A study of high calcium limestone around lenggong Perak to produce type–G Portland cement

By

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ABSTRACT

This project carried out on Portland cement using high calcium limestone, and other minor raw materials such as clay and iron ore. The raw materials were obtained from a local rock in Lenggong in Perak, Malaysia. Composition of raw materials and mineral phase were investigated or tested by XRF. Portland cement is primary construction materials widely used in oil and gas wells specially class G Portland cement.

Portland cement at least to comply with the standards set by the American Petroleum Institute (API). Chemical compositions of limestone, clay, iron ore and raw materials were determined. Modulus of mixture of raw materials was fixed in IM is 1.7, SM is 2.4 and LSM is 9.4. Raw materials were crushed and ground to fine powder to form a mixture raw material and then put in furnace where it is heated and burning to form Portland cement clinker.

From the expriremmtal results, the four main Portland cement are CS_3, CS_2, C_3A and C_4AF.

ACKNOWLEDGEMENT

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I would also like to thank the head, lecturers and stuff of geosciences and petroleum engineering for all their support and providing me with a good environment and facilities to graduate as a petroleum engineer.

It is a great pleasure to express my deepest appreciation to my parents, Ibrahim Mahamat Dahlob and Fatma Hassan Oumar who prayed for me and stood by my side in a long this journey of studies.

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CHAPTER 1

INTRODUCTION

1.1.Project background

Portland cement is a hydraulic product made by burning and grinding a mixture of calcareous and argillaceous materials, such as limestone and clay, limestone and shale. Portland cement is primarily known as a construction cement but it is also being used extensively in oil well cementing operations which helps to seal the annulus between the wall of the wellbore and the casing to provide zonal isolation, to protect the casing against aggressive wellbore fluids and to protect the casing against collapse by rock creeping in on the wellbore.

In order to be able to used as oil well cement, Portland cement must comply in terms of their physical and chemical properties to the standards set by the American Petroleum Institute (API).

In Malaysia, class G cement is used widely in cementing the oil well. The components of Portland cement are Tricalcium Silica (C_3S), Dicalcium Silicate (C_2S). Tricalsium Alumina (C_3A), Tetracalcium Aluminopherite (C_4AF), and Gypsum (CSH_2). In general, this cement has low hydration rate and forms a tight bond between the pebbles and the casing. It holds it properties at oil well temperature and pressure because it is made in such away to suite the usage in a depth of 2440m and temperature between 80 200 F. It protects the casing from any aggressive oil well liquid [Ariffin S, Surej K, S]

1.2.Problem statement

Portland cement, which is primary a construction material, is used extensively in oil well cement, and the use of local cement in oil well application as a means to save drilling cost. Additionally, API class G cement can cost three times more than local construction cement.

1.3. Objective of the project

The objectives of this research is to study and understand the chemical compositions of local major raw materials limestone and minor raw materials , clay and iron ore for producing G-Portland cement which might be used in oil field.

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1.4. Scope of study

The study involves literature review on utilization of Portland cement in oil wells and chemical compositions for raw materials and mixture of raw materials of Portland cement clinker.

Quarrying local samples of limestone from Lenggong in PERAK, Malaysia. The laboratory experiments are also be performed to test samples of ground limestone, clay and iron ore using XRF tool.

Furthermore, the scope of study focused on using local technical background to support the use of local raw materials for Portland cements.

The scope of study also focused on procedures of making (crush sample of limestone, clay, and iron ore, grinding and sending them to XRF laboratory).

1.5. Feasibility of the Project within the Scope and Time frame

- With proper planning beforehand to project will be kept inside to scope of the project and the project can be finished within the timeframe.

- Gantt chart created will assist in planning of the activities done during whole planning course of project.

- Besides, under the supervision and guidance of my supervisor, I am confident this project would be achieved the scope and time frame set beforehand.

CHAPTER 2

LITERATURE REVIE

2.1. Manufacture of Portland cement

Portland cement is produced by partially fusing powdered blends composed of limestone with materials like clay, shale, blast-furnace slag, siliceous sands, and iron ores.

From a chemical standpoint, these blends may be considered to be mixtures of the oxides of calcium (CaO), aluminum ($Al2O_2$), silicon (SiO_2), magnesium (MgO), iron ($Fe2O_3$), potassium (K_2O), and sodium (Na_2O).

During heating to about 2700F, these oxides combine to form calcium silicates and aluminates (commonly referred to as “clinker”).

Portland cement is known as hydraulic cement. When hydraulic cements set and harden by reacting chemically with water, this reaction, called hydration, forms a stone like mass. Hydration begins as soon as cement contacts water. Each cement particle forms a type of growth on it surface that gradually spreads until it links up with the growth from other cement particle or adheres to adjacent substances. Thus progressive stiffening, hardening, and strength development result. The stiffening of well cement slurries can be recognized by an increase in consistency that depends on time, temperature/pressure conditions, and the composition and fineness of the cement and slurry formulations [SPE, Halliburton Services]

The chemical composition of the raw materials and the type of cement to be produced as showing in figure 1, 2.

2.2. Classification of Cement

The raw materials used to manufacture Portland cements are limestone (calcium carbonate) and clay or shale. Iron and alumina are frequently added if they are not already present in sufficient quantity in the clay or shale. These materials are blended together, either wet or dry, and fed into a rotary kiln, which fuses the limestone slurry at temperatures ranging from 2,600 to 3,000°F into a material called cement clinker. After it cools, the clinker is pulverized and blended with a small amount of gypsum to control the setting time of the finished cement.

Oxide	Class G, wt%	Class H, wt%
Silicon dioxide, SiO_2	21.7	21.9
Calcium oxide, CaO	62.9	64.2
Aluminum oxide, Al_2O_3	3.2	4.2
Iron oxide, Fe_2O_3	3.7	5
Magnesium oxide, MgO	4.3	1.1
Sulfur trioxide, SO_3	2.2	2.4
Sodium oxide, Na_2O		0.09
Potassium oxide, K_2O		0.66
Total alkali as Na_2O	0.54	0.52
Loss on ignition	0.74	1.1
Insoluble residue	0.14	0.21
Phase Composition		
C_3S	58	52
C_2S	19	24
C_3A	2	3
C_4AF	11	15
Physical Properties		
% passing 325 mesh	87	70
Blaine fineness, cm^2/gm	3,470	2,610
Physical Requirements		
Thickening time, min, Sch 5	1:40	1:38
B_c at 30 min	14	15
8 hr compressive strength, 110°F (38°C)	928 psi (6.4 MPa)	650 psi (4.5 MPa)
8 hr compressive strength, 140°F (60°C)	2,247 psi (15.5 MPa)	1,650 psi (11.4 MPa)
Free fluid, mL[13]	4.4	4.0

Figure 1: Typical mill run analysis of Portland cement

	Compounds, %				
API Class	C_3S	C_2S	C_3A	C_4AF	Wagner Fineness, cm^2/g
A	53	24	8+	8	1,500 to 1,900
B	47	32	5–	12	1,500 to 1,900
C	58	16	8	8	2,000 to 2,800
G & H	50	30	5	12	1,400 to 1,700

Property	How Achieved
High early strength	By increasing the C_3S
Better retardation	By controlling C_3S and C_3A
Low heat of hydration	By limiting the C_3S and C_3A content
Resistance to sulfate attack	By limiting the C_3A content

Figure 2: typical composition and properties of API classes of Portland cement

2.2.1. Eight types of Portland cement provided by ASTM

1. Type I
2. Type IA
3. Type II
4. Type IIA
5. Type III
6. Type IIIA
7. Type IV and
8. Type V

Where the “A” denotes air-entraining cement. These cements are designed to meet the varying needs of the construction industry. Cements used in wells are subjected to conditions not encountered in construction, such as wide ranges in temperature and pressure. For these reasons, different specifications were designed and are covered by API specifications. API currently provides specifications covering eight classes of oil well cements, designated Classes A through H. API Classes G and H are the most widely used. Oil well cements are also available in either moderate sulfate-resistant (MSR) or high sulfate-resistant (HSR) grades. Sulfate-resistant grades are used to prevent deterioration of set cement down-hole caused by sulfate attack by formation waters.

2.4. API Classifications

API cement is manufactured specifically to meet the needs of the oil industry. The American Petroleum Institute (API) established a set of standards that a Portland cement must meet to be considered API cement. The oil industry purchases cements manufactured predominantly in accordance with API classifications as published in "API *Spec. 10A" The* different classes of API cements for use at down-hole temperatures and pressures are defined as the following:

2.4.1. Class A

This product is intended for use from surface to 6,000 feet when special properties are not required. The properties and performance of Class A cement may be tailored with additives to meet special requirements beyond basic performance. It is similar to American Society for Testing and Materials (ASTM) Type I construction cement. [Normal density = 15.6 ppg]

2.4.2. Class B

This product is intended for use from surface to 6,000 feet when conditions require moderate to high sulfate-resistance. Class B is similar to ASTM Type II construction cement [Normal density = 15.6 ppg].

2.4.3. Class C

This product is intended for use from surface to 6,000 feet when conditions require high early strength. Class C is similar to ASTM Type III cement and available in ordinary, moderate and high sulfate resistance types. [Normal density = 14.8 ppg].

2.4.4. Class G

This product is intended for use from surface to 8,000 feet as basic cement, as manufactured, or it can be modified with additives to cover a full range of well depths and temperatures. No additions other than calcium sulfate or water, or both, shall be inter-ground or blended with the clinker during manufacture of Class G Cement.

Class G cement is available in moderate and high sulfate-resistance types. Class G is similar to ASTM Type IV cements [Normal density = 15.8 ppg].

Chemical Requirements	**API Class G Requirements**
MgO max %	6.0
SO_3 max %	3.0
Loss on Ign. max %	3.0
Insoluble Res. max %	0.75
C_3S max %	48 - 58
C_3A max %	8.0
Total Alkali as Na20%	0.75
Physical Requirements	**API Class G Requirements**
Water % by wt. of cement	44.0
Soundness % max	0.8
Free water max ml	5.8
Min compr. str. MPa (8 hours) at temp. 38C, Atm. pressure at temp. 60C, Atm. pressure	2.1 10.3
Max consistency	30.0
Thickening Time (schedule 5) minimum (minutes)	90 - 120

Figure 3: Class G oil cement [API specification for material and testing for well cementing]

2.4.5. Class H

This product is intended for use from surface to 8,000 feet as basic cement, as manufactured, or it can be modified with additives to cover a full range of well depths and temperatures. No additions other than calcium sulfate or water, or both, shall be inter-ground or blended with the clinker during manufacture of Class H Cement. Available in moderate and high sulfate-resistance types. Class H is similar to ASTM Type IV cements. [Normal density = 16.5 ppg]. [Andrew R. Barron]

2.4. Properties of Cement provided by API Specifications

Chemical properties and physical requirements are summarized in table 3 and 4 respectively. Typical physical requirements of the various API classes of cement are shown in table 5. Although these properties describe cements for specification purposes, oil well cements should have other properties and characteristics to provide for their necessary functions down-hole.

API provides standards for testing procedures and special apparatus used for testing oil well cements and includes slurry preparation, slurry density, compressive, strength
tests and nondestructive sonic testing, thickening-time tests, static fluid-loss tests, operating free fluid tests, permeability tests, rheological properties and gel strength, pressure-drop and flow-regime calculations for slurries in pipes and annuli, arctic (permafrost) testing procedures, slurry stability test, and compatibility of wellbore fluids [Larry W, Lake, Petroleum Engineering Handbook]

2.4.1. Physical properties of Portland cement

Portland cements are commonly characterized by their physical properties for quality control purposes. Their physical properties can be used to classify and compare Portland cements.

2.4.1.1.Fineness

Fineness or particle size of Portland cement affects hydration rate and thus the rate of strength gain. The smaller the particle size, the greater the surface area-to-volume ratio, and thus, the more area available for water-cement interaction per unit volume. The effects of greater fineness on strength are generally seen during the first seven days [PCA, 1988].

2.4.1.2.Soundness

When referring to Portland cement, "soundness" refers to the ability of a hardened cement paste to retain its volume after setting without delayed destructive expansion [PCA, 1988]

2.4.1.3.Setting Time

Cement paste setting time is affected by a number of items including: cement fineness, water-cement ratio, chemical content (especially gypsum content) and admixtures. Setting tests are used to characterize how a particular cement paste sets. For construction purposes, the initial set must not be too soon and the final set must not be too late. Additionally, setting times can give some indication of whether or not cement is undergoing normal hydration [PCA, 1988]. Normally, two setting times are defined [Mindess and Young, 1981]

2.4.1.4.Strength

Cement paste strength is typically defined in three ways: compressive, tensile and flexural. These strengths can be affected by a number of items including: water-cement ratio, cement-fine aggregate ratio, type and grading of fine aggregate, manner of mixing and molding specimens, curing conditions, size and shape of specimen, moisture content at time of test, loading conditions and age [Mindess and Young, 1981]

2.4.1.5.Compressive Strength

The most common strength test, compressive strength, is carried out on a 50 mm (2-inch) cement mortar test specimen. The test specimen is subjected to a compressive load (usually from a hydraulic machine) until failure. This loading sequence must take no less than 20 seconds and no more than 80 seconds. Table 3.15 shows ASTM C 150 compressive strength specifications.

2.4.2. Chemical properties of Portland cement

Portland cements can be characterized by their chemical compositions. A basic understanding of Portland cement chemistry can help someone to understand how and why it behaves as it does. The basic chemical compositions of a typical Portland cement are briefly described in table 12, and how the how the Portland cement hydrates.

	Cement Class				
	A	B	C	G	H
Ordinary Grade, O					
Magnesium oxide, MgO, maximum, %	6.0	—	6.0	—	—
Sulfur trioxide, SO_3, maximum, %	3.5[1]	—	4.5	—	—
Loss on ignition, maximum, %	3.0	—	3.0	—	—
Insoluble residue, maximum, %	0.75	—	0.75	—	—
Tricalcium aluminate, $3CaO \cdot Al_2O_3$, maximum, %	—	—	15	—	—
Moderate-Sulfate-Resistant Grade, MSR					
Magnesium oxide, MgO, maximum, %	—	6.0	6.0	6.0	6.0
Sulfur trioxide, SO_3, maximum, %	—	3.0	3.5	3.0	3.0
Loss on ignition, maximum, %	—	3.0	3.0	3.0	3.0
Insoluble residue, maximum, %	—	0.75	0.75	0.75	0.75
Tricalcium silicate, C_3S maximum, %	—	—	—	58[2]	58[2]
minimum, %	—	—	—	48[3]	48[3]
Tricalcium aluminate, C_3A, maximum, %[2]	—	8	8	8	8
Total alkali content expressed as sodium oxide, Na_2O, equivalent, maximum, %[3]	—	—	—	0.75	0.75
High-Sulfate-Resistant Grade (HSR)					
Magnesium oxide, MgO	—	6.0	6.0	6.0	6.0
Sulfur trioxide, SO_3, maximum, %	—	3.0	3.5	3.0	3.0
Loss on ignition, maximum, %	—	3.0	3.0	3.0	3.0
Insoluble residue, maximum, %	—	0.75	0.75	0.75	0.75
Tricalcium silicate, C_3S, maximum, %	—	—	—	65[2]	65[2]
minimum, %	—	—	—	48[2]	48[2]
Tricalcium aluminate, C_3A, maximum, %[2]	—	3	3	3	3
Tetracalcium aluminoferrite, C_4AF, plus twice the tricalcium aluminate, C_3A, maximum, %[2]	—	24	24	24	24
Total alkali content expressed as sodium oxide, Na_2O, equivalent, maximum, %[3]	—	—	—	0.75	0.75

[1] When the tricalcium aluminate content (expressed as C_3A) of the Class A cement is 8% or less, the maximum SO_3 content shall be 3%.
[2] The expressing of chemical limitations by means of calculated assumed compounds does not necessarily mean that the oxides are actually or entirely present as such compounds. When the ratio of the percentages of Al_2O_3 to Fe_2O_3 is 0.64 or less, the C_3A content is zero. When the Al_2O_3 to Fe_2O_3 ratio is greater than 0.64, the compounds shall be calculated as $C_3A = (2.65 \times \% Al_2O_3) - (1.69 \times \% Fe_2O_3)$, $C_4AF = 3.04 \times \% Fe_2O_3$, $C_3S = (4.07 \times \% CaO) - (7.60 \times \% SiO_2) - (6.72 \times \% Al_2O_3) - (1.43 \times \% FeO_3) - (2.85 \times \% SO_3)$. When the ratio of Al_2O_3 to Fe_2O_3 is less than 0.64, the C_3S shall be calculated as $C_3S = (4.07 \times \% CaO) - (7.60 \times \% SiO_2) - (4.48 \times \% Al_2O_3) - (2.86 \times \% Fe_2O_3) - (2.85 \times \% SO_3)$.
[3] The sodium oxide equivalent (expressed as Na_2O equivalent) shall be calculated by Na_2C equivalent $= (0.658 \times \% K_2O) + \% Na_2O$.

Figure 4: chemical requirements for API cements

Well cement class:				A	B	C	G	H
Mix water, wt% of well cement:				46	46	56	44	38
Fineness tests (alternative methods):								
Turbidimeter (specified surface, minimum, m_2/kg):				150	160	220	—	—
Air permeability (specified surface, minimum, m_2/kg):				280	280	400	—	—
Free-fluid content, maximum, mL:				—	—	—	3.5	3.5
Compressive-strength test, 8-hour curing time	Schedule number, Table 7	Curing temp., °F (°C)	Curing pressure, psi (kPa)	Minimum Compressive Strength, psi (MPa)				
	—	100 (38)	Atmos.	250 (1.7)	200 (1.4)	300 (2.1)	300 (2.1)	300 (2.1)
	—	140 (60)	Atmos.	—	—	—	1,500 (10.3)	1,500 (10.3)
Compressive-strength test, 24-hour curing time	Schedule number, Table 7	Final curing temp., °F (°C)	Final curing pressure, psi (kPa)	Minimum Compressive Strength, psi (MPa)				
	—	100 (38)	Atmos.	1,800 (12.4)	1,500 (10.3)	2,000 (18.8)	—	—
Pressure/temperature thickening-time test	Specification test schedule number, Table 10		Maximum consistency, 15 to 30 min stirring period, B_c	Minimum Thickening Time, min				
	4		30	90	90	90	—	—
	5		30	—	—	—	90	90
	5		30	—	—	—	120 max.	120 max.

B_c = Bearden units of consistency, obtained on a pressurized consistometer, as defined in Sec. 9 of API *Spec. 10A* and calibrated as per the same section.[8]

Figure 5: Physical requirements for API cements

Type of Additive	Use	Chemical Composition	Benefit	Type of Cement
Accelerators	Reducing WOC time Setting surface pipe Setting cement plugs Combating lost circulation	Calcium chloride Sodium chloride Gypsum Sodium silicate Dispersants Seawater	Accelerated setting High early strength	All API classes Pozzolans Diacel systems
Retarders	Increasing thickening time for placement Reducing slurry viscosity	Lignosulfonates Organic acids CMHEC Modified lignosulfonates	Increased pumping time Better flow properties	API Classes D, E, G, and H Pozzolans Diacel systems
Weight-reducing additives	Reducing weight Combating lost circulation	Bentonite/attapulgite Gilsonite Diatomaceous earth Perlite Pozzolans Microspheres (glass spheres) Nitrogen (foam cement)	Lighter weight Economy Better fill-up Lower density	All API classes Pozzolans Diacel systems
Heavyweight additives	Combating high pressure Increasing slurry weight	Hematite Limenite Barite Sand Dispersants	Higher density	API Classes D, E, G, and H
Additives for controlling lost circulation	Bridging Increasing fill-up Combating lost circulation Fast-setting systems	Gilsonite Walnut hulls Cellophane flakes Gypsum cement Bentonite/diesel oil Nylon fibers Thixotropic additives	Bridged fractures Lighter fluid columns Squeezed fractured zones Treating lost circulation	All API classes Pozzolans Diacel systems
Filtration-control additives	Squeeze cementing Setting long liners Cementing in water-sensitive formations	Polymers Dispersants CMHEC Latex	Reduced dehydration Lower volume of cement Better fill-up	All API classes Pozzolans Diacel systems

Figure 6: Summary of oil well cement additives

2.5. Portland cement raw materials

The raw materials that used for the manufacture of Portland cement are limestone, clay, iron ore, shale and gypsum.

2.5.1. Limestone

The limestone used in the manufacture of cement contains between 85% and 95% calcium carbonate, and small quantities of magnesium carbonate, silica, alumina and iron. Limestone and clay or shale are quarried and transported to the crushing plant by rear- dump trucks.

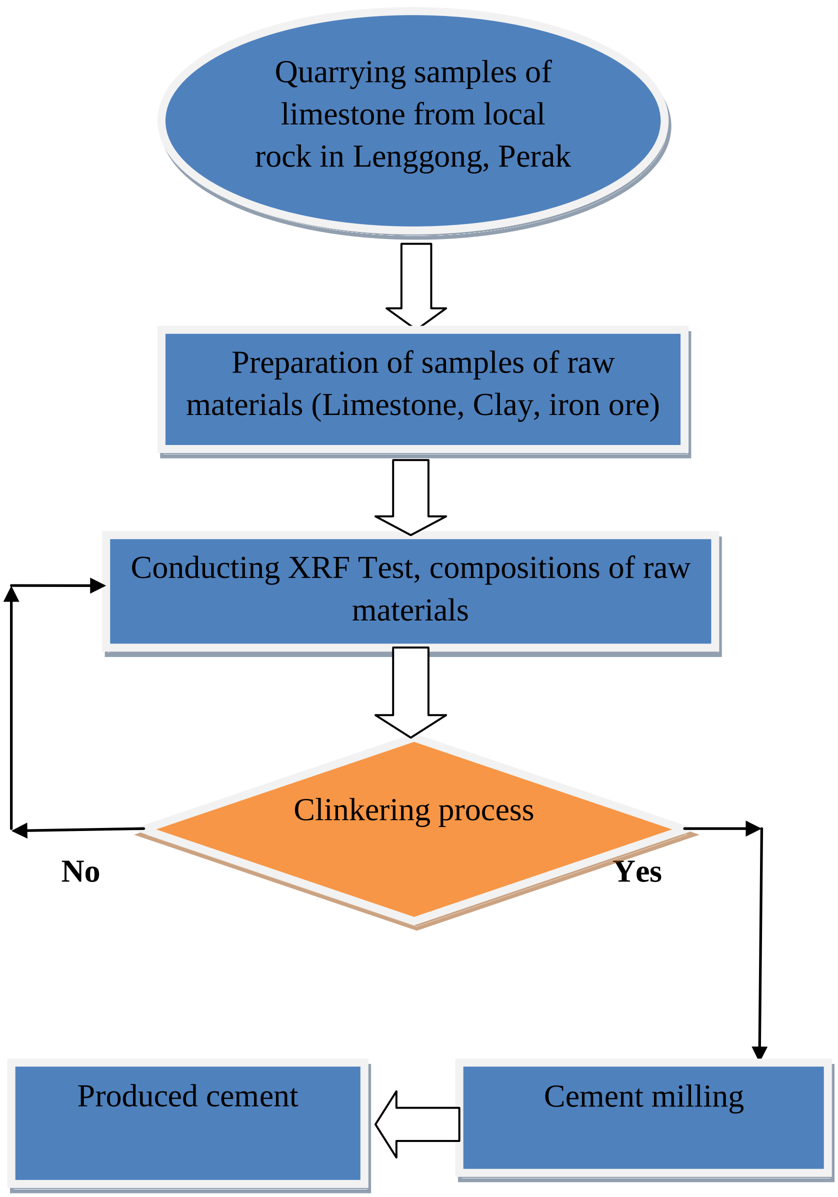
Figure 7: limestone blocks taken away for crushing

CHAPTER 3

METHODOLOGY

In the build-up of achieving the main objective of this project, research and study has been carried out and technical Papers, textbook references, have been studied to acknowledge the past and current applications for Portland cements.

Project low Chart



3.1. Quarrying samples of raw material (Limestone) from local rocks

In this project research, the raw material is limestone taken from Lenggong around Perak, Malaysia. The raw material for producing Portland cement are mixture of materials containing calcium oxide, silicon oxide, aluminium oxide, ferric oxide, and magnesium oxide.

Figure 8: sample of limestone taken from local rock, Lenggong, Perak, Malaysia

3.2. Preparation of samples of raw materials for XRF analysis

Firstly the raw material (limestone) is crushed to small grains using hummer, and then grinded by aggregate impact value test (AIV). The grinded material passed to SIVE shaker machine to make powder form 63 micron.

Figure 9: Aggregate Impact Value Test machine (AIV), civil engineering lab, blocks13.

Figure 10: SIVE Shaker, Civil Engineering, Block13

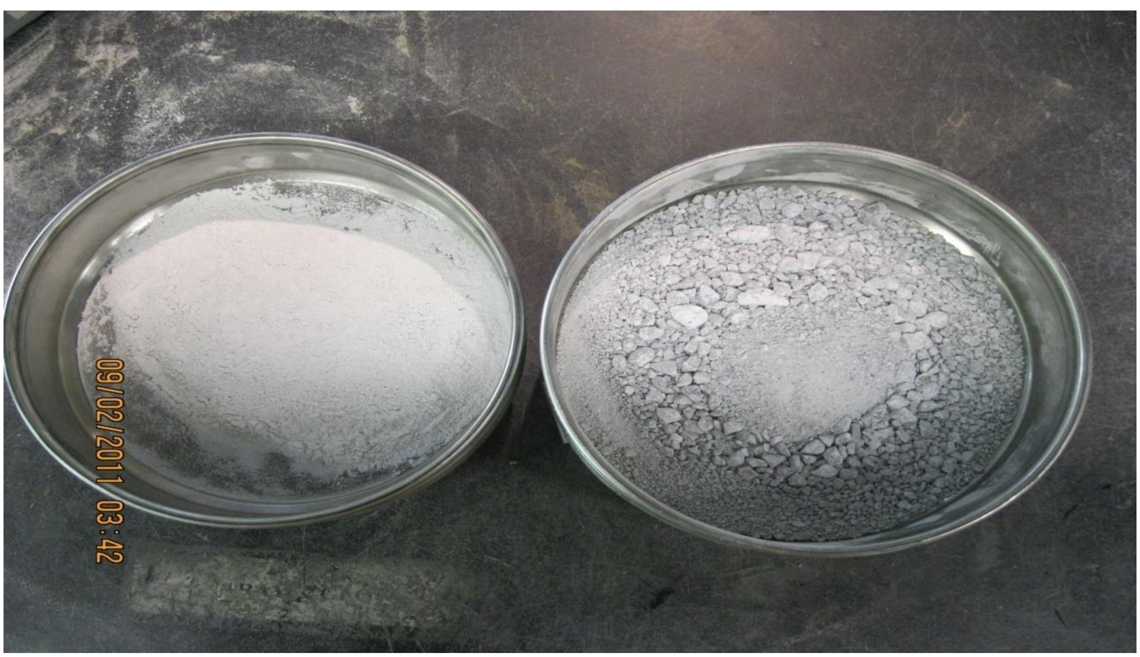


Figure 11: Limestone powder form 63 micron, and small grains

The powder sample is sent to the laboratory for testing their chemical compositions using X-ray fluorescence (XRF) tool which is to identify the material content.

3.2.1. Minor raw materials (Clay, and Iron ore)

Figure 12: Minor raw material, Clay

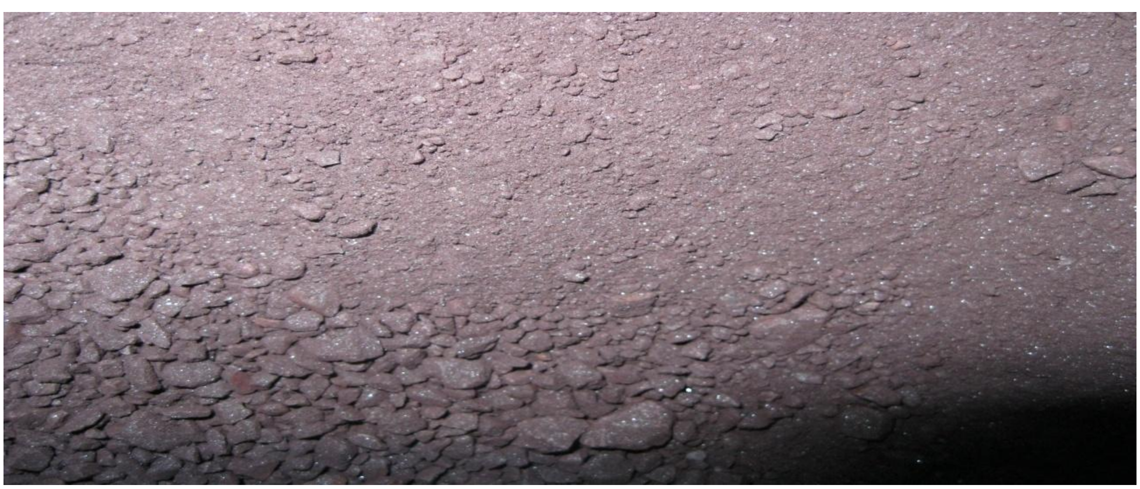


Figure 13: Iron ore powder as additive materials for producing Portland cement

3.2.2. Dry process

The dray process is one of the main cement manufacturing processes used. The quarried limestone and clay are crushed separately until nothing bigger than tennis ball remains. Samples of both rocks are then sent off to the laboratory for mineral analysis. If necessary, minerals are then added to either the clay or the limestone to ensure that the correct amounts of aluminum, iron are present. The clay and limestone are then fed together into a mill where the rock is ground until more than 85% of the material is less than 90μm.

3.3. Laboratory Tools using in this project

3.3.1. X-ray fluorescence (XRF)

An x-ray fluorescence (XRF) spectrometer is an x-ray instrument used for routine, relatively non-destructive chemical analyses of minerals, fluid, sediments and rock.

Figure 14: X-ray fluorescence lab machine

3.4.Clinkering Process

The major raw material for the clinker-making is usually limestone ($CaCO_3$) mixed with a second raw materials containing clay as source of alumino-silicate, and the Portland cement clinker is a dark grey nodular material made by heating ground limestone and clay at a temperature of about 1400 C-1500 C. The nodules are ground up to a fine powder to produce cement, with a small amount of gypsum added to control the setting properties [10]

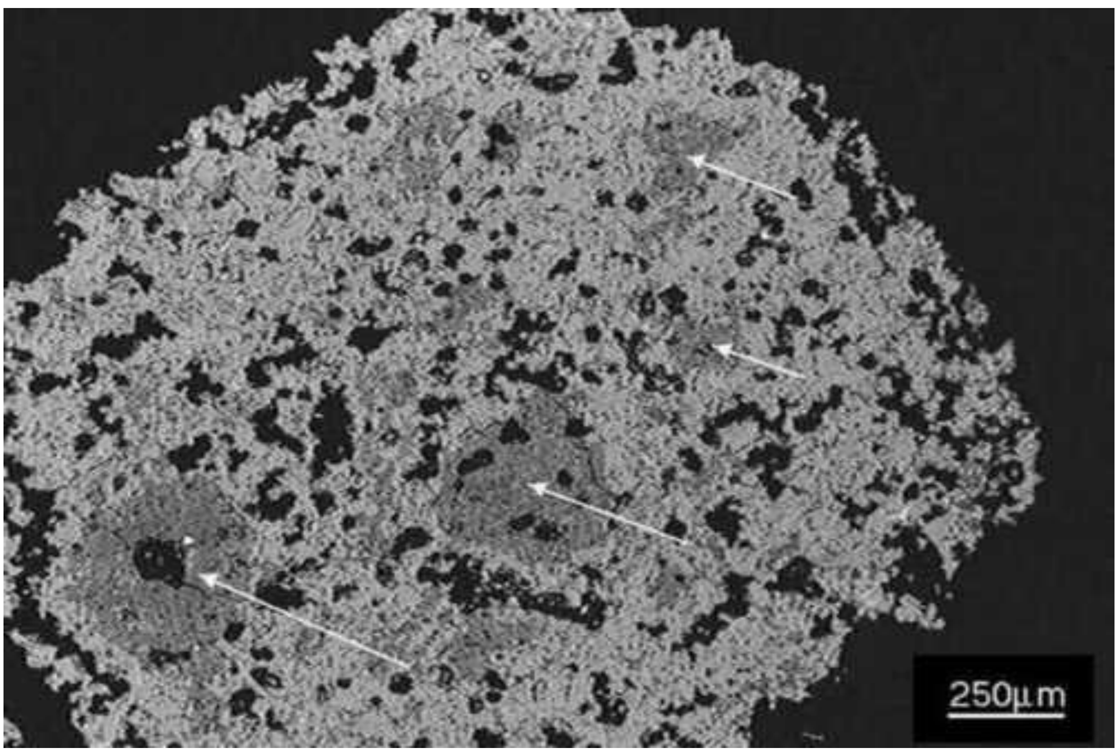


Figure 15: polished section of nodules, light grey color [10]

3.4.1. Nodules ranges

Nodules range in size from 1mm to 25mm or more and are composed mainly of calcium silicates, typically 70%-80%. The strength of concrete is mainly due to the reaction of these calcium silicates with water [10]

3.5. Cement milling

In cement milling stage the clinker cement is mixed with gypsum which added as a set retarder and then ground.

3.6. Project Milestone / Gant Chart of FYP2

No	Detail/Week	1	2	3	4	5	6	7	Mid-semester break	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	Briefing & update on student progress																						
2	Project work commences																						
3	Submission of Progress Report																						
4	PRE-EDX combined with seminar/ Poster Exhibition/ Submission of Final Report (CD Softcopy & Softbound)																						
5	EDX																						
6	Final Oral Presentation																						
7	Delivery of Final Report to External Examiner / Marking by External Examiner																						
8	Submission of hardbound copies																						

Milestone
Process

CHAPTER 4

RESULT & DISCUSSION

Major raw material, limestone is crushed to small grains, and then grinded to powder form 63 microns using SIVE shaker at civil engineering department laboratory. The powder is sent off to XRF laboratory for testing components or elements of limestone as showing in the table below.

4.1. Chemical composition of limestone

Limestone is a major of raw materials of producing Portland cement and its chemical compositions showed in table 1.

O	Al	Si	Ca	O	MgO
-100.0 KCps	1.9 KCps	2.4 KCps	460 KCps	-1000.0 KCps	0.3 KCps
30	2.4	1.5	65.94	6.200	0

Table 1: chemical compositions of limestone

4.2. Chemical composition of clay

Clay is considered as a minor of raw material of producing Portland cement, type G class. The clay is also grinded to powder and sent to XRF test.

O	Al	Si	P	K	Ca	Ti	Mn	Fe	Co	Eu	P_2O_5	K_2O
- 1000.0 KCps	21.6 KCps	9.8 KCps	1.9 KCps	5.2 KCps	5.6 KCps	6.8 KCps	22.0 KCps	642.3 KCps	19.1 KCps	50.7 KCps	1.9 KCps	5.2 KCps
41	23.8	7.97	0.92	0.663	0.641	0.553	0.844	17.68	0.173	5.76	4.585	0.798

Table 2: chemical compositions of clay

4.3. Chemical composition of iron ore

Iron ore is also considered as third minor raw material for producing Portland cement, the iron ore is ground and sent a sample to XRF analysis as showed in the table 3. From this raw material alumina (Al_2O_3) and ferrous oxide (Fe_2O_3) are obtained.

O	Al	Mn	Fe	Co	Eu	SiO_2
-100.0 KCps	3.2 KCps	5.9 KCps	1376.1 KCps	39.8 KCps	12.0 KCps	0.9 KCps
32	6.62	0.253	59.33	0.316	1.67	0

Table 3: chemical composition of iron-ore

4.4. Chemical composition of raw mixture (limestone +clay + iron ore)

The proportions or chemical compositions of raw mixture raw materials for manufacture of Portland cement were fixed such as in LSF is 94.0, SM is 2.4 and IM is 1.7 and then were ground together. The process of mixing raw materials for producing Portland cement G class as showed below

Lime Saturation Factor	Silica Modulus	Iron Modulus
94.0	2.4	1.7

Lime Saturation Factor	Silica Modulus	Iron Modulus
1.00Kg	0.026Kg	0.018Kg

Where lime saturation factor is taken as a base for division to reached a suitable proportion of each raw material (limestone, clay and iron-ore).

Figure 16: A mixture of raw materials ready for clinkering

Before the clinker process took place, a sample of mixture of raw material sent to XRF. In addition, the raw materials are mixed manually since no a mixture machine for a small scale of producing cement. The XRF chemical analysis result of mixture raw materials is showed in the table 4

O	Al	Si	Ca	Fe	Co	SiO_2
-1000.0 KCps	5.9 KCps	3.4 KCps	311.7 KCps	330.7 KCps	10.2 KCps	3.4 KCps
33	7.33	2.42	38.41	18.92	0.146	5.18

Table 4: chemical composition of raw material.

4.5. Clinker process

Figure 17: outside view of Furnaces, civil Engineering laboratory

Figure 18: inside view of furnace, Civil Engineering laboratory

The mixture of raw material is put inside the furnace with maximum temperature 1200C^{o} for two hours. As known, the requested temperature degree for Portland cement clinker is at least 1450C^{o} therefore, the chemical reaction could not take place as the temperature is less than 1450C^{o}. the cement clinker is showed in the figure 20 below

Figure 19: Portland cement clinker at temperature 1200C^{o}

4.6. Clinker analysis

A sample of clinker cement is sent to XRF analysis, and the mineral compositions as in showed in table 5

O	Al	Si	Ca	Cr	Mn	Fe	Co	Ni	Al_2O_3	Cl
32	4.72	15.5	48.93	1.05	1.05	19.91	0.144	0.340	5.251	0

Table 5: XRF clinker analysis

From table 5, we have

a) Ca= 48.93, O = 32

Then $Ca+O_2 \longrightarrow CaO$

Using chemical formula to find the weight percentage of Ca

CaO = 48.93+ 32 = 80.93

Therefore, the weight percentage of Ca is

(48.93/80.93) * 100 = 61%

b) Si = 15.5, O = 32

So, $Si+O_2 \longrightarrow SiO_2$

Using the chemical formula to get weight percentage of Si

SiO_2 = 15.5+ 2(32) = 79.5

Thus, Si = (15.5/79.5) * 100 = 19.5%

c) Al= 4.72 , O = 32

$Al + O_2 \longrightarrow Al_2O_3$

Using the chemical formula, we get

$Al_2O_3 = 2(4.72) + 3(32) = 105.44$

Weight percentage of Al is

(4.72/105.44) * 100 = 4.48%

d) Fe = 6.7, O = 32

$Fe + O_2 \longrightarrow Fe_2O_3$

$Fe_2O_3 = 2(6.7) + 3(32) = 109.4$

Hence, we get

Fe = (6.7/109.4) * 100 = 4.21%

e) Compound of oxide as a summary

CaO	Si_2O	Al_2O_3	Fe_2O_3	Unit
61	19.5	4.48	4.21	wt%

5.6.1. Bogue calculation

Bogue equation is used to calculate the approximate proportions of the four main minerals in Portland cement as per the following formula below.

1. $C_3S = 4.0710CaO-7.6024SiO_2-1.4297Fe_2O_3-6.7187Al_2O_3$
2. $C_2S = 8.6024SiO_2+1.1Fe_2O_3+5.0683Al_2O_3-3.0710CaO$
3. $C_3A = 2.6504Al_2O_3-1.6920Fe_2O_3$
4. $C_4AF = 3.0432Fe_2O$

i. Calculate Tricalcium silica (C_3S)

C_3S = 4.0710(61) – 7.6024(19.5) – 1.4297(4.21) – 6.7187(4.48) = 63.97

ii. Calculate Dicalcium silica (C_2S)

8.6024(19.5) +1.1(4.21) +5.0683(4.48)-3.0710(61) = 7.75

iii. Calculate Tricalcium aluminate (C_3A)

C_3A = 2.6504(4.48)-1.6920(4.21) = 4.74

iv. Calculate Teracalcium almunio-ferrate (C_4AF)

C_4AF = 3.0432(4.21) = 12.81

5.6.2. Comparison

The comparison between expected and obtained results for clinker analysis in table 6 and 7

Expected Oxide	Unit , wt%	Obtained oxide
CaO	65.6	61
SiO_2	21.5	19.5
Al_2O_3	2.8	4.48
Fe_2O_3	5.2	4.21

Table 6: compound oxide

Compound	C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
Clinker expected	64.7	12.9	9.0	8.5
Clinker obtained	63.79	7.75	4.74	12.81

Table 7: Composition of Portland cement clinker for making the cement

Figure 20: gypsum ground to fine powder form

It is about 9% of gypsum is added to the clinker and then ground together to fine at least 63 micron. The figure 22 is referred to the produced cement.

Figure 21: produced cement

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The objective of this project is to study compositions of raw materials (limestone, clay and Iron ore) of producing Portland cement type G class. The first chapter of this report started with project background study, problem statements, objective and scope of work.

In second chapter of this report, literature review about cement manufacture, API cement classification, and raw materials of Portland cement. The third was under title “Methodology”. Methodology discussed about procedures of production cement started with quarried raw materials, preparation of raw materials to XRF test, clinkering process, and mil cement. Furthermore, the Methodology is presented flow chart of the project. This report followed by result and discussion about chemical compositions of raw materials, limestone, clay, iron ore and mix raw materials for Portland cement clinker .

It may be possible to obtain Portland cement form lenggong limestone as a major raw material combining with other minor raw materials such as clay and iron ore.

5.2. Recommendation

The final year project has been useful in cultivating and enhancing the skills and knowledge at hand. As final year student, the experience gained throughout this final year project process increase the student understanding in field of petroleum engineering. Furthermore, other skills were also developed in the process or methods of producing Portland cement,communication skills and individual work instead of deepening all the time on others. However, there were few areas needs improvements in solving some of problems faced such as lack of equipments (furnace with high temperature at least $1450C^{o,}$ and mixture machine of raw materials) for mixing, clinkering and milling cement.

For future study, it is recommended to continue on this research using a furnace with high temperature to complete the process of making Portland cement clinker which means the main process of producing cement flow-line, and then to proceed for physical properties of Portland cement class G, compressive strength, thickening time and fluid loss.

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Appendix A

Chemical symbols are abbreviated form of the names of chemical elements

Element	Symbol	Atomic weight
Hydrogen	H	1
Carbon	C	12
Oxygen	O	16
Neutron	N	18
Sodium	Na	23
Magnesium	Mg	26
Aluminium	Al	27
Silicon	Si	28
Phosphorus	P	31
Sulfur	S	32
Chlorine	Cl	35.5
Potassium	K	39
Calcium	Ca	40
Titanium	Ti	48
Chromium	Cr	52
Manganese	Mn	55
Iron	Fe	56