screen in the “Cube Height” field. The file data is selected from the “ Edit File”. Relevant information related to the testing are filled I and “OK” button is clicked. The loading rate of “4000 Psi/min” is selected for this experiment.
5. To start the test, click the “PUMP On” button. Then, “ Run Test”, is clicked and is hold to begin test while observing the specimen.
6. When the specimen is crushed, the “ Run Test” button is released to stop the test and pressure is released. The maximum load will be shown.
7. The results obtained for 3 samples will be averaged.

3.3.2 Fluid Loss Test

Fluid Loss is the measurement of the water loss of the cement expressed in volume per unit time under reservoir pressure and temperature. The fluid loss will be directly proportional to the water cement ratio. In this experiment, we will fix the water cement ratio as **44%.** API fluid loss is double the filtration volume as long as blowout is not occurred during the test.

The volume of water obtained from the slurry will be collected and recorded manually using the OFITE Low Pressure Low Temperature (LPLT) Filter. The fluid loss tester is not advisable to be used for slurry samples which are to be tested below 250°F because the OFITE LPLT Filter will yield similar result with lesser and simple procedures. The water loss through a 325 mesh screen is measured as a function of time. The following is the calculation of fluid loss of blowout occurs.

API Fluid Loss for Blowout: $2 \times Q_t \frac{5.477}{\sqrt{t}}$

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

t is the time of blowout,(min)

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

Procedures:

1. The OFITE LPLT filtration tester is used for measurement of fluid loss.
2. Two O-rings are placed in between the filter to prevent leakage of cement which will plug the filter mesh that allows flow of water during the test.
3. After that, the filter paper is places above the filter mesh 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 at 100 psi
5. 350 ml of slurry is poured into the vessel immediately after mixing.
6. A cylinder tube is placed directly below the water outlet to measure the volume of water loss. Start the time with a stopwatch. Volume of water collected is observed at 0.25, 0.5, 1, 2, 5, 10, 15, 20, 25 and 30 min interval.
7. If there is blowout occurred, stop the test immediately and record the time and amount of fluid loss. If no blowout, the amount of fluid loss will be double the filtrate volume as stated in API standard.

3.3.3 Thickening Time Test

Thickening time is a measurement of time during which cement slurry remain in a fluid state and is capable of being pumped. This is assessed under simulated down hole conditions using a pressurized consistometer that can measure the consistency of slurry over time. The end of thickening time is considered to be 100 Bc. Bearden Unit of Consistency (Bc) is a rheological properties of matter which is related to cohesion of individual particles of material ability to deform and resistance to flow.

Procedures:

1. The POWER is turned ON position on the Pressurized Consistometer.
2. The temperature ramp and soak parameters are programmed at the curing chamber to be 100^0 F for first 15 minutes and the soaked to 150^0 F for another 15 minutes and soaked until the Bc unit reached 100 Bc.
3. The inner portion of slurry cup including the blade of the rotator and suction ring is slightly greased and assembled.
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 opened and slurry is poured 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 to provide the temperature increase.
7. The HEATER and TIMER are turned ON at the touch screen. Pressure is adjusted to 600 psi until the consistency of 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.

3.4 Requirement for cement slurry (API Recommended Practice 10B-2)

a) Minimum & Maximum Density

For onsite requirement, the density of the cement slurry should has to be at least

+ 0.5 - 1.0ppg greater than drilling fluid density.
Lower than the Equivalent Circulating Density (ECD) to prevent formation fracture.

b) Maximum fluid loss of the slurry(classified based on different casing)

Surface Casing ≤ 500 ml/ 30 min
Production Casing ≤ 100ml/30min
Intermediate Casing ≤ 250 ml/30 min

c) Minimum Thickening Time

In field, the thickening time should include mixing time, pumping displacement time, time for plug and a safety factor. Thickening time varies based on the depth of the well.

d) Minimum Compressive Strength

≥500 psi after 24 hours (curing at atmospheric condition)

3.5 Gantt Chart

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Research Study															
2	Grinding of Lawin Tuff and sieve															
3	XRF Test															
4	Compressive Strength Test															
5	Fluid Loss Test															
6	Thickening Time Test															
7	Analysis of Result															
8	Progress report Submission															
9	Analysis of Result and Discussion															
10	Report Preparation															
11	Submission of Interim Report															
12	Oral Presentation (study week)															

3.6 Tools and Equipment Require

Laboratory Equipments

Figure 10 : Electronic Balance

Figure 11 :*Curing Chamber*

Figure 12: *Slurry Compartment*

Figure 13: *Consistometer*

Figure 14 *Compressibility strength tester*

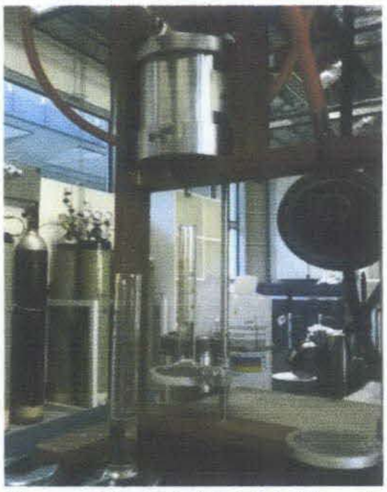


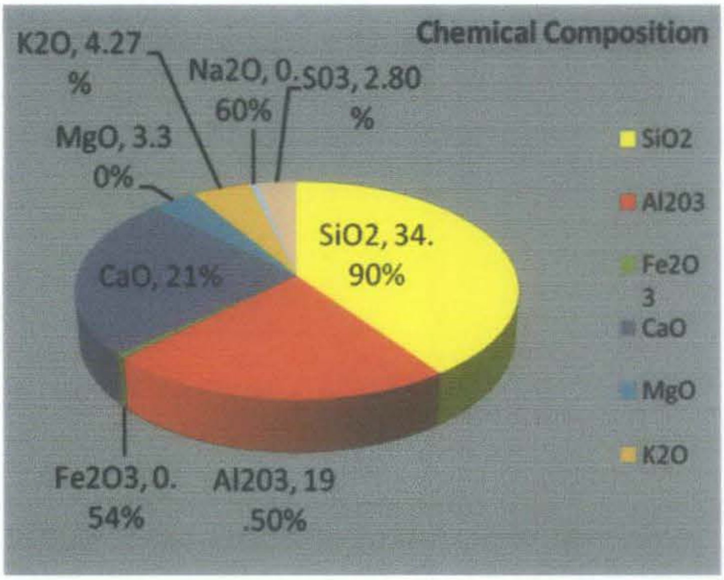
Figure 15:*OFITE LPLT Filtration Loss*

Figure 16: *High speed cement mixer*

CHAPTER 4: Results and Discussion

4.1 XRF Analysis

XRF to determine chemical composition of Lawin tuff had been performed by technician in Block 17 using XRF machine. The measurement method was STG2-S4-CHECK.



SiO_2	34.90%
Al_2O_3	19.50%
Fe_2O_3	0.54%
CaO	21%
MgO	3.30%
K_2O	4.27%
Na_2O	0.60%
SO_3	2.80%

Table 7: XRF Result

From the result, the composition of SiO_2 is about 34.9%. The value is less than the expected value because previous tuff collected from same location has shown average 50%-60% of SiO_2. The total silica composition which include Al_2O_3 and SiO_2 account for 54.4% and are suitable to be used as cement admixture. Studies has shown that the amount of SiO_2 is proportional to the compressive strength. The higher the SiO_2 content, the higher the compressive strength. Since the amount of SiO_2 is less, the compressive strength of the cement in the test is definitely less if compared to other types of volcanic tuff. However, the compressive strength of cement largely depends on the finest of the ash particles as well.

Chemical Compound	Pozzolan Type(Fly Ash)				Type G Cement
	Class F	Class C	Class N	Lawin Tuff	
SiO_2	54.9	39.9	58.2	34.9	24.3
Al_2O_3	25.8	16.7	18.4	19.5	4.3
Fe_2O_3	6.9	5.8	9.3	0.539	4.1
CaO	8.7	24.3	3.3	21	62.3
MgO	1.8	4.6	3.9	3.3	1.8
SO_3	0.6	3.3	1.1	2.8	1.9

Table 8 : *Comparison of chemical compound between Lawin Tuff and other cement*

The comparison table between different types of fly ash cement and type G cement are show in above table. From the comparison table we can observe that SiO_2 of Lawin Tuff is much less than the other types of fly ash cement. The CaO content is quite high compared to other types of fly ash and it can contribute to the compressive strength of cement.

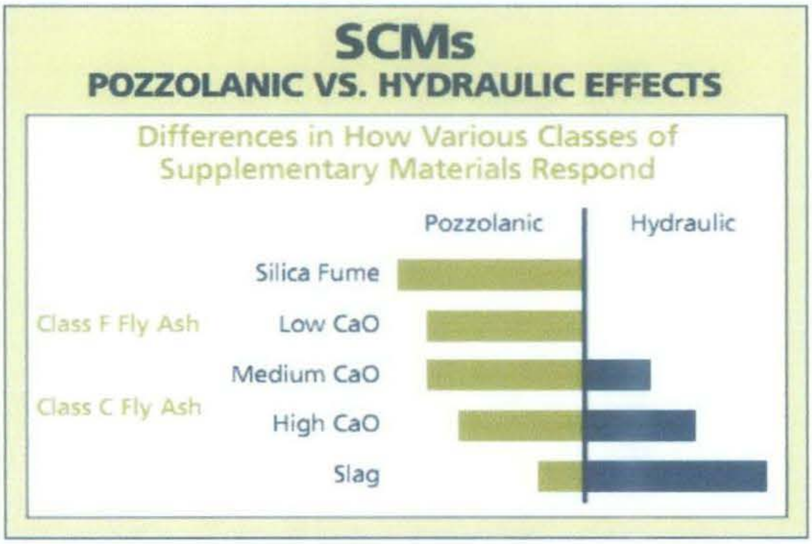


Figure17 : Pozzolanic Vs Hydraulic

As shown in the above figure, there are two types of cement. Normal cement is hydraulic cement while those using ash is pozzolanic. From the XRF chemical analysis, the CaO content is quite high thus the Lawin tuff will poses both between pozzolanic and hydraulic reaction.

4.2 Compressive Strength Test

In oil cementing, there are generally 2 types of cementing. One is lead slurry and the minimum compressive strength required to hold the casing is around 250-300psi while for tail slurry it requires higher density and larger minimum compressive strength of 500 psi for 8 hours. Below shows the table of result for curing at atmospheric pressure and temperature.

Volcanic Ash Content	Average Strength Psi		
	8 hours	24 hours	7 days
0%	900	1537	3916
10%	780	1350	4018
20%	750	1250	4130
30%	620	1100	3915
40%	450	1030	3840

Table 9 : Average Compressive Strength of different percentage of ash

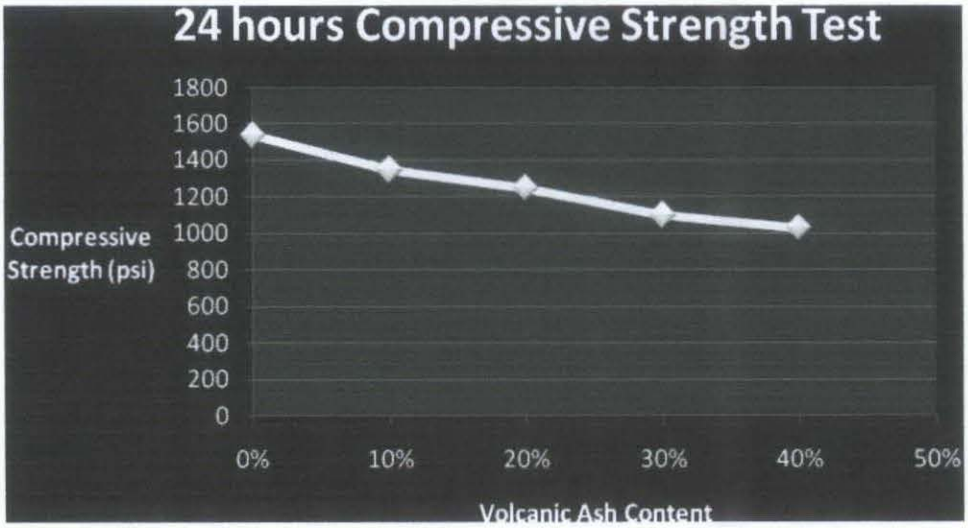


Figure 18: 24 hours compressive strength test (Short Term Strength)

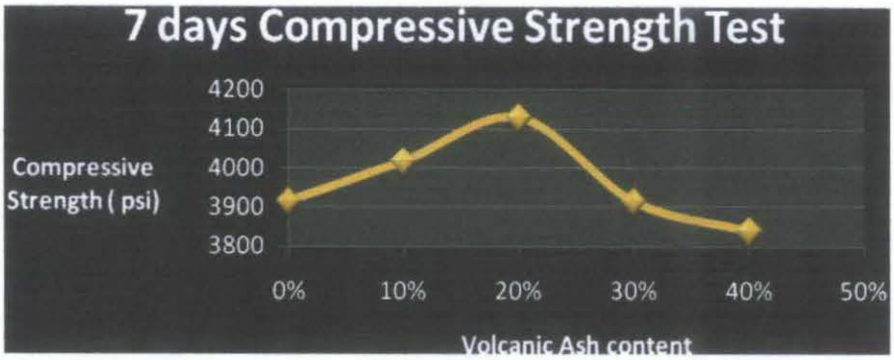


Figure 19 : *7 days Compressive Strength Test (Long term Strength)*

When cement and water react, the process is called **hydration**. Hydration of cement produces C-S-H gel, the strongest part of the "paste" in concrete, and it also produces calcium hydroxide, or free lime. Theoretically, excessive free lime can cause concrete to be too porous, but volcanic ash binds free lime over a long period of time, *increasing* compressive strength. Thus, adding volcanic ash *generally* creates a longer lasting concrete structure.

Benchmarks evaluating cement performance with respect to strength and permeability show that adding ash makes concrete *denser* by reducing water demand in cement. Cement with ash reaches its maximum strength more slowly than traditional cement, but the compressive strength is generally *greater* due to reduced permeability. Also, it substantially contributes to chemical resistance of concrete.

From the graph plot, the reduce strength for the 24 hours compressive strength test after mixing cement and ash can be explained by the lower SiO_2 content in Lawin tuff. Calcium and silicon are present in order to form the strength-producing calcium silicates. Besides, due to equipment limitation, the mortar grinder could not used to grind rocks into fine powder as compared to grinder in cement industry. Since finest of ash will greatly affect the compressive strength of cement because ash will fill the void space between cement. From the 7 days compressive strength graph, we can see that 20% of volcanic ash will increase the long term compressive strength of cement. Thus, we can conclude that substitution of volcanic tuff will increase the long term compressive strength. If the volcanic tuff is able to grind finer, the compressive strength might reach higher value.

Figure 20 : Cement Cube

Figure 21: Cement cube with 40% ash content.

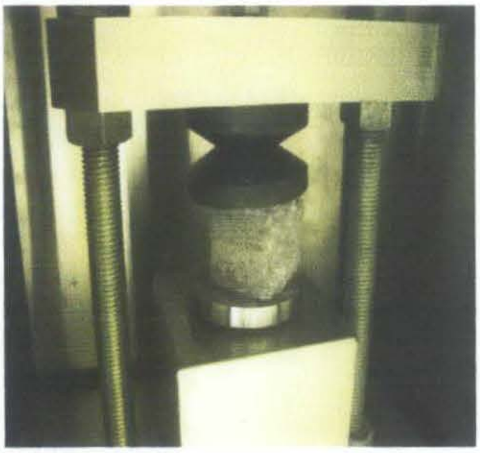


Figure 22 : Compressive Strength Test

4.3 Fluid Loss

Figure 23 : Fluid Loss Test

Higher Fluid loss indicates that the when cement is pumped into the well, it might require secondary cementing. The fluid will escape faster from cement and cause the hole to slough. In the fluid lost test, OFITE LPLT is preferred because no fluid lost material is added into the cement slurry and no pressure will be required to drain out the free water in the slurry. The amount of fluid lost is shown at the following table and graph.

The table shown fluid loss of each cement slurry with different percentage of ash added at atmospheric temperature. It was found that cement slurry with ash will released less water as compared to the class G cement. The minimum fluid loss is cement with 20% ash and at 30-40% fluid loss start to increase due to insufficient strength. It proves that during the cement reaction with water, fine particles of ash will react with excess calcium oxide and calcium hydroxide produce during the early reaction to form additional cementitious material of tricalcium silicate hydrates which filled the existing voids and thus reduce the porosity and also permeability of the cement slurry.

Ash Percentage	Density(ppg)	Time Min	API Fluid Loss (double of filtrate volume)										Fluid loss(%)
			0.25	0.5	1	2	5	10	15	20	25	30	
0%	12.41		1	4	7.5	10.1	17.1	24.4	33.2	37.2	42.4	50.7	19.20
10%	12.45		1.1	2.8	4.6	8	15.4	22.7	29.5	34.2	38.4	42.5	16.10
20%	12.48		0.4	1.8	3	6.1	14	17.1	20	23.5	25.4	28.5	10.80
30%	12.52		0.7	2.2	3	7.7	14	20.5	25	30.7	35.2	38.4	14.55
40%	12.56		0.8	2.8	5.8	10.5	16.9	24.5	30.9	38.8	45.2	52.9	20.04

Table 10: Fluid loss

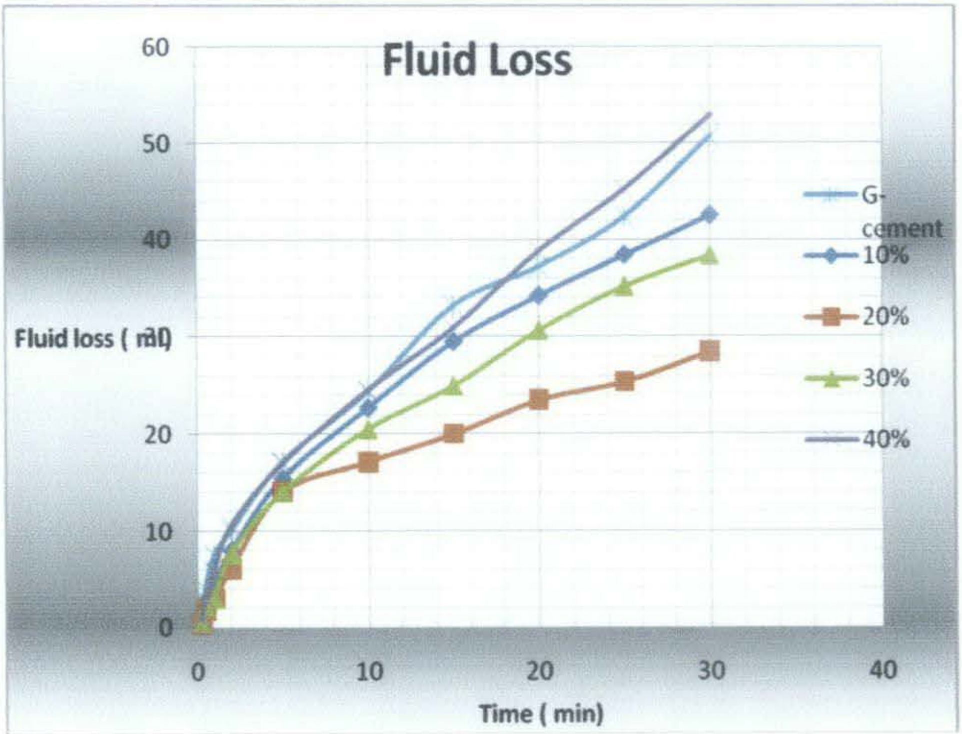


Figure 24: Fluid Loss graph

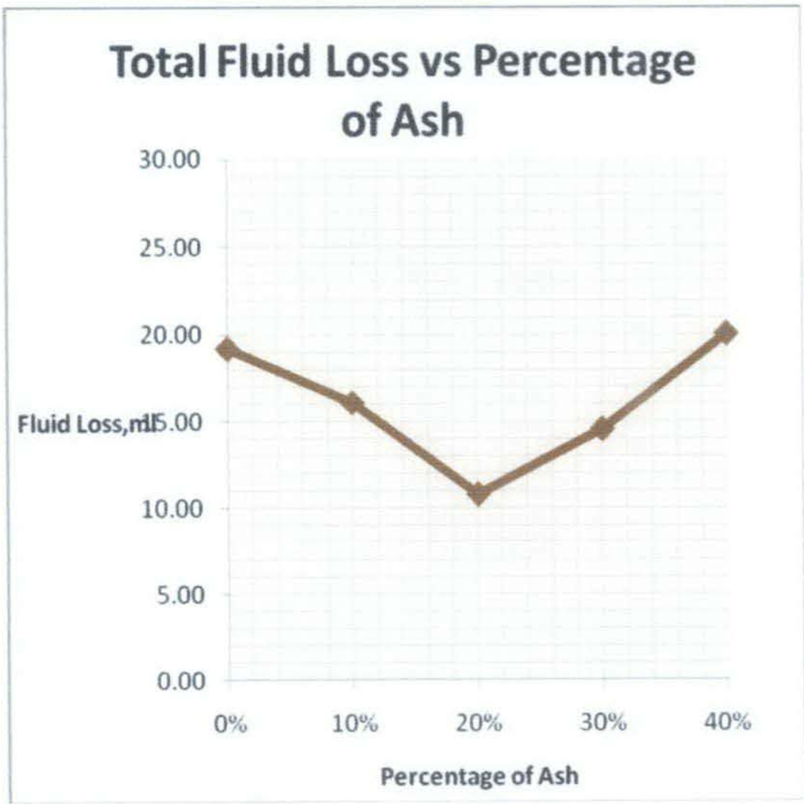


Figure 25: Total Fluid Loss vs Percentage of Ash

4.4 Thickening Time

Thickening time is time measurement where the cement slurry reaches the consistency of 100 BC. At field or laboratory, the slurry must be tested within 5 minutes after mixing. The cement slurry is placed in. It was found that 10% of ash cement will set at a faster time than Portland Type G cement. One key note here is Portland Type G cement is a slow reacting cement due to low heat of hydration. The reason is because in oil well, the depth of the well is very deep and require time to be pumped into the desired depth. Thus, we would choose cement that has a longer thickening time or set longer. With the difference in the content of fast reacting substance between ash and G- cement which is tricalcium aluminate- higher rate of reaction during hydration period and therefore set at a faster time.

Ash Percentage	Density(ppg)	Pressure (psia)	Temperature (F)	Time(hours)
G cement	12.41	750	150	3.6
10%	12.45	750	150	3.2
20%	12.48	750	150	4.3
30%	12.52	750	150	4.5
40%	12.56	750	150	5.6

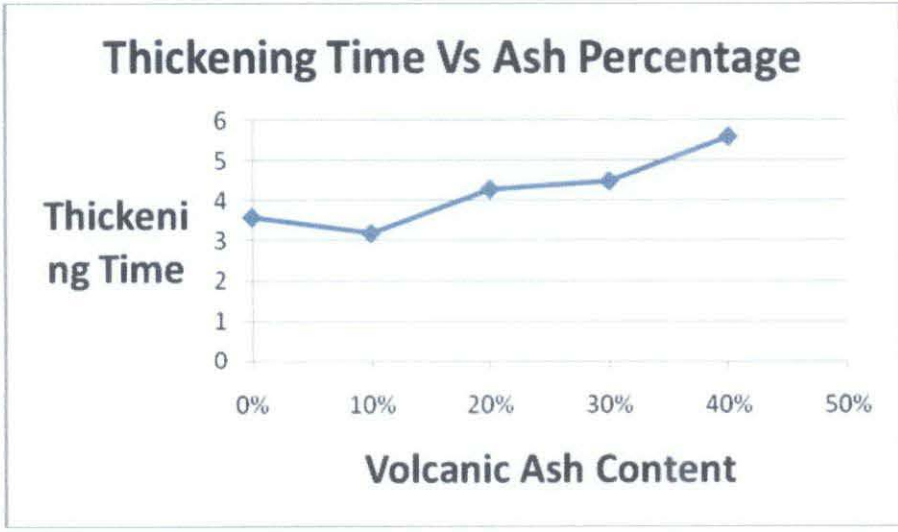


Figure 26: Thickening time at higher pressure and temperature.

4.5 Problems and Recommendation

a) Initially, grinder in Highway Lab was used to grind rocks into powder form but the size of the powder still does not meet the criteria. Thus, the mortar grinder in block 17 was used and manages to grind rocks into more fine.

b) The sieve in Block 14 only has minimum size of 63 μM and the require size is 45 μM or smaller. Thus, this will affect our experiment because finest of powder will greatly affect the result of testing.

c) The OFITE Compressive Strength Tester always breaks down and delay testing of sample cube. For recommendation, we can use Ultrasonic Strength Tester or Compressive Strength tester in block 14. Unfortunately, strength tester in block 14 has low accuracy because the machine always uses to test larger cement cube.

4.6 Economic Evaluation

The economic potential of a new aggregate source is gauged against the economic indicators

listed below:

- It is accumulated or distributed in large enough deposits to be economically viable
- It is near to market areas
- It is located near to existing or projected aggregate shortages
- It is located in areas with a growing demand for aggregates

The volcanic ash deposits largely fulfill these requirements. The costs associated with using the ash are small. Processing of the material may involve some size control to limit the amount of fines or the proportion of the weaker large particles and stockpiling of the volcanic ash may also be necessary to provide uniform sources. Nevertheless, when compared with using more conventional aggregate sources, then the volcanic ash is much cheaper primarily because of the lower haulage distances.

4.7 Future Study

The suitability of lawin tuff to be used in oil well cementing still require further analysis investigation of the chemical and mineralogical composition, including morphology, amount of glassy phase and fineness, and the mechanical properties of the material. Pozzolans are also highly dependent on external factors such as the additional admixtures and thermal treatments they are exposed to. In general, pozzolans have high silicon oxide and aluminum oxide content with a glassy / amorphous structure for reactivity with lime or cement.

5.0 Conclusion

Volcanic tuff in Lawin can increase the long term compressive strength of cement with addition of tuff up to 20%. However, finest of the tuff is important because it will greatly affect the compressive strength. For fluid loss, 20% of ash will have minimum fluid loss . In terms of thickening time, 10% of ash added to cement will increase the setting time.

Further analysis can be done to further confirm whether Lawin tuff is suitable to produce fly ash cement such as chemical and mineralogy analysis, pozzolanic activity test, strength activity index . Finally, economic evaluation can be done to estimate the profitability of using volcanic tuff in Lawin for generating Portland Fly ash cement.

Reference:

1. *"Recommended Practice for Testing Well Cements"*, ANSI/API Recommended Practice 10B-2 (Formerly 10B), First Edition, July 2005. (Identical to ISO 10426-2:2003 including ISO 10426:2005/FDAM 1:2005)

2. Elizabeth L White, *1984, "Effect of Fly Ash on the Rheology of Cement Slurry"*, Materials Research Laboratory, Pennsylvania State University.
3. *N C Ludwig , "Portland Cement and Their Application in Oil and Gas Industry"*
4. Hossain, K. M. A., "*Blended Cement using Volcanic Ash and Pumice*," Cement and Concrete Research, V. 33, No. 10, 2003, pp. 1601-1609
5. Hossain, K. M. A, 2005, "*Development of Volcanic Ash Concrete: Strength, Durability and Microstructure Investigation*, Cement and Concrete Research .
6. Ahmet Cavdar, Sukru Yetgin, 2005," Availability of Tuffs from Northeast of Turkey as natural pozzolan on cement, Some Chemical and Mechanical Relationships, Department of Civil Engineering, Karadeniz Technical University,Turkey.
7. Shahrin Shahrudin, Ariffin Shamsuri, *"Possibilities Studies of using Local Cement in Oil and Gas Well Cementing Operation in Malaysia"*, Cement Research Group, Petroleum Engineering Department UTM
8. Ashok Santra, B.R.Reddy , *"Reaction of CO2 with Portland Cement at Downhole Conditions and the Role of Pozzolanic Supplements". Halliburton.2009*
9. B.E.Morgan. *API Specification for Oil-well Cements*, Drilling Practices, API, pg 83-90
10. Citing Websites. *What is Tuff?* Retrieved August 6, 2010, from http://www.wisegeek.com
11. Citing Websites. Volcanic Rock Types. Retrieved August 7,2010, from http://geology.about.com/od/more_igrocks/ig/extrusives/tuffsalvador.htm
12. Citing Websites. Volcanic Ash. Retrieved August 10,2010, from http://volcanoes.usgs.gov/ash/properties.html
13. *Journal of Hazardous Materials, Volume 131, Issues 1-3, 17 April 2006, Pages 126-130* Y. Abali, S.U. Bayca, S. Targan.
14. Hossain, K. M. A, 2004, "*Volcanic ash and pumice as cement additives: pozzolanic,alkali-silica reaction and autoclave expansion chatacteristics.*"Department of Civil Engineering, Ryerson University.

15. Citing websites. Pozzolanas-Calcined clays and shales, and volcanic ash. Retrieved October 10,2010,from

http://en.howtopedia.org/wiki/Pozzolanas_Calcined_Clays_and_Shales,_and_Volcanic_Ash_-_Technical_Brief

16. Citing websites. General Description of Pozzolans .Retrives October 15 2010 from http://www.todaysconcretetechnology.com/general-description-of-pozzolans.html
17. Citing Websites. Volcanic Ash as Binding Agent in Green Concrete by Kathrine Schmeichel . Retrives 22 Feb 2011 from http://www.cowi.com/menu/NewsandMedia/News/IndustryandEnergy/Pages/volcanicasheyedasbindingagentingreenconcrete.aspx
18. Citing websites. Green Cement has Cebu Volcanic Ash. Retrived 25 Feb 2001 from http://globalnation.inquirer.net/cebudailynews/enterprise/view/20100706-279485/Green-cement-has-Cebu-volcanic-ash-not-coal-ash
19. Citing websites. Green Concrete Technology .Retrived 25 Feb 2011 from http://greenmanplanet.blogspot.com/