CIVIL ENGINEERING DEPARTMENT

FINAL YEAR PROJECT II

FINAL DISSERTATION

INVESTIGATION ON THE USE OF THERMAL TREATED REFINERY SLUDGE AS CEMENT REPLACEMENT MATERIAL

Prepared by

Wan Nur Hasniza Binti Wan Mustapha

14886

Supervisor:

ASSOC. PROF. DR. MOHAMED HASNAIN ISA

INVESTIGATION ON THE USE OF THERMAL TREATED REFINERY SLUDGE AS CEMENT REPLACEMENT MATERIAL

by

WAN NUR HASNIZABINTI WAN MUSTAPHA

14886

Dissertation submitted in partial fulfillment of

the requirements for the

B.ENG. (HONS) CIVIL ENGINEERING

FYP II JANUARY 2015

Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar,

Perak Darul Ridzuan,

Malaysia

ACKNOWLEDGEMENT

My deepest gratitude to Allah The Most Gracious and Merciful for the guidance and blessings I am able to complete my final year project successfully and succeed to produce this report for Universiti Teknologi Petronas (UTP).

I would like to thanks to my supervisor, Assoc. Prof. Dr. Mohamed Hasnain Isa for being very proactive assisting and supporting throughout 8 months of final year project. It has been a valuable experience working under his supervision because he gave the best guidance, attention and encouragement throughout this course.

Not to forget, a million thanks to Assoc. Prof. Dr. Nassir Shafiq who had provided me with all the required information and for motivating me to perform my very best for this project.

My most sincere appreciation is also dedicated to all staff of Universiti Teknologi PETRONAS especially Civil Engineering Department staff member: Miss Rahimah, Mr Zaaba, Mr. Anuar, Mr Johan, Mr Ruzaimi, for their continued support, supervision and involvement to the success of this project. With the full cooperation from them, I have successfully accomplished the objective of final year project. I would like to thank PETRONAS Penapisan Terengganu Sdn. Bhd. through Mr. Hisham Mustapa for his kind cooperation in collecting refinery sludge.

Last but not least, I would like to express my deepest appreciation to my parent and siblings for their true support, understanding and keep motivating me in whatever I do in my life.

It would not be possible for me to go through my working environment without the uncountable help and support from all of them and thus completing the final year project.

ABSTRACT

Nowadays, oil and gas industry is one of the major industry that give the highest beneficial in economy for every country. However, petrochemical industry that conducting refining process produces refinery sludge which normally contaminated waste products that contains high hydrocarbons as well as heavy metals. The effluents are produced during the refining processes which have to be treated in systematic process and procedures.

Refinery sludge is the major solid wastes that have been produced in the oil and gas industry. Because of its hazardous and bad effects towards humans and environment, the best initiatives and treatments of refinery sludge have the serious attention around the world. Countless methods have been explored for handling and treating with refinery sludge. Some of the traditional methods and processes to treat refinery sludge are commonly practiced such as mechanical methods, biological methods and physicochemical treatment. During the refining process, an amount of refinery sludge was collected to be treated. The refinery sludge has numerous quantities that mix of solids, water, and oil.

In this research, the author has explored the effectiveness of thermal treatment process by using Furnace in order to treat refinery sludge. An experimental works have been done on the refinery sludge that would be reused as partial replacement of Ordinary Portland Cement in concrete. In order to do research, the author has collected the refinery sludge samples from the sludge treatment plant of petroleum refinery in Terengganu, Malaysia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1: INTRODUCTION

1.1 Background Study

Oil sludge is defined as designated waste generated due to storage of crude, which contains oil, water and solids. The characteristics of the sludge changes depending on the ratio of different phases, the origin of the crude oil, or location of the accumulation. There are two types of sludge; sludge from Crude Oil and sludge from products [1].

Refinery sludge can be categorized as Hazardous Wastes under the Environment Protection Act and Hazardous Wastes Handling Rules. Refinery sludge cannot be disposed on landfill unless it has been treated [1].

Figure 1.1 shows polycyclic aromatic hydrocarbon as a compound of petroleum hydrocarbon.

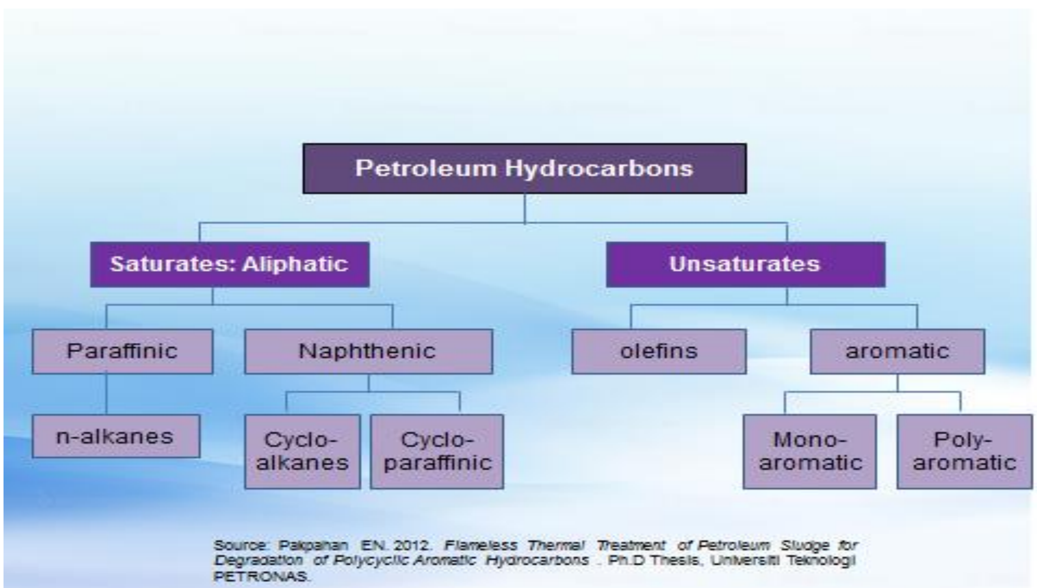


FIGURE 1.1 Polycyclic Aromatic Hydrocarbons (PAH)

FIGURE 1.2 A site sludge pit

Figure 1.2 shows disposal of refinery sludge to a landfill which leads to an unsafe environment.

Refinery sludge is a major solid waste from petroleum industry. It is a complex mixture of many petroleum hydrocarbons (PHCs), heavy metals, water and solid particles. The worlds start to give their attention to prevent and cure the hazardous effect of refinery sludge by having the most effective process of refinery treatment [2].

Petroleum sludge is a hazardous waste which contains Polycyclic Aromatic Hydrocarbons (PAH), which contains toxic and carcinogenic-mutagenic characteristics. Thermal treatment has been proven to be a good method that could completely degrade all priority PAH. [3].

Moreover, the thermal treatment is beneficial saving about 40% in cost operation compares to common incineration methods. Incineration by using diesel fuel is approximately cost about RM 6.80 per hour of operation while thermal treatment process cost about RM4.00. [3].

Some of conventional disposal methods of refinery sludge waste are such as landfills or incineration. However, this kind of method may require huge space while the soil needs to be sealed properly in order to avoid the leaching of harmful and chemical compounds. Refinery sludge normally has mainly heavy organic matters and high amount of combustible matters [4].

Incineration is one of the thermal treatments of refinery sludge. It commonly reduces a huge amount of sewage or refinery sludge and can increase thermal efficiency. However, usually the costs to control the air pollution are very high because of the treatment of large volume flue gas. With its unique characteristics to break down large molecules into smaller ones, pyrolysis has been proven to be an alternative to the disposal of many wastes such as plastic waste, biomass, municipal solid waste, and other solid wastes [4].

Table 1.1 shows the 16 PAHs as priority compounds that have been identified byThe US Environmental Protection Agency (USEPA).

TABLE 1.1 The 16 priority of PAH

Table 1—16 priority polycyclic aromatic hydrocarbon (PAH) compounds

Compounds	Abbreviation	Formula / mol wt	Number of rings	TEF
Naphthalene	Nap	$C_{10}H_8$ / 128	2	0.001
Acenaphtylene	Acy	$C_{10}H_8$ / 152	3	0.001
Acenaphthene	Ace	$C_{10}H_{10}$ / 154		0.001
Fluorene	Flu	$C_{13}H_{10}$ / 166		0.001
Phenanthrene	Phe	$C_{13}H_{10}$ / 178		0.001
Anthracene	Ant	$C_{13}H_{10}$ / 178		0.01
Fluoranthene	Fla	$C_{16}H_{10}$ / 202	4	0.001
Pyrene	Pyr	$C_{16}H_{10}$ / 202		0.001
Benzo[a]Anthracene[a]	BaA	$C_{18}H_{12}$ / 228		0.1
Chrysene[a]	Chr	$C_{18}H_{12}$ / 228		0.01
Benzo[b]Fluoranthene[a]	BbF	$C_{20}H_{12}$ / 252	5	0.1
Benzo[k]Fluoranthrene[a]	BkF	$C_{20}H_{12}$ / 252		0.1
Benzo[a]Pyrene[a]	BaP	$C_{20}H_{12}$ / 252		1.00
Indeno[1,2,3-cd]Pyrene[a]	Ind	$C_{22}H_{12}$ / 276	6	0.1
Dibenzo[a,h]Anthracene[a]	DbA	$C_{22}H_{14}$ / 278		5.0
Benzo[g,h,i]Perylene	BPer	$C_{22}H_{12}$ / 276		0.01

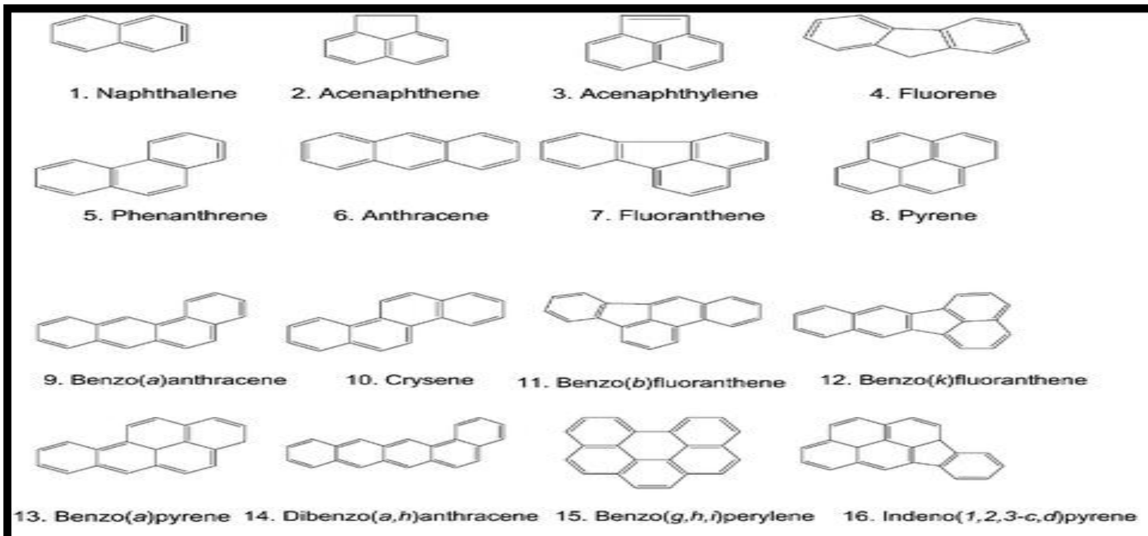


FIGURE 1.3 Chemical structures of the 16 priorities PAH compounds

1.2 Problem Statement

There are various methods in refinery sludge treatment that have been studied in order to deal with PHCs in oily sludge such as the treatment through oil recovery and sludge disposal. During the past years, a lot of studies have been made in refinery sludge treatment for example landfarming, incineration, solidification/stabilization, solvent extraction, ultrasonic treatment, pyrolysis, photocatalysis, chemical treatment, and biodegradation. The application of these methods may reduce or eliminate the contents of hazardous constituents, and environmental and health effect can be controlled. However, due to the recalcitrant nature of oily sludge, few technologies can reach a compromised balance between satisfying strict environmental regulations and reducing treatment costs [2].

Solvent extraction has been widely used in order to remove semi volatile and non-volatile organic compounds in soil/water matrices. This method signifies a simple and efficient method to separate refinery sludge into valuable hydrocarbon and the volume of a solid or semi-solid residue can be reduced. One major challenge in applying solvent extraction to field-scale refinery sludge treatment is that organic solvent has to be collected in large amounts. This definitely may give the impact in economic and environmental concerns [2].

Other than that, centrifugation is another treatment of refinery sludge that has been applied in this oil and gas industry for recent years. However, this method may need high energy consumption in order to produce strong centrifugation force to discrete oil from petroleum sludge. Moreover, it will also increase the cost of treatment process as well as give bad impact towards environmental [2].

Other than that, thermal treatment using oxygen-containing gas use the refinery sludge from a petroleum refinery plant as the raw material. Unfortunately, the result shows that the effects of oxygen at the concentrations studied are not significant at temperatures below 613 K [5].

Research has proved that three to five percent of all crude oil that have been produced are not usable. When the crude oils are transported in ships or stored in tanks, the sludge will settle to the bottom of the tank. The problem is when the sludge cannot be drained from the tanks and must be removed and transported which may result in high cost. That expense is, in part, the cost of hiring crews to remove the sludge from the tanks. A greater part of the expense is the disposal fee associated with the environmentally-unfriendly material. Large volumes of sludge are also formed at refineries and oil extraction sites. Accidents in the transportation of oil and petroleum products also add to environmental contamination. In a less-than-wise regime of environmental protection and resources conservation, large open spaces and easily accessible raw materials made the situation perverse on a national scale [6].

In Malaysia, a typical petroleum refinery with a production capacity of 105, 000 barrels per day produces about 50 tons oil sludge per year. [9]

1.3 Objectives

There are two main objectives of this research are discussed below:

1. To characterize ash obtained from thermal treatment of petroleum sludge.

2. To assess the potential for reuse of petroleum sludge as partial replacement material for Ordinary Portland Cement (OPC).

1.4 Scope of Study

The research involved thermal treatment of refinery sludge using furnace. Other than that, it focused on characterization of residue (ash) and last but not least systematically investigated the potential reuse of residue as cement replacement material in concrete.

CHAPTER 2: LITERATURE REVIEW

Petroleum sludge in Malaysia is regulated in year 2005 under the Environmental Quality Act Regulation as a restricted schedule waste f its storage, transportation and disposal. Therefore the refinery sludge must be notified when dispose, treatment (residue), and recovery shall be at prescribed premises only. The waste has the potential consequences of release of toxic substances in certain cases. [3]

2.1 Degradation of Refinery Sludge Using Thermal Treatment

In the thermal treatment or incineration process, the effectiveness of PAH degradation mainly depends on factors such as temperature, air (oxygen) availability and catalyst inclusion as then a number thermal treatment studies employing additives for enhanced degradation of PAH.

The optimum condition for PAH degradation from petroleum sludge cake was obtained Ca(OH)2 (1.13mole) + NaHCO3 (1.13mole) (1:1) additive and 496^{0}C treatment temperature. Thermal process is beneficial saving of abut 40% in cost operation compares to conventional incineration technique [3].

Pyrolysis of oil sludge first by thermogravimetry/mass spectroscopy (TG/MS) and then in a horizontal quartz reactor with an electrical laboratory furnace under different pyrolysis conditions was carried out. The influence of heating rate from 5 to 20 °Câmin-1, final pyrolysis temperature from 400 to 700 °C, various interval holding stage, and catalyst on the products were investigated in detail. The TG/MS results show that pyrolysis reaction of oil sludge starts at a low temperature of about 200 °C, and the maximum evolution rate is observed between the temperatures of 350-500 °C. Pyrolysis conversion can be promoted by a higher final pyrolysis temperature, an interval holding stage, and adding catalyst [4].

The thermal treatment, the effectiveness of PAH degradation is based on the temperature, air and additives that have been used in the treatment. Table 2.1 shows the effect of temperature on thermal treatment of refinery sludge.

TABLE 2.1 Effect of temperature on formation and degradation of PAH

Table 2.1 Effect of temperature on formation and degradation of PAH

Temperature	Formation				Degradation				Reference
	Selected PAH (number of rings)								
	3	4	5	6	3	4	5	6	
T ≤ 100°C	not discussed				●	●			(Magoha, 2004)
300°C ≤ T ≤ 500°C	thermodesorption								(Kopinke and Remmler, 1995)
		●	●		●	●			
	polymer degradation								(Kwon & Castaldi, 2005)
	●	●		●	not discussed				
600°C ≤ T ≤ 1000°C	fluidized bed, excess air								(Liu et al., 2001)
	●	●	●		not discussed				
	without additive								(Wheatley & Sadhra, 2004)
	●	●			not discussed				
600°C ≤ T ≤ 1000°C	with additive								(Wheatley & Sadhra, 2004)
			●		not discussed				
T ≥ 1000°C	pyrolysis (oxygen-free heating under He~1000°C)								(Pope et al., 2000)
	●	●				●	●		
	pyrolysis ~1100°C								(Pope et al., 2000)
		●					●		
	direct burning (calcination ~1300°C)								(Pope et al., 2000)
	●	●					●	●	

2.2 Oxidative Thermal Treatment

In this research paper, the refinery sludge from a petroleum refinery plant which situated at northern Taiwan is used as the raw material in thermal treatment using oxygen-containing gas. The treatment of refinery sludge is done by the use of carrier gas with various concentration of oxygen in the temperature range of 380-1123 K and at various constant heating rates of 5.2, 12.8, and 21.8 K/min. This study greatly assists the utilization of oil sludge as an energy resource [5].

2.3 Polycyclic Aromatic Hydrocarbon (PAH) in Refinery Sludge

Polycyclic aromatic hydrocarbons (PAH) can be defined as chemicals that can be found in two groups or more. PAH can be found in the natural environment and PAH can also be created by human. PAH is created by the incomplete burning process of products like oil, gas, and garbage.

According to Environmental Protection Agency of United States (2008) stated that the National Waste Minimization Program defines this group using the Toxic Release Inventory reporting category for polycyclic aromatic compounds. Chemicals included in this category, by name and CAS number, are:

I. Benzo(a)anthracene, 56-55-3
II. Benzo(a)phenanthrene (chrysene), 218-01-9
III. Benzo(a)pyrene, 50-32-8
IV. Benzo(b)fluoranthene, 205-99-2
V. Benzo(j)fluoranthene, 205-82-3
VI. Benzo(k)fluoranthene, 207-08-9
VII. Benzo(j,k)fluorene (fluoranthene), 206-44-0
VIII. Benzo(r,s,t)pentaphene, 189-55-9
IX. Dibenz(a,h)acridine, 226-36-8
X. Dibenz(a,j)acridine, 224-42-0
XI. Dibenzo(a,h)anthracene, 53-70-3

XII. Dibenzo(a,e)fluoranthene, 5385-75-1
XIII. Dibenzo(a,e)pyrene, 192-65-4
XIV. Dibenzo(a,h)pyrene, 189-64-0
XV. Dibenzo(a,l)pyrene, 191-30-0
XVI. 7H-Dibenzo(c,g)carbazole, 194-59-2
XVII. 7,12-Dimethylbenz(a)anthracene, 57-97-6
XVIII. Indeno(1,2,3-cd)pyrene 193-39-5
XIX. 3-Methylcholanthrene, 56-49-5
XX. 5-Methylchrysene, 3697-24-3
XXI. 1-Nitropyrene, 5522-43-0
XXII. It should be noted that some PAHs are listed individually on EPA's Priority Chemical list.

They are:

I. Acenaphthene, 83-32-9
II. Acenaphtylene, 208-96-8
III. Anthracene, 120-12-7
IV. Benzo(g,h,i)perylene, 191-24-2
V. Fluorene, 86-73-7
VI. Phenanthrene, 85-01-8
VII. Pyrene, 129-00-0

One research has been done that resulted PAHs can cause tumors to laboratory animals that were exposed to PAHs through their food, by breathing the contaminated air, and when the PAHs were applied to their skin. When pregnant mice ate high doses of a PAH (benzo(a)pyrene) they will have reproductive problems. Moreover, the offspring of the pregnant mice may have birth defects and a decrease in their body weight. Other effects are such as damage to the skin, body fluids, and the immune system. However, these effects have not been seen in humans [6].

PAHs are a concern because they are persistent. PAHS cannot be burn easily, they may stay in the environment for long periods of time. Individual PAHs have different behavior. Some of them can transfer into a vapor in the air very easily. However, most of them do not break down easily in the water [7].

However, many researchers have proved that PAH has their own used especially in the making of dyes, plastics and as ingredient in medicines.

2.4 Reuse of petroleum sludge cake residue ash

Potential application of the residue was investigated to be used as cement replacement material in concrete. Standard mortar cubes were prepared by mixing Ordinary Portland Cement (OPC) with partial replacement of the residue, whereby at 10% replacement exhibited about 100% higher compressive strength at all ages as compared to that of the control mix with 0% ash. [3]

2.5 Cement Replacement Material

Sustainability is an important issue all over the world. Carbon dioxide emission has been a serious problem in the world due to the greenhouse effect. Today many countries agreed to reduce the emission of CO_2. Many phases of cement and concrete technology can affect sustainability. Cement and concrete industry is responsible for the production of 7% carbon dioxide of the total world CO_2 emission. [10]

Sawdust is a waste product from the timber industry. Research work carried out on the ash derived from the sawdust has confirmed its pozzolanic properties with a pozzolanic index value of 75.9%. Performance of the ash–portland cement mixture has been evaluated with respect to setting time, workability and compressive strength. From the results obtained, 10% replacement of cement with SDA shows good performance giving the desired workability and strength. [11]

2.6 Critical Analysis

Based on the previous research papers, every method of PAH degradation has their own advantages and disadvantages. The research has come out to treat the refinery sludge by using thermal treatment with selective additives and at the same time has reused refinery sludge as partial replacement material for Ordinary Portland Cement in concrete.

CHAPTER 3: METHODOLOGY

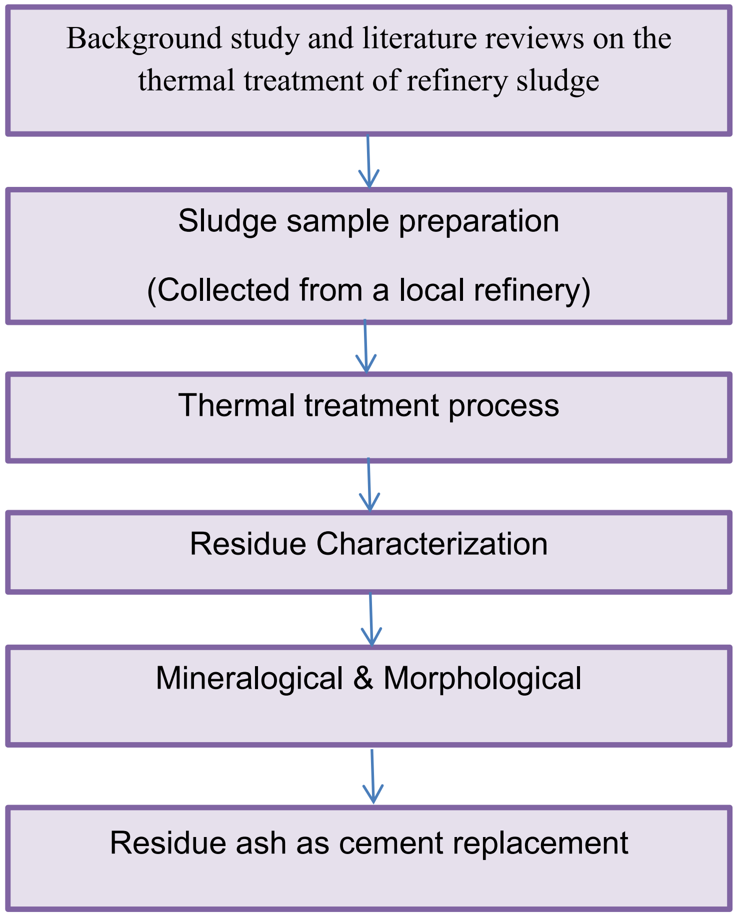


FIGURE 3.0 Flow Diagram of Experimental Work of the Research

3.1 Experimental

3.1.1 Petroleum Sludge Cake Collection

Petroleum sludge cake was collected from the Decanter unit in Waste Water Treatment Plant (WWTP) of a local petroleum refinery in Terengganu, Malaysia.

3.1.2 Petroleum Sludge Cake Thermal Treatment

In the research, 1 kg of petroleum sludge cake was manually mixed with 170.2 g calcium hydroxide (2.3 moles) and 193.2 g sodium bicarbonate (2.3 moles). After that, the sample was placed in a glass crucible. The amount of each batch must not exceed half of the volume of crucible to ensure every surface of the sample was completely heated. The sample was then heated in a furnace at 500 ^{0}C for 40 minutes duration. If the sludge was mixed with the additives, it must be treated on the same day because the sample will not have the same condition and texture on the next day.

The use of Calcium Hydroxide and Sodium Bicarbonate as additives was beneficial and a temperature of 450 ^{0}C was suitable for PAH degradation. [8]

FIGURE 3.1 Furnace

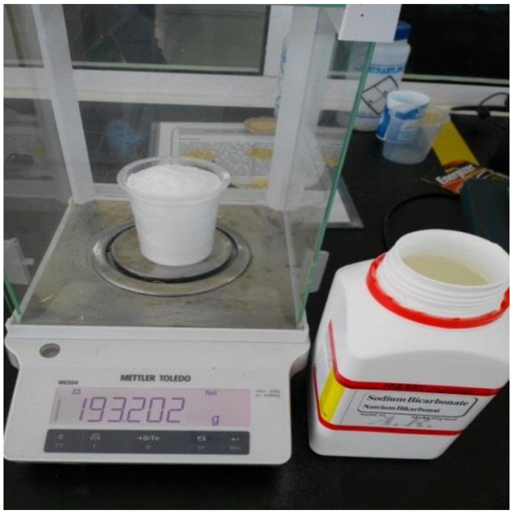


FIGURE 3.2 Sodium Bicarbonate

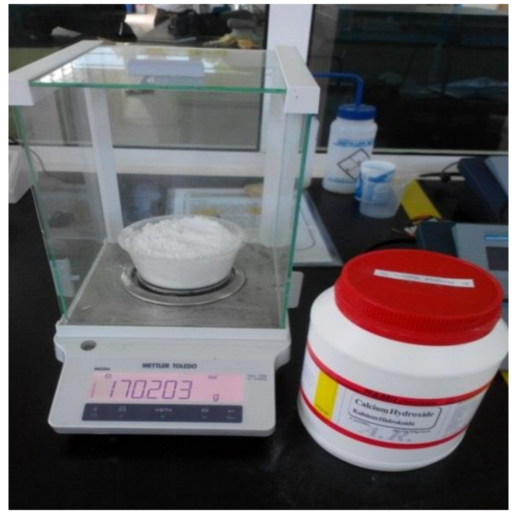


FIGURE 3.3 Calcium Hydroxide

FIGURE 3.4 Mix of Petroleum Sludge with Additives

FIGURE 3.5 Treated Residue Ash

FIGURE 3.6 Residue Ash before Grinded

FIGURE 3.7 Residue Ash after Grinded

3.1.3 Reuse of Petroleum Sludge Cake Residue

The residue was obtained from the thermal treatment at 500 ^{0}C of petroleum sludge cake in the presence of additive Calcium Hydroxide and Sodium bicarbonate (1:1). After that, the residue have been grinded by using grinder machine and passed through sieve 250 micrometers. The experiment conducted by mortar made with varying amounts of residue ash as cement replacement. With exception of the control, the cement and residue were mixed prior to mixing with sand and water. After addition of water, the mixture was re-mixed and placed in the mould, then vibrated three times in order to achieve homogenous and compacted mortar.

Mortar cubes were casted in prismatic standard steel mould of dimensions 50 mm x 50 mm x 50 mm. After casting the mixtures moulds, they were exposed, covered and left for 24 hours. On the next day, the cubes were de-mould and transferred into water-bath for curing treatment.

After characterization of ash, the next step is to determine its viability and sustainability as cement replacement material. For that reason, first thing first is to determine its effect on compressive strength development until the age of 28 days. Other than the compressive strength, other mechanical properties have been investigated such as the compressive strength test for the mortar followed ASTM C-109. Moreover, the residue has been tested by using X-ray fluorescence (XRF) technique, X-ray Diffractometer (XRD) and FESEM/EDX.

CHAPTER 4 PROJECT PROGRESS & FUTURE WORK

4.1 Project Progress

The project consists of two phase of laboratory work according to two different objectives of this project. First phase is thermal treatment of petroleum sludge and the second phase is reuse of petroleum residue (ash) as cement replacement material in making concrete. The overall progress for this semester went right on track but there were short delay due to circumstances. The first six weeks cover the procurement of apparatus and materials, collection of petroleum sludge from refinery plant in Kerteh, Terengganu and the thermal treatment of the petroleum sludge. On the 7th week, the petroleum residues (ash) were grinded by using grinding machine which passed through the sieve size 250 micrometers. While on the 8th week, the next phase was done by casting the mortar cubes of dimensions 50 mm x 50mm x 50 mm. The cement and residue were mixed with sand and water with different variation composition of mortar mixture. The mortar cubes were placed in water-bath for curing treatment and have been tested after 7, 14, 21 and 28 curing days.

After completing the first and second phase of laboratory work, the samples were tested in Universiti Malaysia Pahang for XRF and XRD test while FESEM test has been carried out in Universiti Teknologi PETRONAS. The compressive strength of the mortar were tested after 7, 14, 21 and 28 curing days.

4.3 Key Milestones

4.3.1 Lab work (Week2-Week7)

4.3.2 Submission of Progress Report to Supervisor (Week 7)

4.3.3 Pre-SEDEX (Week 12)

4.3.4 Dissertation (Week 12)

4.3.5 Technical Report (Week 13)

4.3.6 VIVA (Week 14)

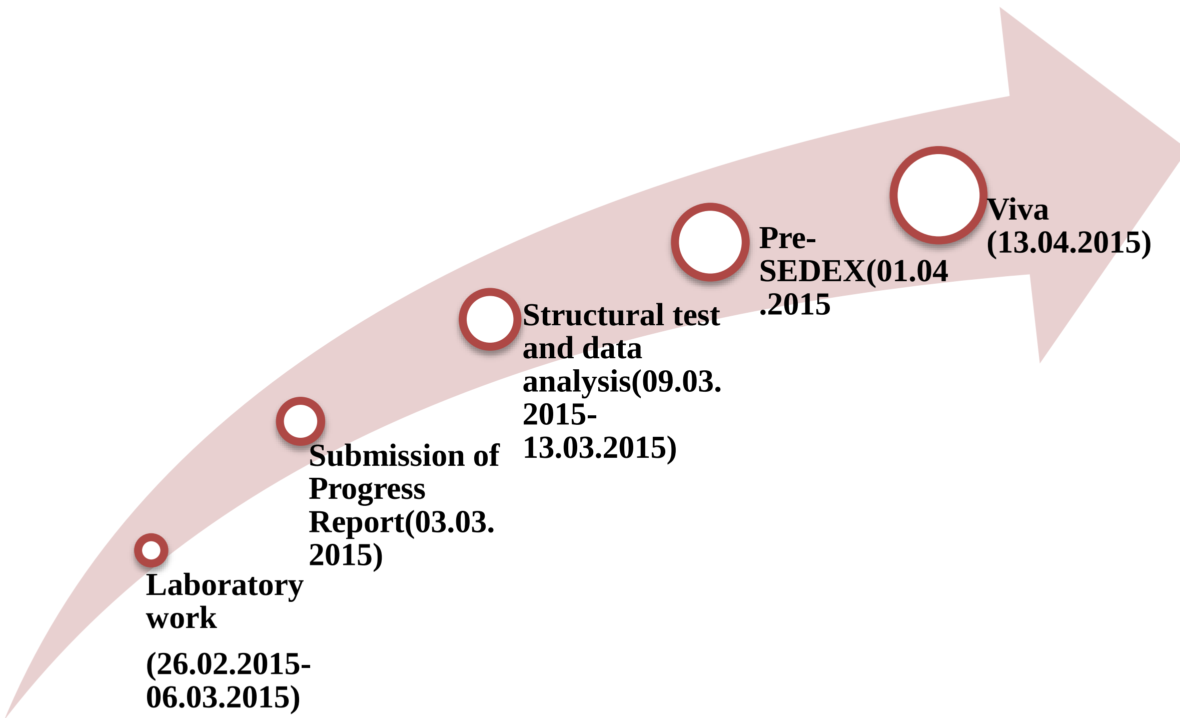


FIGURE 3.8 Key Milestones of The Project

4.4 Project Timeline

4.4.1 Gantt Chart (FYP 1)

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Preliminary Research Work and Preparing proposal														
2.	Submission of Extended Proposal to Supervisor														
3.	Procurement of Split Tube Furnace														
4.	Proposal Defense														
5.	Submission of Final Interim Report After Correction														

4.4.2 Project Gantt Chart (FYP 2)

No.	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Petroleum sludge cake collection														
2.	Petroleum Sludge Cake Thermal Treatment														
3.	Reuse of Petroleum Sludge Cake Residue as cement replacement (Experiment)														
4.	Data Analysis														
5.	Pre-SEDEX														
6	Viva														

CHAPTER 5: RESULTS AND DISCUSSION

After having thermal treatment of the petroleum sludge, the final product of residue ash was produced about 40%-43% of the original weight of petroleum sludge that have been used. This project used 4 kg of petroleum sludge which gave final product of residue ash is 1.75 kg. The original state of petroleum sludge was in aqueous phase and oily but after the thermal treatment, the residue ash produced was in dry powder form.

Pakpahan (2012) stated that at 10% replacement of cement by petroleum residue ash exhibited about 60% higher compressive strength of standard mortar cube compared to the standard mortar cube without any ash.

In this project, the standard mortar cubes were tested for their compressive strength at 5%, 7.5% and 10% replacement of residue ash. The expected results from this test are 10% replacement of residue ash will give the highest compressive strength regarding to its optimum condition from previous study. Table 5.1 and Figure 5.1 show the result of compressive strength of mortar cubes for 7, 14, 21 and 28 days of curing. The results of this final year project (which after this will be stated as ‘2015’) have been compared with the result of Pakpahan et al.,2012 (which after this will be stated as ‘2012’).

The chemical compositions of residue ash were tested by using XRF technique and the amount of crystalline phase of residue ash was tested by using XRD test. FESEM test that has been done gave the images of microstructure of constituents in residue ash.

5.1 Compressive Strength of Mortar Cubes

The result of compressive strength of mortar cubes have been determined to measure the mechanical strength of the mortar cubes following ASTM C-109. The compressive strength results of mortar containing residue ash with variation of curing days were presented in Table 5.1 and Table 5.2. The results of compressive strength were plotted in Figure 5.1 and Figure 5.2 to show the comparison with control mortar (M0). The result in Table 5.1 shows that M0 had highest strength compared to the M5, M7.5 and M10. The higher the percentage of residue ash in mortar cubes, the lower the compressive strength. The trend remains the same up to 28 curing days. On the other hand, the result in Table 5.2 shows M5 and M10 have higher compressive strength compared to M0.

However, the compressive strength of control mortar (M0) in 2012 is higher than compressive strength of M0 in 2015. This is definitely because of the properties and condition of the cement at that different time. Strength of cement would be affected by its surrounding area such as humidity, temperature, time and others.

From this observation, the conclusion that can be made was different batch of petroleum sludge will have different chemical composition that affect the strength of the concrete. The difference in chemical composition will be discussed in the next topic.

TABLE 5.1 Compressive Strength of Mortar (Mpa) in 2015 (This study)

Code	**Curing days**			
	7 days	**14 days**	**21 days**	**28 days**
M0 (0%)	**20.58**	**21.12**	**23.96**	**25.22**
M5 (5%)	**17.46**	**14.16**	**19.56**	**20.50**
M7.5 (7.5%)	**14.24**	**13.25**	**14.36**	**16.70**
M10 (10%)	**9.08**	**13.04**	**12.9**	**15.42**

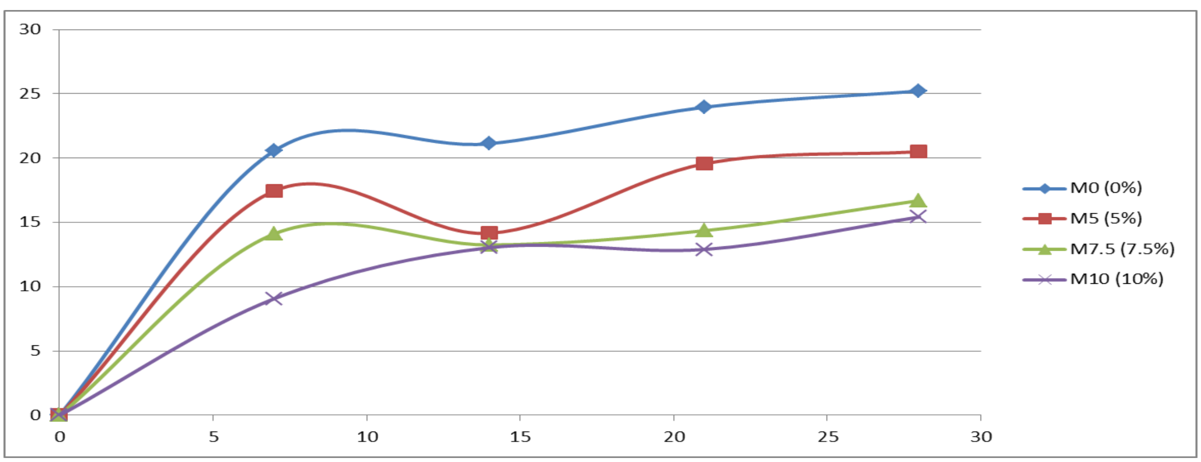


FIGURE 5.1 Compressive Strength of Mortar (MPa) in 2015 (This study)

TABLE 5.2 Compressive Strength of Mortar (Mpa) in 2012 (Pakpahan et al.,2012)

Code	**Curing Days**		
	7 days	**14 days**	**28 days**
M0 (0%)	**4.796**	**4.939**	**5.486**
M5 (5%)	**6.238**	**6.346**	**6.914**
M10 (10%)	**7.769**	**8.011**	**10.548**

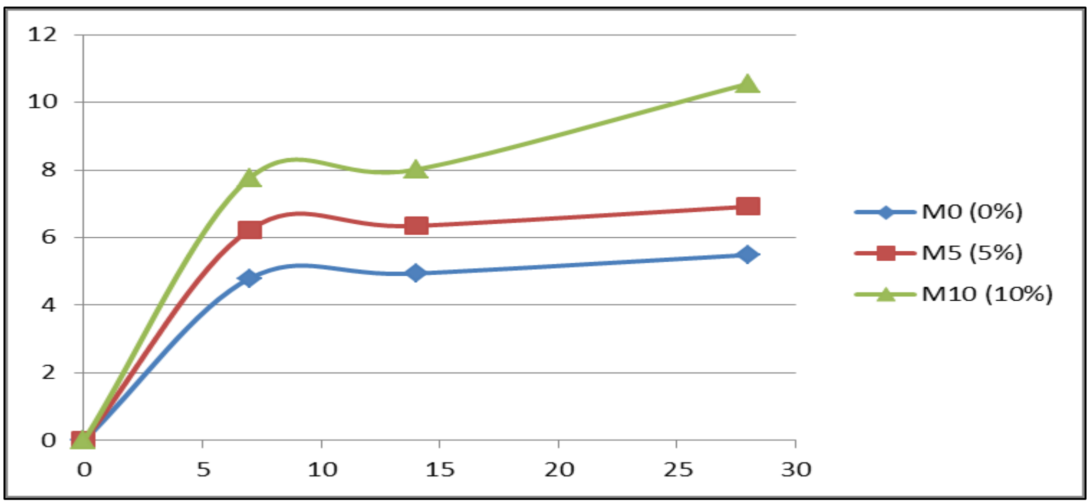


FIGURE 5.2 Compressive Strength of Mortar (MPa) in 2012 (Pakpahan et al.,2012)

5.2 Mineralogical and Morphological Characterization

X-ray fluorescence (XRF) analyzed the chemical composition of petroleum residue ash. Table 5.3 indicates the chemical composition of residue in 2015 while Table 5.4 indicates the chemical composition of residue in 2012. The composition of Silicon (Si), Aluminium (Al) and Iron (Fe) in residue ash during 2012 is about 65.97% while the composition of of Silicon (Si), Aluminium (Al) and Iron (Fe) in residue ash during 2015 is about 25.21%. The presence of these chemical constituents in residue ash is mainly responsible for the strength in concrete. Other than that, potassium (K) and Magnesium (Mg) composition in residue during 2015 are higher than the composition of residue in 2015. These elements will also responsible to improve the strength of mortar.

From this result, it shows the main reason of the difference between compressive strength of mortar in 2012 and in 2015. Even though the compressive strength of mortar in 2015 and in 2012 are different, the residue ash is still considered to be a passive pozzolan and can be used as cement replacement material in concrete.

Furthermore, the compressive strength of mortar in 2015 is higher than in 2012 is because of the Calcium content in the residue. The percentage of Calcium in residue during 2015 is about 52.48% while the percentage of calcium in residue during 2012 is 13.30%. This chemical is considered as a strength factor of mortar and as major factor in mortar quality.

Based on the results of XRF test in Table 5.3 and Table 5.4, it concludes that there is possibility to use the petroleum residue ash as material replacement for cement like fly-ash.

XRF TEST RESULT

TABLE 5.3 Chemical Composition of Residue in 2015 (This study)

Chemical Constituents	Composition (%)
Sodium (Na)	16.78
Potassium (K)	0.22
Magnesium (Mg)	0.29
Aluminium (Al)	7.77
Silicon (Si)	10.93
Iron (Fe)	6.51
Sulphur (S)	2.91
Calcium (Ca)	52.48
Phosphorus (P)	0.90

TABLE 5.4 Chemical Composition of Residue in 2012 (Pakpahan et al.,2012)

Chemical Constituents	Composition (%)
Sodium (Na)	7.53
Potassium (K)	1.93
Magnesium (Mg)	2.22
Aluminium (Al)	12.2
Silicon (Si)	47.28
Iron (Fe)	6.487
Sulphur (S)	3.61
Calcium (Ca)	13.30
Phosphorus (P)	1.93

XRD TEST RESULT

The quantitative analysis of X-Ray Diffraction (XRD) is obtained to characterize the crystalline phase of residue ash. Basically, XRD analysis would quantify the amount of crystalline phase of mineral content. The analysis is made by scanning in the 2-Theta range of 10-60^0 at an angular speed up to 1^0/minute.

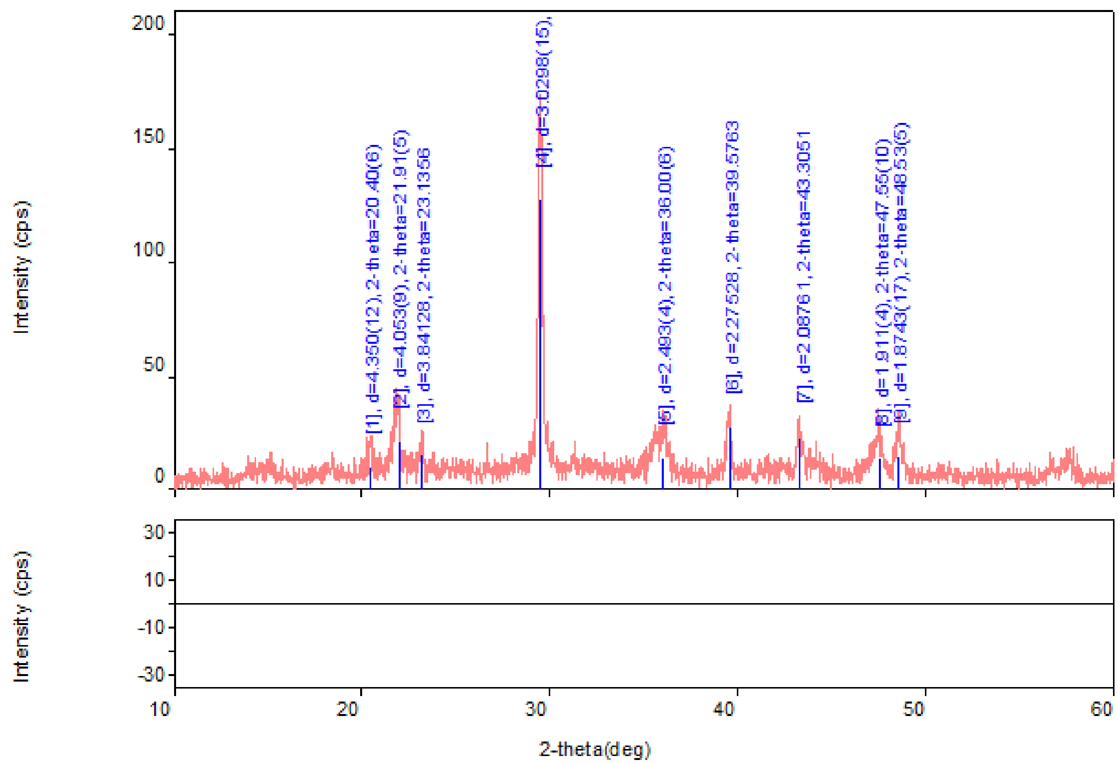


FIGURE 5.3 XRD Analysis of Residue

TABLE 5.5 XRD Analysis of Residue

2-theta (deg)	d (ang.)	Height (cps)	Size	Phase name
20.40(6)	4.350(12)	10(3)	452(98)	Aluminum Phosphate, (2,1,-3)
21.91(5)	4.053(9)	21(5)	261(38)	Boron, (0,0,3)
23.1356	3.84128	15.1935	261.32	Calcite, syn, (0,1,2), Aluminum Phosphate, (2,1,3)
29.457(15)	3.0298(15)	128(11)	520(49)	Calcite, syn, (1,0,4), Aluminum Phosphate, (7,1,2)
36.00(6)	2.493(4)	14(4)	105(8)	Calcite, syn, (1,1,0), Boron, (1,0,4), Aluminum Phosphate, (3,0,-10)
39.5763	2.27528	27.377	105.173	Calcite, syn, (1,1,3), Aluminum Phosphate, (14,1,-3)
43.3051	2.08761	23.2219	105.173	Calcite, syn, (2,0,2), Boron, (1,1,3)
47.55(10)	1.911(4)	13(4)	167(28)	Calcite, syn, (0,2,4)
48.53(5)	1.8743(17)	15(4)	304(37)	Calcite, syn, (1,1,6)

FESEM/EDX RESULT

FESEM/EDX images indicate the microstructure of constituents. Morphological character of the residue ash is shown in Figure 5.4. the micro-structure of residue ash magnified 1000 times, 5000 times and 10,000 times. The percentage of oxides in residue ash is high which is about 46.63% . The development in the properties of concrete with cement is attributed to the pozzlonic reactions taking place between the oxides content in the ash and the hydration products of ordinary portland cement (OPC). Figure 5.4 also shows the small size of particles as well as irregularly shape of residue that could decrease the void space of mixture and minimize the deformation.

Figure 5.6 shows the distribution of each elements in the residue ash. The well distributed elements such as Oxides, Carbon and Calcium indicates their huge amounts in the residue.

Figure 5.7 and Figure 5.8 show morphological images of residue ash in 2015 and 2012. Smaller particle sizes distribution as shown in Figure 5.8 compared to Figure 5.7 indicates that its better quality and ability to fill the pores of mixture.

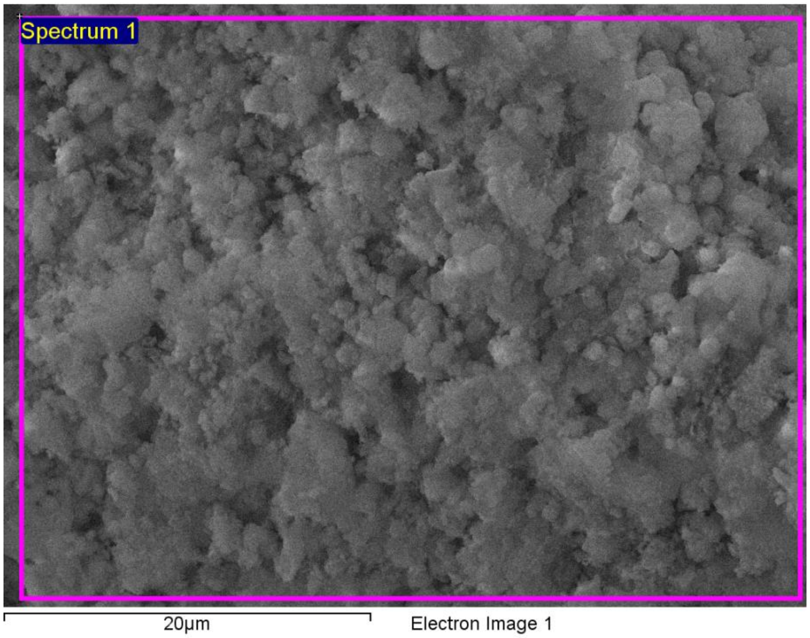


FIGURE 5.4 Electron Images of Residue

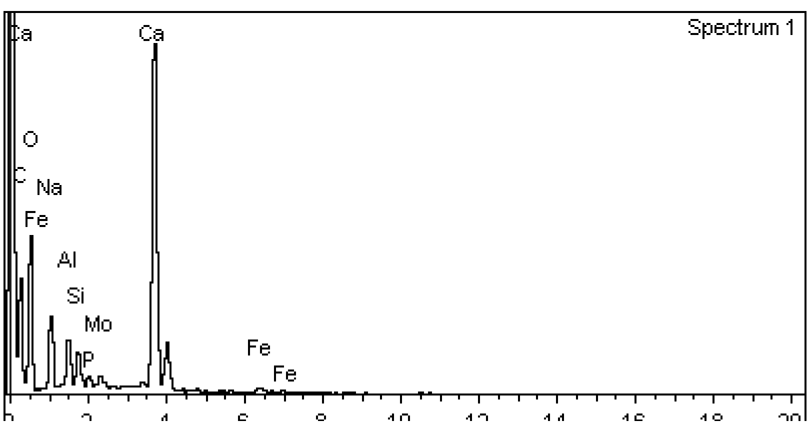


FIGURE 5.5 FESEM/EDX Analysis of Residue

TABLE 5.6 Element Composition of Residue

Element	Weight%	Atomic%
C K	20.76	31.03
O K	46.63	52.33
Na K	5.28	4.12
Al K	1.99	1.32
Si K	1.34	0.86
P K	0.43	0.25
Ca K	21.34	9.56
Fe K	0.86	0.28
Mo L	1.37	0.26
Totals	100.00	

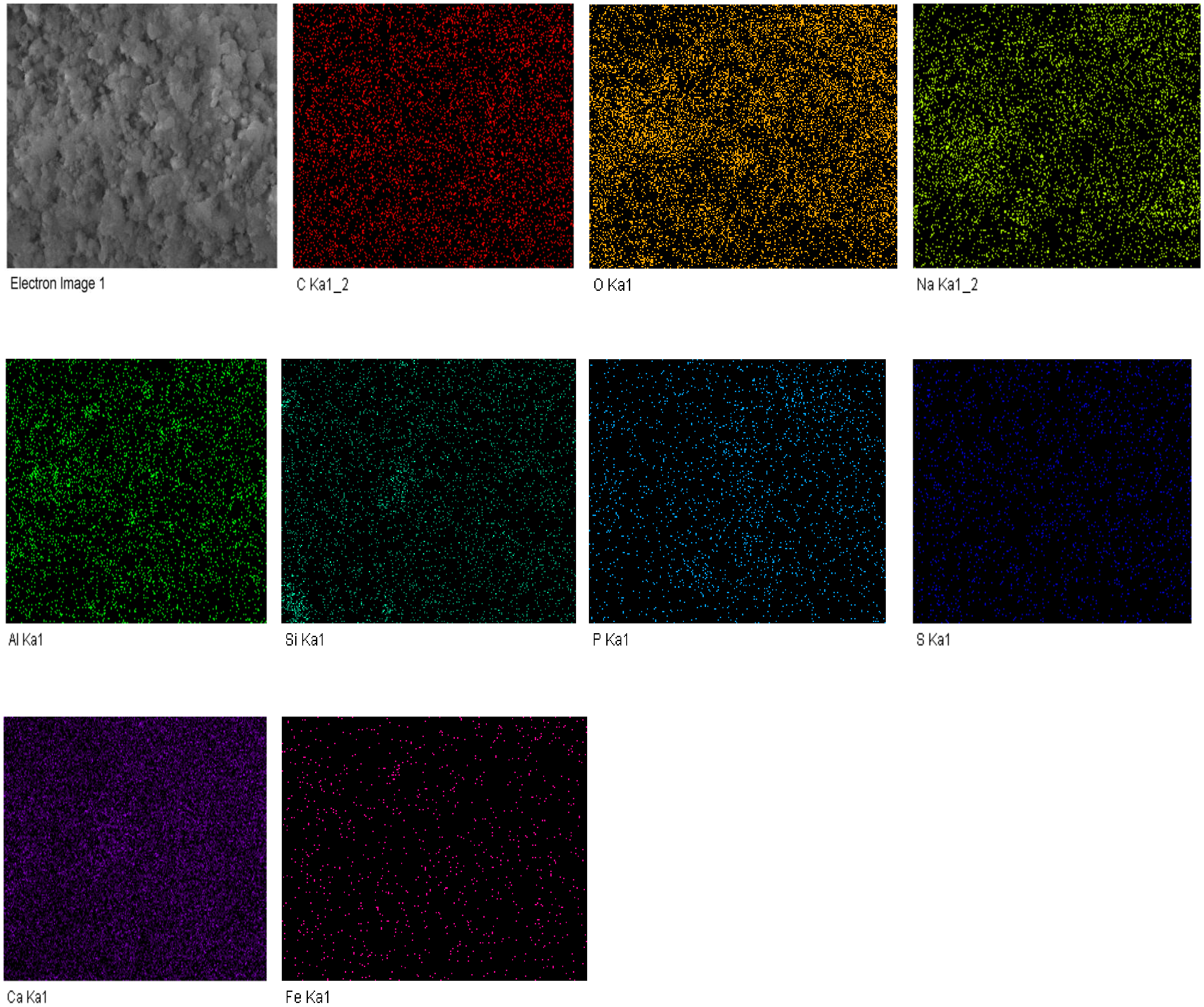


FIGURE 5.6 Mapping Images of Element in Residue

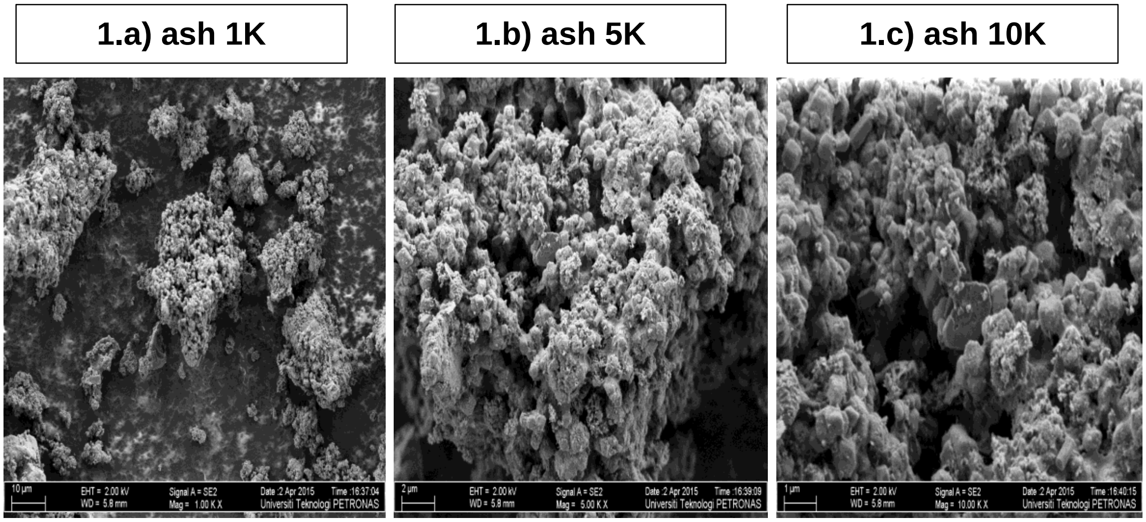


FIGURE 5.7 Scanning Electro Microscopy of Residue in 2015

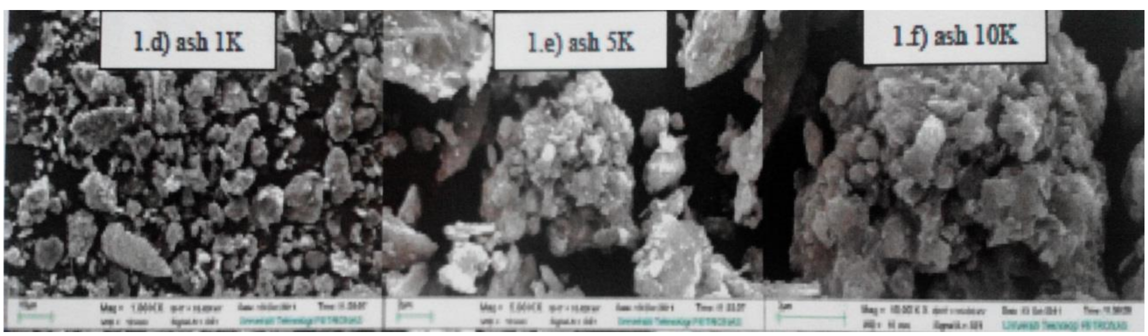


FIGURE 5.8 Scanning Electro Microscopy of Residue in 2012

CHAPTER 6: CONCLUSION

As a conclusion, the author really hope the research will benefit to the nation especially in oil and gas area.

This study prove that the suitability to use treated refinery sludge as cement replacement material in concrete. However, the compositions of chemical constituents in the residue ash need to be investigated in order to achieve high strength of concrete.

The alternative to replace the cement in concrete is good for our environment and Earth as cement is not environmental friendly and dangerous to our health.

We as an engineer have to find a solution for the betterment of human life and give value in engineering and design.

By computing the residue or refinery sludge to partial replacement material of Ordinary Portland Cement in concrete, it would be a huge advantage for oil and gas industry in our country.

CHAPTER 7: RECOMMENDATIONS

This research work has open up opportunities for further study. The following issues are recommended for enhancement of the research in the future.

1. Another parameter such as additives or heating temperature could be investigated in thermal treatment of refinery sludge.

2. Research in detail of characterization of concrete that contains residue ash as cement replacement such as porosity, durability, tensile strength and others.

3. Study the characterization of residue ash such as particle size and relate it with the properties of residue ash.

REFERENCE

[1] Oil Field Tekniks. Petroleum Sludge. Retrieved from: http://www.oilfieldtekniks.net/

[2] G. J. Hu, J.B. Li, G.M. Zeng, Recent development in the treatment of oily sludge from petroleum industry: a review, Journal of Hazardous Materials 261 (2013) 470-490.

[3] Pakpahan E.N. 2012. Flameless Thermal Treatment of Petroleum Sludge for Degradation of Polycyclic Aromatic Hydrocarbons . Ph.D Thesis, Universiti Teknologi PETRONAS.

[4] Wang ZQ, Guo QJ, Liu XM, et.al, Low Temperature Pyrolysis Characteristics of Oil sludge under Various Heating Conditions, Energy & Fuels 21(2): (2007) 957-962.

[5] Shie, J.-L.; Lin, J.-P.; Chang, C.-Y.; Wu, C. -H.; Lee, D.-J.; Chang, C.-F.; Chen, Y.-H., Oxidative Thermal Treatment of Oil Sludge at Low Heating Rates. Energy Fuels 18 (2004) 1272–1281.

[6] R-A Business staff. (2010). Oil-sludge-processing industry overview. Retrieved from http://russianamericanbusiness.org/web_CURRENT/articles/654/1/Oil-sludge-processing-industry-overview

[7]United States. Office of Solid Waste. Environmental Protection Agency Washington, Polycyclic Aromatic Hydrocarbons (PAHs) DC 20460 (January 2008).

[8] Pakpahan, E.N. and Isa, M.H. and Kutty, S.R.M. and Chantara, S. and Wiriya, Wan (2013) Polycyclic aromatic hydrocarbon removal from petroleum sludge cake using thermal treatment with additives.

[9] C.C. Ling and M.H. Isa, Bioremediation of oil sudge contaminated soil by co-composting with sewerage sludge, J. Sci. Ind. Res. 65 (2006), pp. 364-369

[10] Ramezanianpour Ali Akbar. Cement replacement materials: properties, durability, sustainability. Springer London Limited; 2013.

[11] Elinwa, A.U and Mahmood, Y.A (2002): Ash from Timber Waste as Cement Replacement Material. Cement and Concrete Composites, 24(2), 219-222.

APPENDICES

APPENDIX A

Calculation of mass of additives to be used in every 1kg of Petroleum sludge:

<u>Sodium Bicarbonate ($NaHCO_3$)</u>

Molar mass of $NaHCO_3$ = 84.007 g/mol

Mass of NaHCO3 = 2.3 moles x 84.007 g/mol= 193.2 g

<u>Calcium Hydroxide ($Ca(OH)_2$)</u>

Molar mass of $Ca(OH)_2$ = 74.093 g/mol

Mass of $Ca(OH)_2$ = 2.3 moles x 74.093 g/mole = 170.2 g

APPENDIX B

Calculation of Variation Composition of Mortar Mixture

Volume of 1 cube mortar = 50mm x 50 mm x 50 mm = 0.000125 m^3

Volume of 21 cubes mortar = 21 x 0.000125 m^3 = 0.002625 m^3

Wastage= 10% of volume of cubes mortar = 0.0002625 m^3

Total volume = Volume of 21 cubes mortar + Wastage = 0.0028875 m^3

Code	% of ash, % of cement	Mass of Cement (kg)	Mass of Residue Ash (kg)	Mass of sand (kg)	Mass of water (kg)
M0	0;100	1.126	O.000	4.274	0.866
M5	5;95	1.070	0.056	4.274	0.866
M7.5	7.5;92.5	1.042	0.085	4.274	0.866
M10	10;90	1.013	0.113	4.274	0.866

APPENDIX C

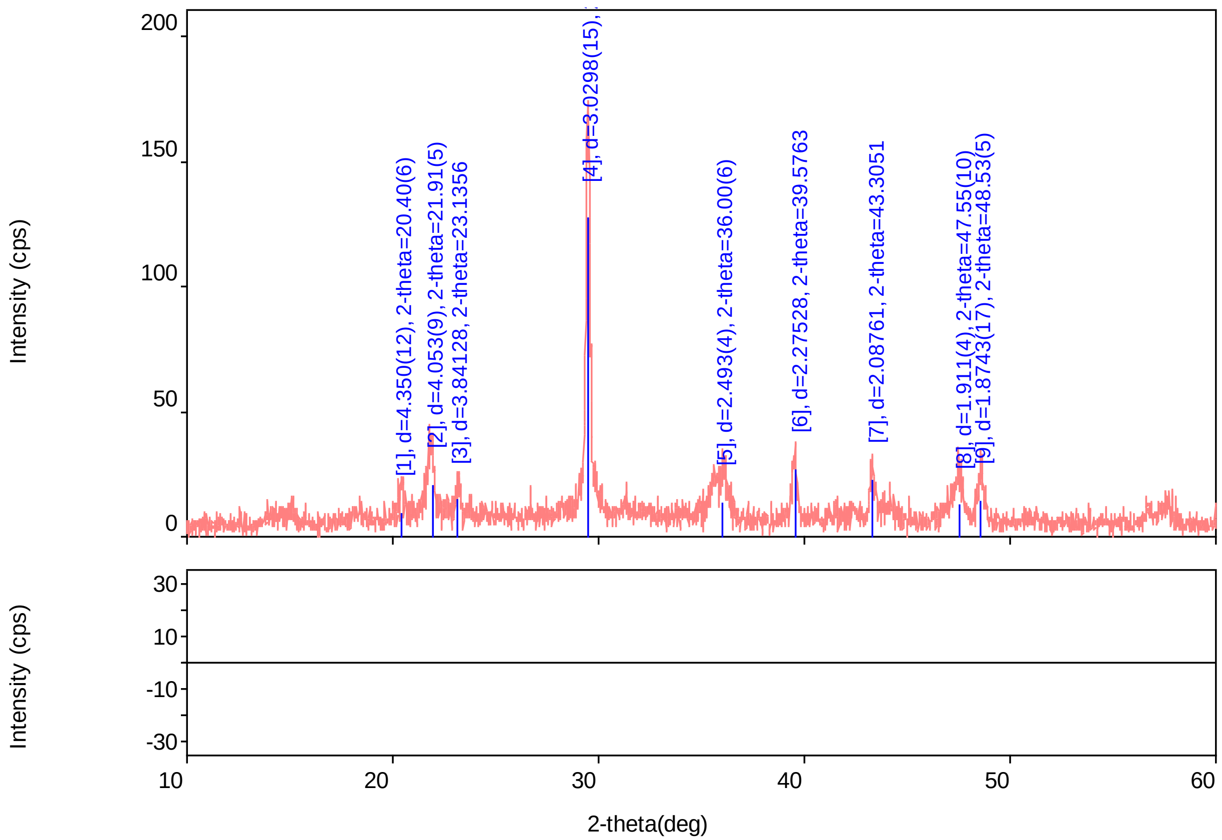
XRD Result

Analysis Results

General Information

Analysis date	3/16/2015 8:42:23 AM		
Sample name	XRD Analysis	Measured time	3/16/2015 7:48:54 AM
File name	UTP-FYP-PRA MARKING.raw	Operator	administrator
Comment	UMP		

Measurement profile



Intensity (cps)
200
150
100
50
0
[1], d=4.350(12), 2-theta=20.40(6)
[2], d=4.053(9), 2-theta=21.91(5)
[3], d=3.84128, 2-theta=23.1356
[4], d=3.0298(15),
[5], d=2.493(4), 2-theta=36.00(6)
[6], d=2.27528, 2-theta=39.5763
[7], d=2.08761, 2-theta=43.3051
[8], d=1.911(4), 2-theta=47.55(10)
[9], d=1.8743(17), 2-theta=48.53(5)
Intensity (cps)
30
10
-10
-30
10
20
30
40
50
60
2-theta(deg)

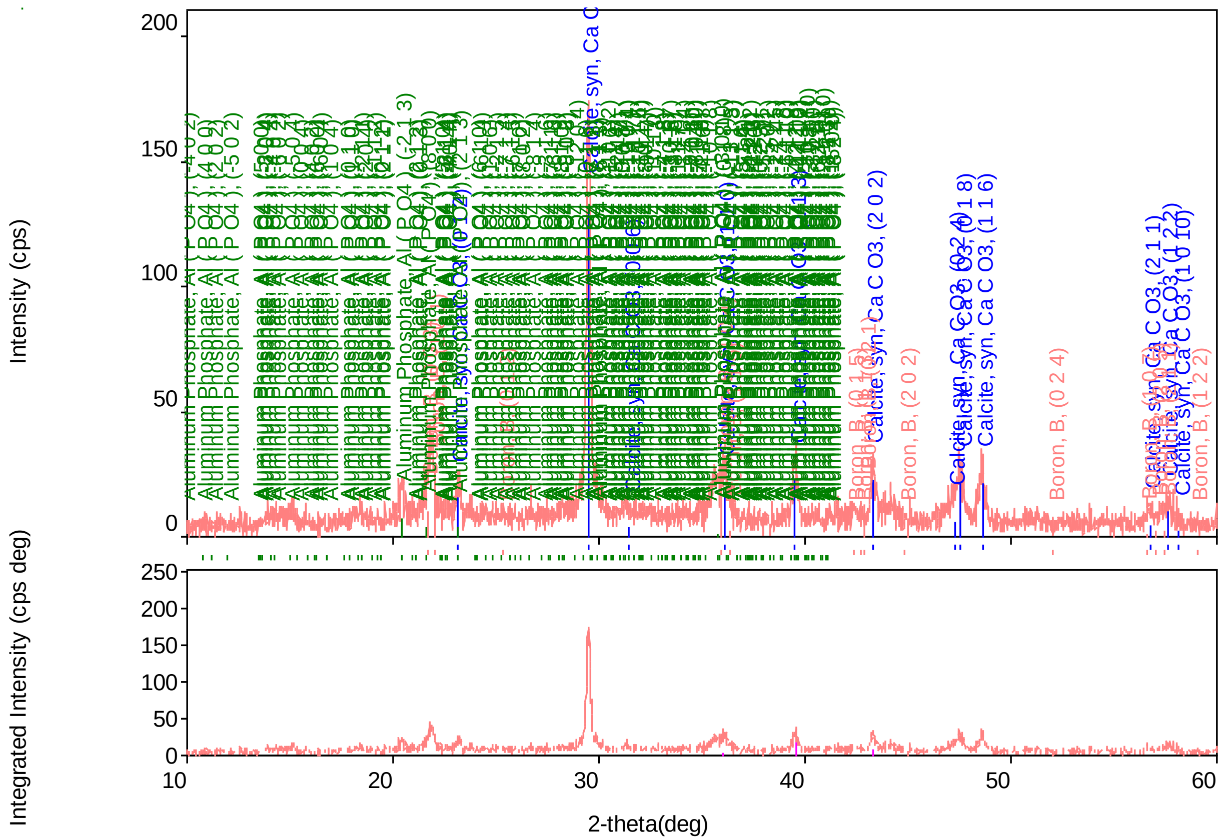
Measurement conditions

XG	Cu/30 kV/15 mA	Duration time / Scan speed	1 deg/min
Goniometer		Step / Sampling step	0.02 deg
Attachment	-	Measurement axis	2ƒÆ/ƒÆ
K-beta filter	-	Scan range	10-60 deg
Incident monochromator	-	Incident slit	-
Receiving monochromator	-	Vertical divergence slit	-
Counter	-	Receiving slit #1	-
		Receiving slit #2	-

Qualitative analysis results

Phase name	Formula	Figure of merit	ICDD
Calcite, syn	Ca C O3	0.6456347123195286	50586 (ICDD)
Boron	B	0.9879008556554814	10745416 (ICDD)
Aluminum Phosphate	Al (P O4)	1.154053456283153	10704690 (ICDD)

Phase name	Formula	Space group	ICDD
Calcite, syn	Ca C O3	167 : R-3c,hexagonal	50586 (ICDD)
Boron	B	166 : R-3m,hexagonal	10745416 (ICDD)
Aluminum Phosphate	Al (P O4)	7 : P1c1,unique-b,cell-1	10704690 (ICDD)


Intensity (cps)
Integrated Intensity (cps deg)
2-theta(deg)
0
50
100
150
200
250
10
20
30
40
50
60
Aluminum Phosphate, Al (P O4), (-5 0 2)
Calcite, syn, Ca C O3, (2 0 2)
Calcite, syn, Ca C O3, (1 1 6)
Calcite, syn, Ca C O3, (2 1 1)
Calcite, syn, Ca C O3, (1 0 10)
Boron, B, (2 0 2)
Boron, B, (0 2 4)
Boron, B, (1 2 2)

Peak list

2-theta (deg)	d (ang.)	Height (cps)	Int. I(cps¥deg)	FWHM(deg)	Size	Phase name
20.40(6)	4.350(12)	10(3)	2.0(5)	0.19(4)	452(98)	Aluminum Phosphate, (2,1,-3)
21.91(5)	4.053(9)	21(5)	8.6(7)	0.32(5)	261(38)	Boron, (0,0,3)
23.1356	3.84128	15.1935	4.29475	0.323403	261.32	Calcite, syn, (0,1,2), Aluminum Phosphate, (2,1,3)
29.457(15)	3.0298(15)	128(11)	32.7(8)	0.165(15)	520(49)	Calcite, syn, (1,0,4), Aluminum Phosphate, (7,1,2)
36.00(6)	2.493(4)	14(4)	13.5(10)	0.83(6)	105(8)	Calcite, syn, (1,1,0), Boron, (1,0,4), Aluminum Phosphate, (3,0,-10)
39.5763	2.27528	27.377	18.0132	0.829508	105.173	Calcite, syn, (1,1,3), Aluminum Phosphate, (14,1,-3)
43.3051	2.08761	23.2219	15.3095	0.829508	105.173	Calcite, syn, (2,0,2), Boron, (1,1,3)
47.55(10)	1.911(4)	13(4)	8.8(8)	0.54(9)	167(28)	Calcite, syn, (0,2,4)
48.53(5)	1.8743(17)	15(4)	5.1(4)	0.30(4)	304(37)	Calcite, syn, (1,1,6)

APPENDIX D

XRF Result

No	Parameter	Results	Unit	Test Method
1.	Calcium (Ca)	28.52	%	Quantexpress (Best Detection)
2.	Sodium (Na)	9.12	%	Quantexpress (Best Detection)
3.	Silicon (Si)	5.94	%	Quantexpress (Best Detection)
4.	Aluminium (Al)	4.22	%	Quantexpress (Best Detection)
5.	Iron (Fe)	3.54	%	Quantexpress (Best Detection)
6.	Sulphur (S)	1.58	%	Quantexpress (Best Detection)
7.	Phosphorus (P)	0.49	%	Quantexpress (Best Detection)
8.	Chlorine (Cl)	0.26	%	Quantexpress (Best Detection)
9.	Magnesium (Mg)	0.16	%	Quantexpress (Best Detection)
10.	Zinc (Zn)	0.16	%	Quantexpress (Best Detection)
11.	Potassium (K)	0.12	%	Quantexpress (Best Detection)
12.	Barium (Ba)	0.10	%	Quantexpress (Best Detection)
13.	Titanium (Ti)	0.04	%	Quantexpress (Best Detection)
14.	Strontium (Sr)	0.04	%	Quantexpress (Best Detection)
15.	Nickel (Ni)	0.02	%	Quantexpress (Best Detection)
16.	Manganese (Mn)	0.02	%	Quantexpress (Best Detection)
17.	Copper (Cu)	0.01	%	Quantexpress (Best Detection)
18.	Chromium (Cr)	73	ppm	Quantexpress (Best Detection)
19.	Arsenic (As)	56	ppm	Quantexpress (Best Detection)
20.	Zirconium (Zr)	4	ppm	Quantexpress (Best Detection)

APPENDIX E

Result of Compressive Strength (MPa)

CODE	COMPRESSIVE STRENGTH OF MORTAR (MPa)			AVERAGE
M0	22.39	Error	18.76	20.6
M5	17.04	17.88	20.31	17.46
M7.5	14.21	13.88	14.27	14.24
M10	9.128	12.56	9.032	9.08

7 Curing Days

CODE	COMPRESSIVE STRENGTH OF MORTAR (MPa)			AVERAGE
M0	21.04	22.03	20.29	21.12
M5	14.10	14.21	15.47	14.16
M7.5	15.50	13.63	12.86	13.25
M10	13.12	12.95	Error	13.04

14 Curing Days

CODE	COMPRESSIVE STRENGTH OF MORTAR (MPa)			AVERAGE
M0	29.04	21.52	26.4	223.96
M5	20.4	23.28	18.72	19.56
M7.5	16.4	14.20	14.52	14.36
M10	13.36	10.28	12.44	12.90

21 Curing Days

CODE	COMPRESSIVE STRENGTH OF MORTAR (MPa)			AVERAGE
M0	20.96	26.4	24.04	25.22
M5	23.28	error	17.72	20.5
M7.5	16.48	13.44	16.92	16.7
M10	15.88	14.96	11.12	15.42

28 Curing Days