Permeability and Leachability of Immobilized Petroleum Waste in Metakaolin Cement Binder

by

Logeswarri Nagarajan

(14990)

Dissertation submitted in partial fulfilment of the requirements for the

Bachelor of Engineering (Hons) (Chemical Engineering)

JANUARY 2015

Universiti Teknologi PETRONAS

32610 Bandar Seri Iskandar

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Permeability and Leachability of Immobilized Hydrocarbon Waste in Metakaolin Cement Binder

by

Logeswarri Nagarajan

(14990)

A project dissertation submitted to the Chemical Engineering Department
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons) (CHEMICAL ENGINEERING)

Approved by,

____

(Dr Asna binti Mohd Zain)

UNIVERSITI TEKNOLOGI PETRONAS
32610 BANDAR SERI ISKANDAR, PERAK
January 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

____

(Logeswarri Nagarajan)

ABSTRACT

This research studies the waste management of petroleum sludge that was retrieved from the final decanter outlet of a petroleum refinery complex by the application of a technique known as Solidification and Stabilization (S/S). The S/S technique is a well-established waste disposal technique for hazardous wastes and the study focuses on the treatment of sludge waste using metakaolin. The effectiveness of the process is studied by chemical and physical methods, that is, through permeability, leachability and strength tests. The S/S technique applies a binder, commonly Ordinary Portland Cement, to immobilize and encapsulate the hydrocarbon waste to chemically stabilize it preventing from external chemical reaction with the environment. The purpose of this study is to investigate the factors affecting the strength of the solidified sludge waste and metakaolin cement binder using different mix ratios where the optimum ratio can lead to the strength improvement in waste-binder matrix. The objective is met by optimizing waste to cement and admixture ratio based on the unconfined compressive strength as the main judging criteria. The performance of the S/S is measured through leaching analysis to determine the lowest leachability of metals in the leachate through Toxicity Characteristic Leaching Procedure (TCLP), porosity and permeability properties of the stabilized waste with the unconfined compressive strength and its leaching behavior. It was found the presence of sludge and metakaolin showed that the highest cement to sludge ratio of 60 with highest amount of metakaolin of 15% produces the strongest cement matrix of strength of 85.75 MPa compared to the other lower cement to sludge ratio. Porosity was lowest at 12.09 when the C/Sd was at 40% and C/B at 5%, which however increases rapidly as C/B increases to 15%. A reversal was observed when C/Sd of 60 with increasing C/B ratio. The metals content in the leachate were relatively low and below the regulated metals content and in wastewater as outlined in EQA 1974. The optimum permeability for the solidified matrix of cement and metakaolin was the 15% metakaolin ratio with the aid of the FESEM EDX test method.

ACKNOWLEDGEMENT

I thank God for the courage and patience He provided me to come see through to the end of my first and foremost important Final Year Project. For without His blessings, the work might not have been completed. My endless gratitude and appraisal to Dr. Asna binti Mohd Zain, for without her guidance and endless support, the project would have come never met the end. For all the knowledge that she did not felt stingy to share with her fellow student, it has been a privilege under such talented and knowledgeable person for my project to be completed within the stipulated time frame. Ideas and suggestions provided throughout the course of the journey helped to build the project from scratch into something valuable, which will be proven applicable in the future upcoming days. I am particularly grateful for her willingness to spare some time from her busy schedule to support my project thoroughly till the end.

A heartfelt appreciation is also extended to the coordinator, Dr. Asna herself, for providing support from time to time and accommodating to the students' queries. Without the complete guidelines and seminars on matters regarding the final year projects, the student might have found it difficult to handle things. A special gratitude to Ms. Azriha Anuar for her assistance on the Atomic Absorption Spectrometry equipment, Mr. Shahrul, for the assistance on the Compression Test Machine, as well as Mr. Saharuddin for the chemicals and equipment provided throughout the project. All of these would not have materialized without the endless love, motivation and support of my family members and friends. This report is dedicated to my parents, signifying the end of the remarkable journey in my undergraduate life, and I thank them for being there with me, supporting and encouraging through my ups and downs and lastly in completing my final year project successfully.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Hydrocarbon (HC) wastes basically are waste generated from the processed streams or crude oil stock (API 2010). They are made up of substances that may consist of mobile oil, greasy sludge, suspended or lumped oily substances and maybe some organic solvent. While a variety of useful products are obtained from crude oil refinery, the waste generated from the process is known as hydrocarbon waste. The generated waste basically represents the complexity of the products obtained from the crude oil refinery. Provided the degree of harmfulness the combined mixture may be, releasing it to the environment might cause a chain of chemical reaction, which either dissipates, dissolves or maybe vaporizes into the ecosystem, which in turn might be deadly.

To overcome this, solidification and stabilization technology comes in place. Solidification/Stabilization (S/S) is typically a process that involves the mixing of a waste with a binder to reduce the contaminant leachability by both physical and chemical means to convert the hazardous waste into an environmentally acceptable waste form for land disposal or construction use (Malviya and Chaudhary 2006). “Stabilization” refers to techniques that chemically reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile or toxic forms (Roger and Caijun 2005). “Solidification” refers to techniques that encapsulate the waste, forming a solid material, and does not necessarily involve a chemical interaction between the contaminants and the solidifying additives (Jeffery et al. 1995). The technology is mostly applied in segments that immobilizes soils or sludge which contain one or more metal contaminants. High volumes of waste that are difficult to treat using other using existing technologies are recommended to apply this technique. The technology though is affected by certain factors that have to be taken into consideration before proceeding further into the implementation stage. One of the criteria involved is the presence of admixtures in the cement based matrix. The presence of admixtures may help to improve the immobilization of specific contaminants which in this study case, hydrocarbon waste. The efficiencies of the encapsulation of the waste sometimes can be enhanced with the addition of additives.

Certain existing admixtures proved its efficiencies in improving the cement physical or chemical behavior which results in better outcome. However, the application of admixtures under this technology is still under study. This study describes the treatment of immobilized waste with a mixture of metakaolin and Portland cement in order to emulate a stable earth-like material with solidified cement containing entrapped pollutants. Since the solid has high interior strength, it prevents the leaching of heavy metals as leachates from the wastewaters, solid wastes and contaminated soils (Geysen, 2001). The admixture of Portland cement and metakaolin is expected to have reduced heavy metals leachability. According to the CANMET Materials Technology Laboratory, metakaolin when used in cement produces significant pore refinement, modifies the waste transport properties and diffusion rates of harmful ions as opposing to the high porosity and poor durability of Portland cement alone.

The application of metakaolin generally results with cement matrix with increased strength, decreased permeability, and increased durability in tests such as freeze-thaw and wet dry resistance (PCA 2002). However, with the combination of hydrocarbon waste in the cement mixture, the properties of the metakaolin might be altered which may result in better S/S cement matrix. Current sludge disposal methods include land filling, incineration and release into the ocean, which causes groundwater contamination through the leaching of the heavy metals into the soil. With the aid of nature through rainfall, the wastes containing heavy metals are transported far beyond.

1.2 Problem Statement

Hydrocarbon waste which originates from crude oil processing refineries are classified under the nonspecific source wastes, which is called as F list wastes specified under USEPA.

This may cause handling difficulty leading to equipment failure during mixing process. The disruption of the cement matrix due to presence of hydrocarbon waste may reduce the efficiencies of the S/S technology to immobilize the waste. Reduction in permeability, decrease in compressive strength and weak leaching behavior may prove the technology not suitable for hydrocarbon based waste. The treatment of hazardous waste through immobilization has become increasingly important due to the increased amount of wastes produced by the oil and gas, metal and sand dredging industries. The leaching of heavy metals from sludge waste is a major concern for waste management in order to reduce adverse effects to both the environment and humans alike. In addition, the existing leachate treatment plant in Malaysia with the capacity of 180,000 m^3 is almost full and therefore new inventions in waste treatment such as the immobilization of the inorganic compounds (heavy metals) using binders has to replace the traditional landfilling methods.

1.3 Objectives

1. To study the effects of the absence and presence of metakaolin on the permeability, leachability, porosity and unconfined compressive strength of the immobilized petroleum waste.
2. To determine the optimum sludge waste to metakaolin cement binder ratio for effective immobilization of heavy metals
3. To study the relationship of cement to metakaolin ratio, C/B, cement to petroleum waste ratio, C/Sd and water to cement ratio, W/C towards the permeability, leachability, porosity and unconfined compressive strength behavior.

1.4 Scope of Study

Throughout the research, the student was exposed to the following:

1. Characterization and classification of hazardous, radioactive and mixed waste based on the physical and chemical reactivity as outlined by the Unites States Environmental Protection Agency (USEPA).
2. The basics of hydraulics cement system and the effect of admixtures on cement formation for solidification and stabilization.
3. Interaction between the binders, admixtures and the waste.
4. Chemical tests and analysis techniques on the waste, binder as well as the admixture.
5. Laws, regulations and standards required to be fulfilled for the S/S technology.
6. Solidification and Stabilization technology overview, applications and screening procedures.
7. Leaching process and evaluation tests for inorganic release from cement based matrix.

CHAPTER 2

LITERATURE REVIEW

2.1 Stabilization and Solidification Technology

The stabilization and solidification technology is a waste management technology which involves the process of mixing the waste with a binder to reduce the contaminant leachability by both physical and chemical means and indirectly convert the hazardous waste into an environmentally acceptable waste form, which goes to a landfill or used in construction. Both terms carry different function towards the contribution in this technology. By changing its chemical state or by physical entrapment, stabilization attempts to reduce the solubility or chemical reactivity of a waste. The physical nature and handling characteristics of the waste are not necessarily changed by stabilization (Conner and Hoeffner 1998). On the other hand, converting the waste into an easily handled solid with reduced hazards from volatilization, leaching, or spillage is what solidification is about. S/S technology was originally developed for treatment of nuclear waste in 1950s and later on different types of hazardous wastes. From around 1980s the technology also was applied for treatment of contaminated soil and sediments (Laugesen 2007). The development in the solidification was mainly originated from the low-level radioactive waste disposal. The regulations derived from this technology was slowly begun to be applied to other waste provided certain standards are met. The standards are achieved by applying few pretreatments to prevent contaminant leaching, such as neutralization, oxidation/reduction, physical entrapment, chemical stabilization and binding of the stabilized solid into a monolith.

2.2 Hydrocarbon Waste

Crude oil is a combination of multiples substances with different organic hydrocarbon molecule. Petroleum crude may be made up of 83-87% carbon, 11-15% hydrogen, and 1-6% sulphur (API 2010). Paraffin (saturated chains), naphthene (saturated rings), and aromatics (unsaturated rings) are the three types of most commonly existing hydrocarbons. The waste material chosen for this project is the petroleum sludge, the residue of crude oil processing. The petroleum sludge is derived from crude oil, where it is formed by three groups of hydrocarbons, namely, paraffins, aromatics and naphthenes. The paraffins or linear alkanes, form 10-30% of crude oil and the naphthenes including saturated hydrocarbons arranged in five to six carbon atoms, from 30-60% of crude oil. The remaining constituents of the crude oil are nonhydrocarbons such as sulphur, fatty acids, nitrogen and metals (Zain et. al, 2014). The crude oil components in terms of its elements are listed in Table 2.1.

Table 2.1: Crude Oil Components

Source: Leachability of Solidified Petroleum Sludge by Zain et. al (2014)

Element	Weight Percent (%)
Carbon, C	84 - 87
Hydrogen, H	11 - 14
Sulphur, S	< 0.1 - 8
Oxygen, O	< 0.1 – 1.8
Nitrogen, N	< 0.1 – 1.6
Nickel, Ni	Trace to 1000 ppm
Vanadium, V	Trace to 1000 ppm
Selenium, Se	Trace to 510 ppb

Stringent standards are involved in the processing of crude oil and it falls under the European Union (EU) requirements known as the Restriction of Hazardous Substance Directive (RoHS) adopted in February 2006. The RoHS determines the maximum allowable concentration of hazardous materials released to the environment and the requirements are summarized in Table 2.2.

Table 2.2: RoHS Requirement for Manufactured Substances

Source: Leachability of Solidified Petroleum Sludge by Zain et. al (2014)

Hazardous Material	Regulating Standard
Lead, Pb	Maximum concentration of 0.1% or 1000 ppm for all elements except Cadmium with maximum concentration of 0.01% or 100 ppm
Mercury, Hg	
Cadmium, Cd	
Hexavalent chromium, Cr	
Polybrominated biphenyl, PBB	
Polybrominated biphenyl ether, PBDE	

The petroleum sludge has numerous contaminants such as organic substances, inorganic metals and other minor components. The sludge has heavy metals contents including mercury (Hg), arsenic (As), lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd), chromium (Cr), nickel (Ni) and aluminium (Al). Most of these metals are toxic when found in excess or exceeded the regulating standards. Pb and Hg ions are mobile metal ions, where they easily migrate to water reservoir and affect aquatic life and other living species in contact with or consuming the water. The organic components in the sludge include naphthalene, phenanthrene, anthracene, oil and grease (Zain et. al, 2014). The typical organic and inorganic components are tabulated in Table 2.3.

Table 2.3: Typical Petroleum Waste Components

Source: Leachability of Solidified Petroleum Sludge by Zain et. al (2014)

Component	Common Ranges (µg/L)
Mercury, Hg	< 0.2
Cadmium, Cd	< 5
Lead, Pb	< 50
Zinc, Zn	< 500 - 1000
Copper, Cu	3 - 500
Nickel, Ni	6 - 500
Chromium, Cr (Total)	< 500 or < 1000 C (IV)
Arsenic, As	0.55 - 100
Cobalt , Co	< 500
Iron , Fe	< 3000 - 5000
Vanadium, V	< 1000
Naphthalene	1.15
Phenanthrene	1.11
Anthracene	1.10
Oil	50 - 5000

For a process plant, waste streams are often mixed and stored together with other forms of waste. This results in variation of the waste composition. Multiple sources have cited information pertaining the composition of waste oils and sludge. However, most of the information retrieved is either specified to their respective process waste or a mere simple assumption model on the particular type of waste (Bojes and Pope, 2007). Currently, different refinery operations which produce different forms of waste streams are yet to be systematically grouped or characterized for further understanding. Codified in regulation at 40 CFR 261.31, the nonspecific source wastes which are also known as the F list waste consist of seven groups. One of the groups is known as the petroleum refinery wastewater treatment sludge. Waste classified under this group is from the gravitational and physical/chemical separations of oil/water/solids/ during the storage or treatment of process wastewaters and oily cooling wastewaters from petroleum refineries.

This group can be further subdivided into 2 which are coded by EPA as F037 and F038 based on the sludge stage of separation which is either primary or secondary. Resource Conservation and Recovery Act has classified the listed below industry waste streams from petroleum refining as harmful (IPIECA 2010):

1. Dissolved air flotation float
2. Slop oil emulsion solids
3. Heat exchanger bundle cleaning sludge
4. API separator sludge
5. Petroleum refinery primary oil/water/solids sludge
6. Petroleum refinery secondary (emulsified) oil/water/solids separation sludge
7. Clarified slurry oil storage tank sediment

2.3 Metakaolin

Admixtures are ingredients other than water, aggregates, hydraulic cement and fibers that are added to the concrete batch immediately before or during mixing (Ruiz & Irabien, 2004). Different type of admixtures present in the market nowadays provides a variety of benefits to the application in the concrete. Among them includes increase or decrease in setting time, fluid loss reduction, foam prevention, stable strength growth, as well as excellent workability. Concrete produced in North America nowadays are basically made up a combination of these admixtures. According to US Federal Highway Administration, two basic types of admixtures are available: chemical and mineral.

The main process important for production high reactivity pozzolan from kaolin clay is calcination. The heating process drives off water from the mineral kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate ($Al_2O_3 \cdot 2SiO_2$), metakaolinite.

The process is known as dehydroxylation, and may be presented by simple Equation 1:

$$Al_2O_3.2SiO_2.H_2O \rightarrow Al_2O_3.2SiO_2 + 2H_2O \quad (1)$$

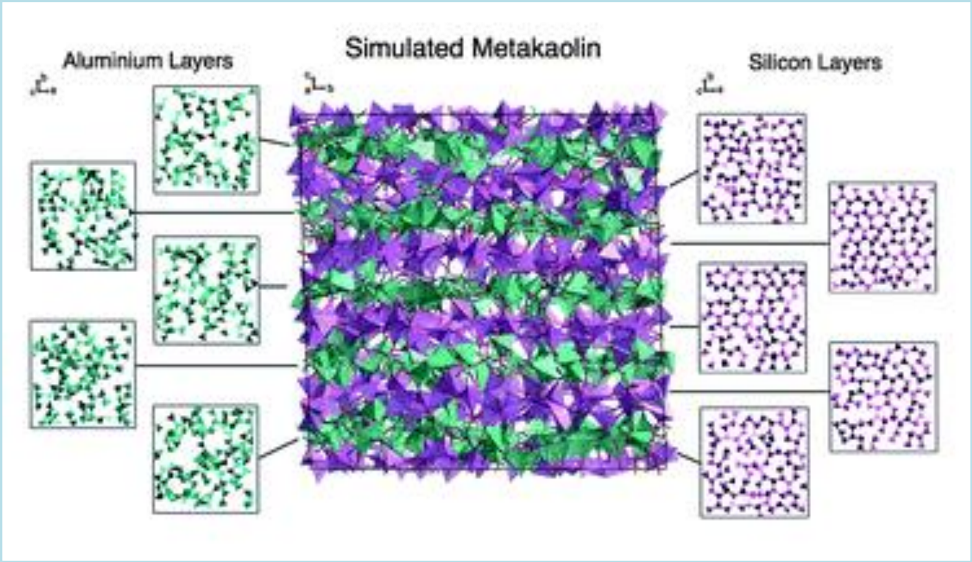

Figure 2.1: Metakaolin Structure

According to Qian, Sun, and Tay (2003), metakaolin is defined as a highly reactive metastable clay mineral, in which it was dehydroxylated from the clay mineral kaolinite. This process in highly endothermic due to the large amount of energy required to remove the chemically bonded hydroxyl ions. Meta kaolin has high reactivity where it forms strong slow-hardening cement with the presence of moisture. In addition, it is considered to have twice the reactivity of most of the pozzolans. Therefore, it is a valuable admixture for cement applications especially in waste disposal. The advantages of this material include reduced permeability, increased durability and compressive strengths, and resistance to chemical attack. The Table 2.4 shows the chemical composition and physical characteristics of kaolin.

Table 2.4: Chemical Composition of Kaolin

Source: Thermal Treatment of Kaolin Clay to Obtain Metakaolin by Ilic et. al (2010)

Component	Content, mass%
$\mathbf{SiO_2}$	48.00
$\mathbf{Al_2O_3}$	31.75
$\mathbf{Fe_2O_3}$	4.38
$\mathbf{CaO}$	1.00
$\mathbf{MgO}$	0.48
$\mathbf{Na_2O}$	0.16
$\mathbf{K_2O}$	1.50

2.4 Permeability

Permeability is defined as the state or quality of a material or membrane that causes it to allow liquids or gases to pass through it (Geankoplis, 2008). According to Zhang (2013), a pozzolanic composition of components such as silicone oxide, aluminium oxide, iron (II) oxide and calcium are needed to be present as these components contribute to creating a low-permeability solidified waste. These components also assist in trapping the wastes and prevent leaching due to its pozzolanic structure.

2.5 Leachability

According to Shi and Fernandez-Jimenez (2006), leaching can be defined as the diffusion of solutes into a solvent. In this study, the process of leaching involves heavy metals which are being removed as leachates at the end of the sludge waste treatment. In order to leach out metal salts, crushing and grinding is essential as it will increase the rate of leaching by increasing the surface area of the soluble metals into the solvent. In order to decrease the leachability of the sludge waste, a highly reactive clay mineral, metakaolin is being used. The testing method for leaching, the TCLP test will be conducted using USEPA method EPA-1311 to evaluate the leaching behaviour of the matrixes.

2.6 Portland Cement

Qian, Sun, & Tay (2003) mentioned in their journal that Portland cement is the most common component for immobilizing purposes that forms a confined matrix with other binding materials. The Portland cement is the binding material commonly used in waste disposal methods. In this study, the Lafarge Portland Type I cement based on Malaysian Standard 522 Part I 2003, supplied by Lafarge Malaysia, would be used as a component of the sludge-cement-metakaolin matrix that is going to be experimented at different ratios. Portland cement is produced from a pulverization of hydraulic calcium silicates and calcium sulfates (Dell'Orso et al., 2012). Portland cement is known to have good strength capacity even under water. Generally, sludge waste is mixed with cement ingredient in proportion such that the weight ratio of aqueous liquid phase of the sludge to the cement ingredient is in the range from 10:1 to 1:3.

2.7 Criteria for Solidified/Stabilized Waste

According to U.S.EPA and Dell'Orso et. al (2012), the properties for solidified and stabilized substance can be divided into two, the chemical properties and physical properties. These properties are vital especially when testing the metal concentration in the leachates after the leachability test is done, in order to ensure that the concentration of metals leached to the environment is in compliance with the governing standards in the actual conditions. The Table 2.5 shows the limits of the chemical and physical properties of the waste after going through the solidification and stabilization process.

Table 2.5: Criteria for Solidified/Stabilized Waste

Source: USEPA SW 872, 1982

	Properties	Criteria
Chemical	Metal concentration in TCLP leachates (mg/L)	
	Cadmium (Cd)	0.5 mg/L
	Chromium (Cr)	5 mg/L
	Lead (Pb)	5 mg/L
	Zinc (Zn)	300 mg/L
Physical	Compressive strength	≥ 0.35 MPa

CHAPTER 3

METHODOLOGY

3.1 Project Methodology

This section outlines the way in which the project is to be undertaken, including the methods to be used. In order for the research to be done successfully, a detailed procedure is required to fulfil all the objectives of the study. The main criterion of the methodology involves the batching of samples and the testing of the solidified sample for permeability, leachability, strength and porosity. Figure 3.1 show the summary of the research methodology.

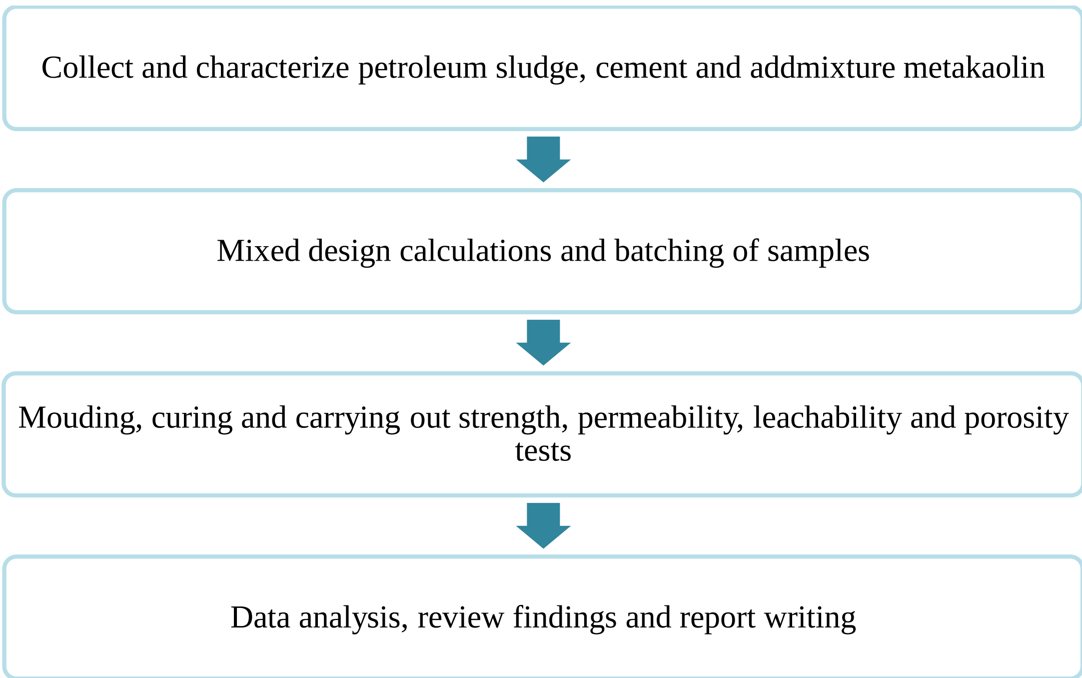

Figure 3.1: Research Methodology Flowchart

3.2 Experimental Design

A mix design template was made to perform calculations in order to determine the best proportion of cement to sludge. Cement and sludge were mixed at different ratios in consistent moisture content. Cement without petroleum sludge is used as the control sample of the experiment. The optimum metakaolin ratio will be determined based on the optimum water to cement and cement to sludge ratios. Figure 3.2 shows the experimental design for stabilization and solidification.

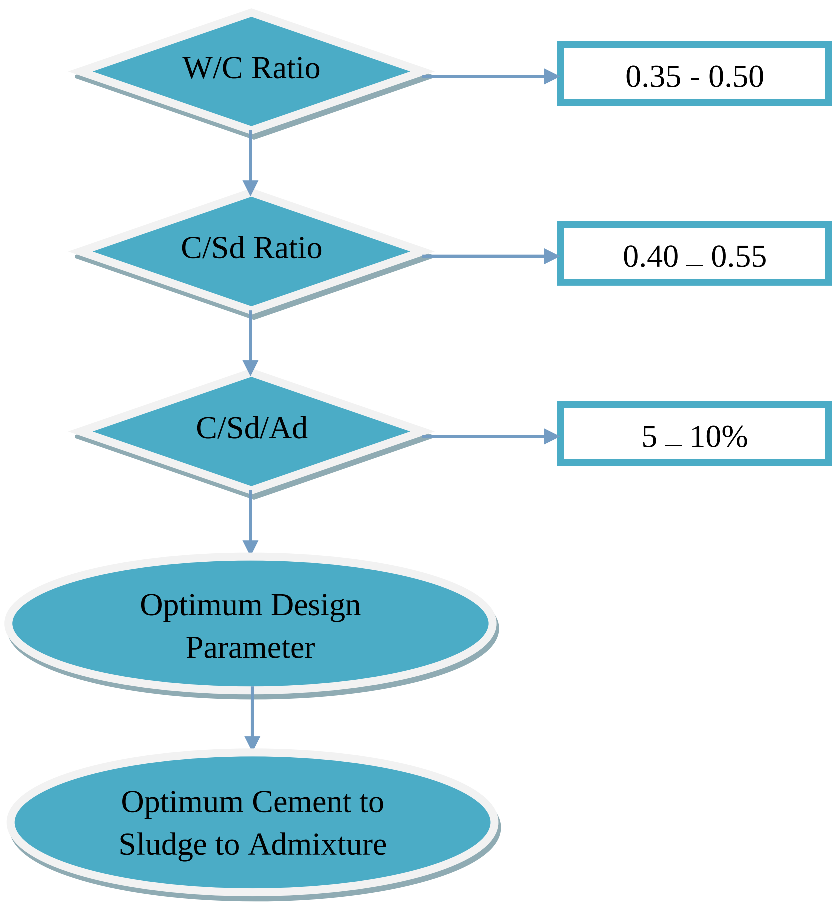

Figure 3.2: Experimental Design of Stabilization and Solidification

3.3 Characterization

A series of procedures is proposed for this experiment. The S/S technology requires characterization of the waste as well as the binder to understand the physiochemical of the cement matrix. The presence of admixture in this mixture must also be specialized to recognize its general properties and applications to justify its purpose or function in the cement based matrix. Once the waste, binder and admixture characterization are specified, according to the standards of the S/S technology, few tests such as the unconfined compressive test (UCS), leaching, porosity and permeability tests will be carried out on the cement based matrix as an evaluation criteria for the S/S technology.

3.3.1 Specific Gravity

Specific gravity of a material is defined as the ratio of the material dry solid portion mass to the mass of the equivalent volume of water. The measurement of specific gravity is for the purpose of the mixing calculation for the cement to sludge ratio. The before and after measurements of the specific gravity are necessary to estimate the extent of waste volume expansion due to treatment. The apparatus required is just a marked flask or container to hold a known volume of sludge. The procedures to estimate the specific gravity of the sample is as per below:

1. Record the sample temperature, T. Weigh empty container and record weight, W. Fill empty container to mark with sample, weigh and record weigh, R. Measure all masses to the nearest 10 mg.
2. If sample got flow readily, add as much of it to container as possible without exerting pressure, record volume, weight, and record mass, P. Fill container to mark with distilled water, taking care that air bubble not trapped in the sludge or container. Weigh and record mass, Q. Measure all masses to nearest 10 mg.

Calculation for the specific gravity for both procedures mentioned above can be done using the formulas shown in Equations 2 and 3.

$Specific\ Gravity\ at\ 4℃\ for\ Procedure\ 1$

$$= \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4℃} = \frac{S-W}{R-W} X\ F \qquad (2)$$

$Specific\ Gravity\ at\ 4℃\ for\ Procedure\ 2$

$$= \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4℃} = \frac{(P-W)}{(R-W)-(Q-P)} X\ F \qquad (3)$$

Based on the temperature, T measured, derived the value of F from the tabulated temperature correction factor shown in Table 3.1.

Table 3.1: Temperature Correction Factor, F

Temperature(℃)	Temperature Correction Factor, F
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

3.3.2 Moisture Content

Moisture content express the amount of free water present in a moist sample. Under the S/S technology, it is necessary to run this procedure to determine the material handling properties and to determine whether pre-treatment is needed. Based on the amount of moisture content in the waste sample, the amount of additional water required for the S/S binder can be calculated.

Moisture content procedure:

1. Record the empty container mass, E.
2. Fill the empty container with raw sludge, weigh and record the mass as C.
3. Keep the container with sample in an oven at about 104 ^{O}C for 24 hours.
4. Weight the container with sample after dried for 24 hours. Record the mass, D.
5. If the sample is in liquid form and contain organic material, leave in the dry sand bed (heated) before keeping in the oven for 24 hours.
6. Measure all masses to the nearest 10 mg.

Based on the procedures mentioned above, calculation of moisture content is given in Equation 4.

$$Moisture\ Content\ (\%) = \frac{(D - C) \times 100}{C - E} \tag{4}$$

3.3.3 Total, Fixed and Volatile Semisolids

Total solids are defined as substance or material left when it undergoes the evaporation or specified drying at designated temperature. The procedure helps to determine the percentage of total solid left after it undergoes specified drying at designated temperature. For the properties determination of the hydrocarbon waste, the total, fixed and volatile solids will help to assist in the cement and binder calculation. The standard applicable for this test is APHA 2540G. When filtered, the sample leaves behind sludge, which classifies the hydrocarbon waste as semisolid. The determination of total solid will to decide the amount of water and sludge added to obtain the desired volume of cement.

Total solid procedure:

1. Use a dry, clean inert container as the evaporating dish for the sample.
2. Place the container in an oven for 1 hour at 103 ^{o}C to 105 ^{o}C and once done, cool the container by placing it in a desiccator till it is being used.
3. Stir the semisolid sample before pouring it into the container. Weigh approximately 50 g and place it into the container.

4. Place the sample into an oven for 1 hour at 103 ^{o}C to 105 ^{o}C. After 1 hour, place the container with sludge into the desiccator and wait for the sample to cool down to room temperature.
5. Measure and record its weight.
6. Repeat procedures 3 to 5 until the weight change is observed to be less than 4 %.
7. Repeat the trial for 3 times to get an average value.

Fixed and volatile solid procedure:

1. The residue from the previous Total Solid test is used in this experiment.
2. Place the sample into the furnace and allow it to burn at 550 ^{o}C for 1 hour.
3. After 1 hour, place the container with sludge into the dessicator and wait for the sample to cool down to room temperature.
4. Measure and record its weight.
5. Repeat procedures 3 to 5 until the weight change is observed to be less than 4 %.
7. Repeat the trial for 3 times to get an average value.

The calculations for the total, volatile and fixed solids were calculated by using Equations 5, 6 and 7 accordingly.

$$\%\ total\ solids = \frac{(A - B) \times 100}{C - B} \tag{5}$$

$$\%\ volatile\ solids = \frac{(A - D) \times 100}{A - B} \tag{6}$$

$$\%\ fixed\ solids = \frac{(D - B) \times 100}{A - B} \tag{7}$$

where:

A = mass of dried residue + dish, g

B = mass of dish, g

C = mass of wet sample + dish, g

D = mass of residue + dish after ignition, g

3.3.4 Metal Content

The leachate obtained after 18 hours undergoes metal test to examine the concentration of metals leached from the S/S treated waste. Metals can be determined in accordance with U.S. E.P.A SW-846 Methods 6100, by atomic absorption spectroscopy (AAS). For this test, only selected optimized ratio will be selected to undergo the AAS. The metals detected are zinc (Zn), manganese (Mn), lead (Pb), chromium (Cr), copper (Cu), nickel (Ni), and iron (Fe). Standard calibration curves were prepared prior to determining the concentration of the metals in the leachate.

3.4 S/S Evaluation

3.4.1 Unconfined Compressive Strength (UCS) Test

This test measures the shear strength of a material without lateral confinement. Before being tested for UCS, the sample surface area must be measured to confirm its dimension. The standard applicable for this test would be according to ASTM C109. Place the sample at the middle of the machine containing upper and lower plates and the sample is not supported laterally. To ensure equal and uniform pressure is applied on the surface in contact with the upper and lower plates aligned the cube with the steel plates. The compressive strength value is determined by compressing the sample until it is deformed or broken. The compressive strength value can be observed from the display meter of the equipment. Average reading must be taken by repeating the procedures with 3 samples of the same mixture component.

3.4.2 Leaching Test

This test is used to evaluate the leaching of metals, volatile and semi volatile organic compounds, and pesticides from wastes that categorized under RCRA as characteristically toxic and can be used on other wastes as well. Leaching procedure must be carried according to the TCLP 1311 procedures. Crush block leaching (CBL) is selected to simulate the leaching behavior of the solidified waste. The simulation of the leaching behavior is done in 2 different environments which is acidic and neutral. Crushed sample recovered from the compressive strength test will be used in this procedure. Samples crushed during the compressive strength test need to be recovered in a sealable sample bag to preserve its condition prior to the leaching test.

3.4.3 Porosity & Permeability Test

Porosity is defined as the void space or pore spaces in solid structures which might be or not available to retain fluids. To measure the porosity of a material, it is the fraction of the volume of pore spaces over the total volume of the solid. The property plays a role to determine the whether the immobilized waste be leached out when it comes in contact with any other external fluids. In this context, if the waste is not completely immobilized, then the chances of the waste being dissipated out of the cement based matrix is high if the porosity is high and interconnected with other pores. The standard applicable for this segment would be according to the ASTM D4404-10 test standards. This test method covers the determination of the pore volume and the pore volume distributions of soil and rock by the mercury intrusion porosimeter method. The range of apparent diameters of pores for which this test method is applicable is fixed by the operating pressure range of the testing instrument. In the oil and gas industry, this property is defined as the ability of porous material to allow fluid to pass through it. This property is crucial in determining the possible movement of the immobilized waste. Although encapsulated with cement, the presence of pores and its interconnection with other pores may increase the permeability of the matrix which easily enable leaching medium to leach away the improperly immobilized hydrocarbon waste. Therefore, the lower the permeability of the matrix, the better quality it is to act as a waste management method.

3.5 Key Milestones

The typical life cycle of this project includes several key milestones that mark significant points along the process of completion of the project. The key milestones of the Final Year Project (FYP II) are the pre-sedex presentation, completion and submission of the dissertation, the technical report submission, viva evaluation, submission of hardbound of the dissertation to the supervisor and coordinator. As for the project milestones, they are summarized in Figure 3.3.

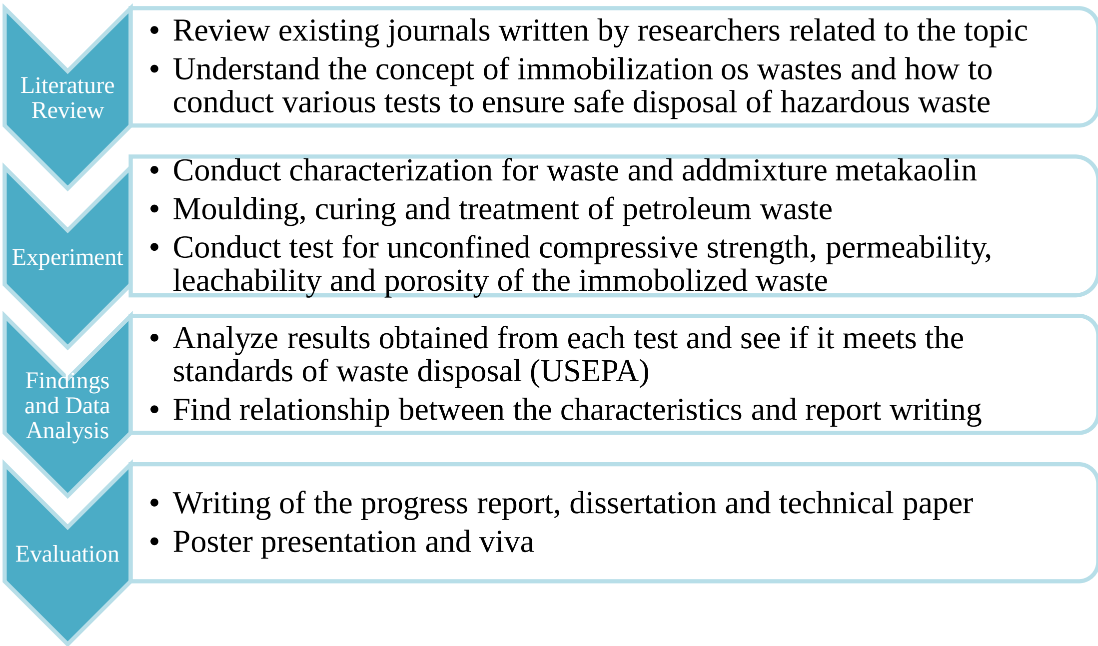

Figure 3.3: Key Milestones

3.6 Design Parameters

There is several design parameters involved in this project. Each of the parameter will be discussed in detail in this section. The first parameter would be the Toxicity Characteristic Leaching Procedure (TCLP) which is the test method for leachability of metal ions in the solidified sludge. In order to release the metal ions from the solidified sludge waste, crushing block leaching, an aggressive method for leaching has to be conducted according to TCLP U.S.EPA SW-846 Method 1311. The TCLP test was conducted using U.S.EPA method in order to evaluate the leaching behaviour of the solidified matrix of sludge waste and metakaolin cement binder. The petroleum sludge is assumed to contain 92% volatile solids with hydrocarbon as the main contaminant (Zain et. al, 2014).

The cement to sludge ratio (C/Sd) of 0.40 to 0.55 for four batches of water to cement ratio of 0.35 to 0.50 will be solidified into 1 litre plastic container and cured at 28 days curing period. The solidified matrix of petroleum sludge waste and metakaolin will be crushed and ground to the size of less than 10 mm. The crushed sample of the solidified and stabilized waste will be mixed with extractant fluid, which will be prepared using glacial acetic acid, CH_3COOH with reagent water (ASTM Type II Standard). The predicted pH value would be approximately 2.88 ± 0.05 of extractant fluid no. 2 of TCLP. A minimum of 100g of waste in solid form for TCLP 1311 and its extraction fluid will be calculated using the Equation (1) below. The extraction fluid has to be agitated by a rotary agitator for 18 ± 2 hours at a rotation speed of 30 ± 2 rpm. The solid and liquid component of the test method will be filtered using a glass fibre filter.

$$Weight\ of\ extraction\ fluid = \frac{(20\ x\ \%\ solid\ x\ weight\ of\ waste\ filtered)}{100} \tag{8}$$

As for the second design parameter of this project, it involves the permeability test, more specifically the permeable porosity test. The test method that will be applied is the high-resolution surface observation of particles down to a few tens of nanometres and elemental analysis by field emission scanning electron microscopy and energy dispersive X-ray spectrometry, or commonly known as (FESEM/EDX). It is beneficial to characterize the particle morphology by comparison of different imaging methods like secondary electron (SE)-, backscattered electron (BSE)- and transmitted electron (TE) detection. In scanning electron microscopy surface topography becomes visible due to the dependency of the SE yield on the angle of electron incidence. Therefore, this method is beneficial to determine the permeability limit of the solidified matrix of sludge waste.

The unconfined strength (UCS) test is the test method chosen to determine the strength of all the batching of the sample including the basic and sludge batching as well as the solidified matrix of petroleum sludge and metakaolin. For this method, a mould of 5cm x 5cm x 5cm for the casting of the material is required as per stated in the ASTM C109-91. The moulded and solidified petroleum sludge will be cured in a curing cabinet with moistened air at relative humidity of more than 64% to allow stabilization to occur. At the end of the curing process, the ELE compression machine that complies with BS 1881: Part 116 will be used to perform the UCS test.

The last test method is the permeable porosity technique to determine the porosity of the samples produced in each batching throughout the project. According to Zain et. al (2014), porosity is measured based on the ASTM C642 for measuring void or empty spaces in solidified and hardened concrete. As a part of this method, a cylindrical sample of 350 cm^3 will be used in the permeable porosity test. In addition, a dry sample has to be used to determine the mass of the sample. At the end of testing, a formula will be used to calculate the percentage of permeable porosity or voids in the solidified cement with cement replacement material, metakaolin.

$$Permeable\ pore\ space\ (voids), \% = \frac{(g_1 - g_2)}{g_2}\ x\ 100 \qquad (9)$$

where g_1 is dry bulk density in Mg/m^3

g_2 is apparent density in Mg/m^3

Table 3.2: Gantt Chart and Key Milestones

WEEKLY TASKS	WEEKS													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1. Obtain Sludge and Experimentation		■	■	■	■	■	■	■	■	■	■			
2. Analysis of Experiment Outcomes * Cement Based Matrix Test * Compressive Strength Test (UCS) * Leaching and Leachate Analysis (TCLP) * Surface Morphology (FESEM/EDX) * X-ray Diffraction (XRD)				■	■	■	■	■	■	■	■			
3. Submission of Progress Report ***** Extensive report writing (Due: 6th March)								■						
4. Results and Discussion Compilation ***** Compiling proposal according to the judging criteria									■	■	■			
5. Pre-SEDEX * Presentation with the aid of poster (Due: 25th March)											◆			
6. Report Draft Submission ***** Compiling report draft according to judging criteria and submission to supervisor for correction												■		
7. Dissertation Submission (Soft bound)													◆	
8. Technical Paper Submission														◆
9. Oral Presentation (Viva)														◆

■	Gantt Chart
◆	Key Milestones

CHAPTER 4

RESULTS AND DISCUSSION

The discussion will cover the results obtained from the characterization tests made throughout the project. The characterization covers mainly the hydrocarbon petroleum sludge. Once the characterization was completed, the main criteria were measured accordingly based on what mentioned previously in the methodology segment.

4.1 Specific Gravity

Based on the procedures mentioned above, calculation of specific gravity for the hydrocarbon waste is given in Equation 9 and the calculated value as per tabulated in Table 4.1.

$$Specific\ Gravity = \frac{Weight\ of\ Sample}{Weight\ of\ Equal\ Volume\ of\ Water\ at\ 4℃}$$
$$= \frac{(S-W)}{(R-W)}\ x\ F \tag{9}$$

Table 4.1: Specific Gravity Calculations

Specific Gravity	**Petroleum Sludge**		
	1	2	3
Temperature (^{o}C)	25.00	25.00	25.00
Mass of Empty Container (g), W	109.7	110.8	109.3
Mass of Empty Container + Sludge (wet) (g), S	120.1	121.1	119.7
Mass of Empty Container + Distilled Water at 4 ^{o}C (wet) (g), R	119.82	120.95	119.51
Mass of Sludge (wet) (g)	10.46	10.29	10.39
Mass of Distilled Water (wet) (g)	10.12	10.10	10.20
Specific Gravity	1.03	1.02	1.02
Average Specific Gravity	1.0		

4.2 Moisture Content

As mentioned previously in the methodology, under the S/S technology, it is necessary to run this procedure to determine the material handling properties and to determine whether pretreatment is needed. Based on the amount of moisture content in the waste sample, the amount of additional water required for the S/S binder can be calculated. The calculated moisture content is as shown in the table below using Equation 10.

$$Moisture\ Content = \frac{Wet\ weight - Dry\ weight}{Wet\ weight}\ x\ 100 = \frac{(C - B)}{B}\ x\ 100 \tag{10}$$

Table 4.2: Moisture Content Calculations

Moisture Content (%)	**Hydrocarbon Waste**		
	1	2	3
Mass of Empty Container (g)	109.72	110.86	109.3
Mass of Empty Container + Sludge (wet) (g)	114.83	115.85	114.3
Mass of Sludge (wet) (g), C	5.11	4.99	5.00
Mass of Empty Container + Sludge (dry) (g)	114.79	115.80	114.2
Mass of Sludge (dry) (g), B	0.05	0.04	0.05
Moisture Content (%)	92.31	90.03	91.8
Average Moisture Content (%)	91.39		

The result showed that sludge is actually made up of water for almost 91 % of its total content. The remaining is considered the waste that is collected from the process respectively.

4.3 Total, Fixed and Volatile Solid

Like the moisture content, the presence of solid covers the remaining percentage of the hydrocarbon waste sample that need to be considered while calculating the expected volume to the cement estimation. The total solid, fixed solid and volatile solid observed in the sample were tabulated in Table 4.3.

Table 4.3: Total, Fixed and Volatile Solid Calculations

Total, Fixed & Volatile Solid		**Hydrocarbon Waste**		
		1	2	3
Mass of Empty Crucible (g)		82.83	83.95	86.50
Mass of Empty Crucible + Sludge (wet) (g)		137.25	138.44	140.98
Mass of Empty Crucible + Sludge (dry) (g)		87.51	88.65	91.19
Mass of Empty Crucible + Sludge (Furnace dry)		85.24	85.65	87.99
Mass of Sludge (wet) (g)		54.43	54.49	54.48
Mass of Sludge (dry) (g)		4.68	4.70	4.70
Mass of Sludge (Furnace dry) (g)		2.42	1.70	1.50
Total Solid (%)		8.60	8.62	8.62
Fixed Solid (%)		51.66	36.28	31.84
Volatile Solid (%)		48.34	63.72	68.16
Average	Total Solid (%)	8.61		
	Fixed Solid (%)	39.92		
	Volatile Solid (%)	60.07		

4.4 Mixing Calculation

Once that was conducted, moisture content analysis was made on the sludge to calculate the amount of water present in the sludge. As mentioned in chapter 3, this moisture content is crucial for mixing calculation for the determination of amount of water required to be added to the cement mixture to prevent dehydration of the mixture during curing in room temperature. Insufficient water in the mixing may lead to difficulties to handle and equipment malfunction as well as brittle properties of the cement block. The dry mass or total solid of the sludge must also be measured to estimate the amount of dry sludge required to mix with cement and binder to estimate the additional amount of water required. Once all information gathered, the number of samples required and their dimension are determined for the volumetric estimation of the cement mixture required to be placed in the mould for the curing and testing procedures.

Density of Water = 1000 kg/m^3

Density of Sludge = 1021.12 kg/m^3

Density of Cement = 3140 kg/m^3

Density of Metakaolin = 2589.23 kg/m^3

Sludge Moisture Content = 0.913859

Total Solid = 0.0861

Volume of Mould = 15 cubes x (0.05 x 0.05 x 0.05) m^3 for UCS

= 0.001875 m^3

Calculation for Cement to Sludge Ratio (C/S_d) = 40 and Cement to Water Ratio (C/W) = 0.45

Assume

Cement Dry Mass = 40 kg

Sludge Dry Mass = 1 kg

Raw Sludge Mass = 1 kg / Total Solid

= 1 kg / 0.0861

= 11.6089 kg

In the presence of cement replacement material which is the metakaolin, the mass of cement reduced according to the percentage of metakaolin added. For example:

Percentage of metakaolin: 15 %

Mass of Metakaolin based on cement mass = 40 kg x 0.15

= 6 kg

Remaining Amount of Cement in Mixture = 40 kg – 6 kg

= 34 kg

Based on the mass calculated for cement, metakaolin as well as raw sludge, the volumes of each component except water was calculated accordingly:

Volume of Cement	$=34\ kg / 3140\ kg/m^3$	$= 0.01083\ m^3$
Volume of Metakaolin	$= 6\ kg / 2634.10\ kg/m^3$	$= 0.00228\ m^3$
Volume of Raw Sludge	$= 11.6089\ kg / 1021.12\ kg/m^3$	$= 0.01137\ m^3$
Total Volume of Mixture	$= 0.01083\ m^3 + 0.00228\ m^3 + 0.01137\ m^3$	
	$= 0.02448\ m^3$	

Ratio of Calculated Volume/ Ratio of Required Volume

$= 0.02448\ m^3 / 0.001875\ m^3$

$= 13.05$

Based on the ratio calculated above, the real mass of cement, metakaolin and raw sludge required for mixing 15 cm^3 moulds of cement block can be calculated as shown below:

Mass of Cement Required	= 34 kg / 13.056	= 2.6042 kg
Mass of Metakaolin Required	= 6 kg / 13.056	= 0.4596 kg
Mass of Raw Sludge Required	= 11.6089 kg / 13.056	= 0.8892 kg

Based on the Water to Cement (W/C) which is 0.45, the amount of water calculated is based on the amount of cement.

Amount of water required = 0.45 x 2.64042 kg = 1.1882 kg

However, water present in the sludge must be considered to prevent too much hydration of the mixture.

Amount of water in sludge = 0.8892 kg x Moisture Content

= 0.8892 kg x 0.9139

= 0.8126 kg of water

Therefore, the real amount of water required is by deducting the amount of water present in the sludge from the amount of water calculated based on cement mass.

Amount of water need to be added: 1.1882 kg – 0.8126 kg = 0.3756 kg

Overall, the mass of each component is tabulated as below in Table 4.4.

Table 4.4: Mass for C/Sd=40 and C/W=0.45

Component	Mass (kg)
Cement	2.6042
Raw Sludge	0.8892
Metakaolin	0.4596
Water	0.3756
Total	4.3286

The sample calculation showed can be computed using Microsoft Excel for better accuracy. The experiment will cover a wider range of cement to sludge ratio as well as cement to water ratio. The expected experiment ratios are as shown in the Tables 4.5, 4.6 and 4.7. The complete calculation for all the selected ratios is included in the appendix section. The calculations were made using the Microsoft Excel Spreadsheet. Once the mixing calculation is complete, the next thing to look into is the mixing procedure for the mixture.

Table 4.5: Proposed Set of Ratios for Cement to Water

Water to Cement Ratio
0.35
0.40
0.45

Table 4.6: Proposed Set of Ratios for Cement, Water & Sludge

Cement to Sludge Ratio (C/Sd)	Water to Cement
40	0.45
50	0.45
60	0.45

Table 4.7: Proposed Set of Ratios for Cement, Sludge & Metakaolin

Cement to Sludge Ratio (C/Sd)	Metakaolin Composition	Water to Cement Ratio
40	5%	0.45
	10%	
	15%	
50	5%	0.45
	10%	
	15%	
60	5%	0.45
	10%	
	15%	

4.5 Mixing

The sludge needs to be homogenized using the electric mixer for approximately 2-3 minutes. During mixing, add cement slowly followed by the addition of the admixture metakaolin. Leave the mixture to homogenize for 5 minutes. Slowly add distilled water to the electric mixer to further homogenize the mixture. Once the homogenous slurries can be observed, quickly add the slurries into the 50 x 50 x 50 cast mould for the UCS test and 1.5 inch x 3 inch cylindrical caste mould for porosity and permeability test. The moulds are then cured at room temperature (25 ^{o}C to 33 ^{o}C) with 92% relative humidity for 24 hours. Cover the mould with Perspex cover to prevent further excessive loss of water from evaporation. After 24 hours, the moulded cubes removed from its caste and must be kept in the curing chamber for further dry curing.

Based on the unconfined compressive strength test for the entire sample, the optimized ratio will be taken from the data and further tested for other properties such as TCLP, metal content, porosity and permeability. Based on these properties, the research will be able to deduce the effect of addition of metakaolin to the S/S cement matrix for waste management purpose. If proven successful, this technique can be certified as one of the promising waste management method rather than incinerating the hydrocarbon waste which results in consumption of energy and natural resources.

4.6 Unconfined Compressive Strength (UCS)

The objective of this test to observe the development of cement strength with different ratios of water to cement, cement to sludge ratio as well as cement to binder ratio. The optimized ratio can be determined from the strength growth curve to further study the characteristics of the stabilized and solidified cement matrix. Once the cube cement was casted, the unconfined compressive strength was measured accordingly based on the different day interval which are day 1, 7, 14, 21 and 28. The measured unconfined compressive strength was taken according to a planned schedule, which can be seen in appendix.

For each measurement, 3 cubes were measured at once, and average value was obtained to reduce the impact of equipment inconsistencies. The average cubes unconfined compressive strength were calculated and tabulated which will be discussed later in this section.

4.6.1 Water to Cement Ratio Unconfined Compressive Strength Development

The preliminary test involves testing for the workability of a selected water to cement ratio before further proceeding adding petroleum sludge waste and metakaolin. The Table 4.8 shows the average unconfined compressive strength for different water to cement ratios.

Table 4.8: Unconfined Compressive Strength for W/C Ratios

Water to Cement Ratio (W/C)	Unconfined Compressive Strength (UCS)				
	Average UCS (MPa)				
	Day 1	Day 7	Day 14	Day 21	Day 28
0.35	16.75	40.83	52.29	60.86	66.17
0.40	14.42	26.38	35.61	43.20	50.57
0.45	13.24	20.79	27.33	34.18	39.85

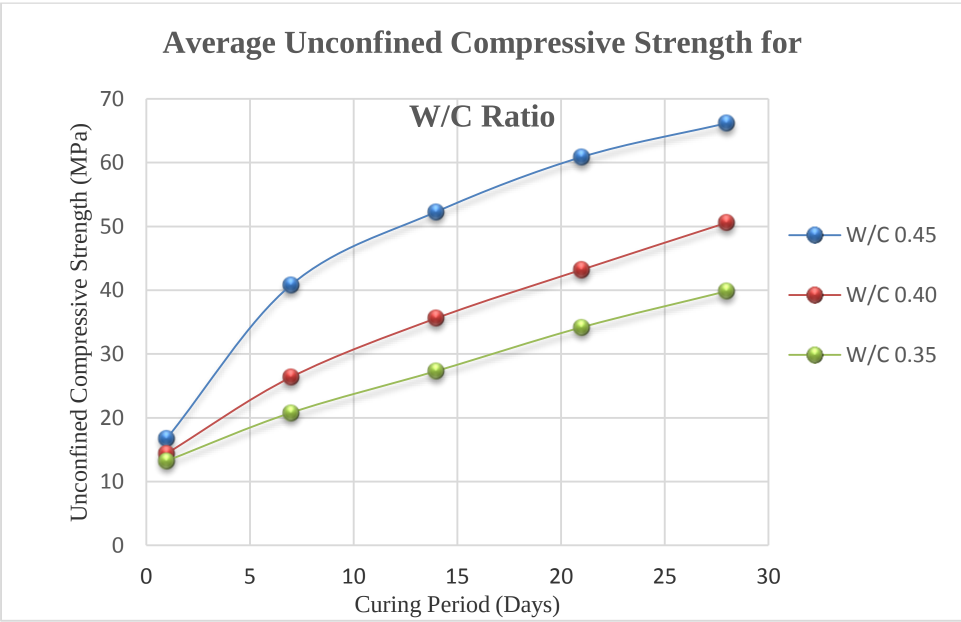

Figure 4.1: Average Unconfined Compressive Strength for W/C Ratios

Figure 4.1 shows the comparisons for unconfined compressive strength (UCS) for different water to cement ratio samples. All samples above showed almost similar development of initial which soon deviates from each other as days passes by. The lowest water to cement ratio pulled out significantly from other batches of samples with sharp increase in unconfined compressive strength. The samples matured on the 28th day with the lowest water to cement ratio prevail with highest unconfined compressive strength of 66.17 MPa. Based on this data, the cement block with the highest UCS will be used as the base compositions for the subsequent test which involves adding in petroleum waste sludge, together with the cement and water. This new batch UCS will also be measured according as what have been done previously. From Figure 4.1, it can be deduced that the next mixing which involves adding in petroleum waste sludge will be based on water to cement ratio of 0.45 as it exhibits the highest unconfined compressive strength as can be observed in Figure 4.9.

4.6.2 Cement to Sludge Ratio Unconfined Compressive Strength Development

Once the optimized ratio for water to cement was decided, petroleum waste sludge was added into the mixture to determine the optimize ratio before adding in the last component which is metakaolin. Three cement to sludge ratios were selected, which are 40, 50 and 60. The detailed calculations for the cement to sludge ratios, as well as water to cement ratio can be seen in the Appendix III.

Table 4.9: Unconfined Compressive Strength for C/Sd Ratios

Cement to Sludge Ratio C/Sd)	Water to Cement Ratio (W/C)	Day 1	Day 3	Day 7	Day 14	Day 28
		Average Stress (MPa)				
40	0.45	13.9	32.0	36.7	41.46	45.7
50	0.45	16.6	34.6	36.7	41.26	46.2
60	0.45	19.1	35.3	38.2	41.24	46.4

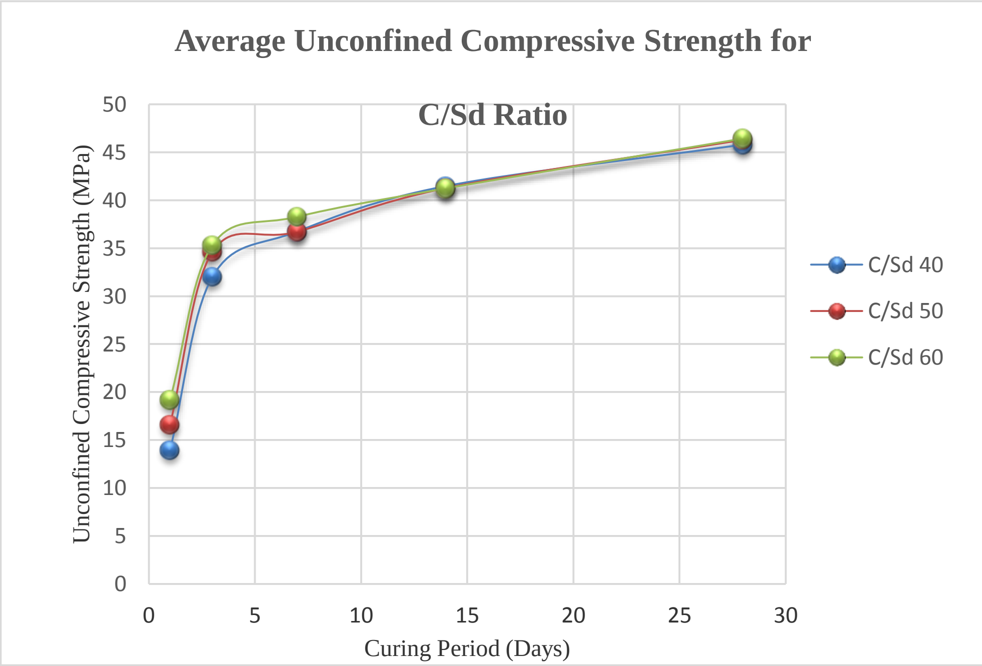

Figure 4.2: Average Unconfined Compressive Strength for C/Sd Ratios

Based on Figure 4.2 above, it can be seen that the strength development for the samples almost shows similar behavior with the same water to cement ratio. The highest cement to sludge ratio proved to give out the highest unconfined compressive which is only slightly above the previous 2 lower cement to sludge ratios. Therefore, it was decided to use the highest cement to sludge ratios together with the binder, metakaolin, and to get the best ratio when for unconfined compressive strength when added with the admixture.

4.6.3 Cement to Binder Ratio Unconfined Compressive Strength Development

Metakaolin is a cement replacement material, which is considered as an additive to the cement and water mixture to either strengthen or weaken the cured cement matrix. For this research purpose, metakaolin will be added in 3 different ratios which is 0.05, 0.10 and 0.15 cement to binder ratio. Since it was decided earlier that the project will consider 0.60 as the cement to sludge ratios, the detailed calculations for all the ratios mentioned can be seen in the appendix section.

In the process of adding metakaolin of cement to binder (C/B) ratio equal to 5% to the mixture, with C/Sd = 40 and W/C = 0.35, it was observed that the sample obtained was dry, thus making the mixing process difficult. Insufficient water in the mixture resulted in the low workability of the mixture. The picture shown in Appendix VII depicts the problem faced when using low water to cement ratio. In this case, it was assumed that metakaolin is a dehydrating agent which absorbs water, thus resulting in low workability of the mixture. To meet the time frame, it was decided that the maximum water to cement ratio, W/C = 0.45 is to be applied to all ratio to prevent dehydration of the samples.

Table 4.10 below shows the tabulated values for all samples mixed with the presence of both petroleum waste sludge as well as metakaolin. From the data obtained, graphs were plotted to depict the relationship between the unconfined compressive strength development as well as the sludge and metakaolin compositions. To begin with, comparison on the matured sample was analyzed as can be seen in Table 4.10.

Table 4.10: Unconfined Compressive Strength Development for Metakaolin Ratios

Water to Cement Ratio (W/C)	Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Days				
			1	7	14	21	28
0.45	0.60	0.00	9.82	23.56	29.22	35.30	48.28
0.45	0.60	0.05	11.16	25.77	32.34	37.49	52.36
0.45	0.60	0.10	12.66	25.98	32.55	42.21	61.67
0.45	0.60	0.15	14.22	27.46	36.36	46.42	79.58

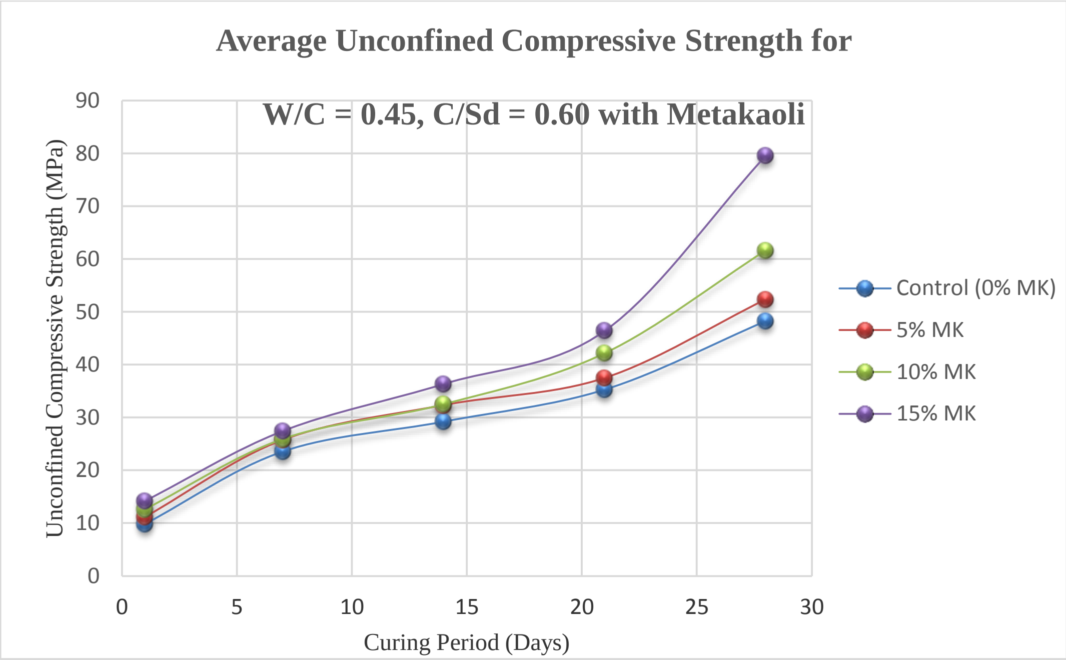

Figure 4.3: Average Unconfined Compressive Strength for W/C=0.45, C/Sd=0.60 with Metakaolin

Figure 4.3 shows the comparison between the unconfined compressive strength for the same water to cement ratio and cement to sludge ratio but different metakaolin ratios. The initial unconfined compressive strength development is almost the same for all three ratios, however it differs at the end for the highest cement to sludge ratio, C/Sd = 0.60. The unconfined compressive strength increases steadily for C/Sd = 60 until the end for all composition of metakaolin with 15% metakaolin ratio showing the highest strength achieved. For C/Sd = 60, the unconfined compressive strength increases as the composition of the metakaolin increases. The figures below show the relationship of the composition of metakaolin and unconfined compressive strength of the samples on days 7, 14, 21 and 28.

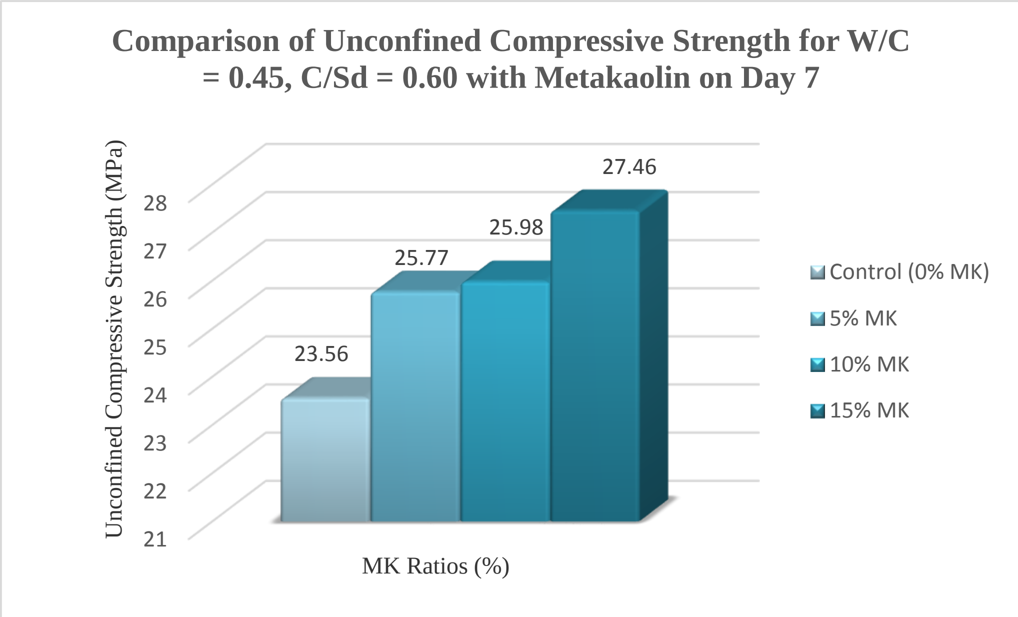

Figure 4.4: Comparison of Unconfined Compressive Strength for W/C = 0.45, C/Sd = 0.60 with Metakaolin on Day 7

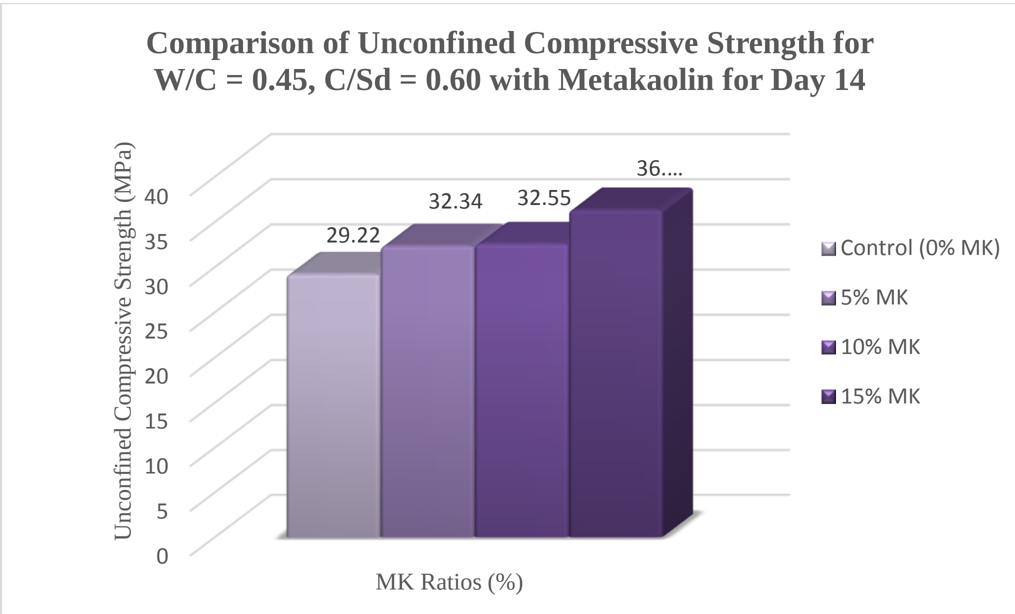

Figure 4.5: Comparison of Unconfined Compressive Strength for W/C = 0.45, C/Sd = 0.60 with Metakaolin for Day 14

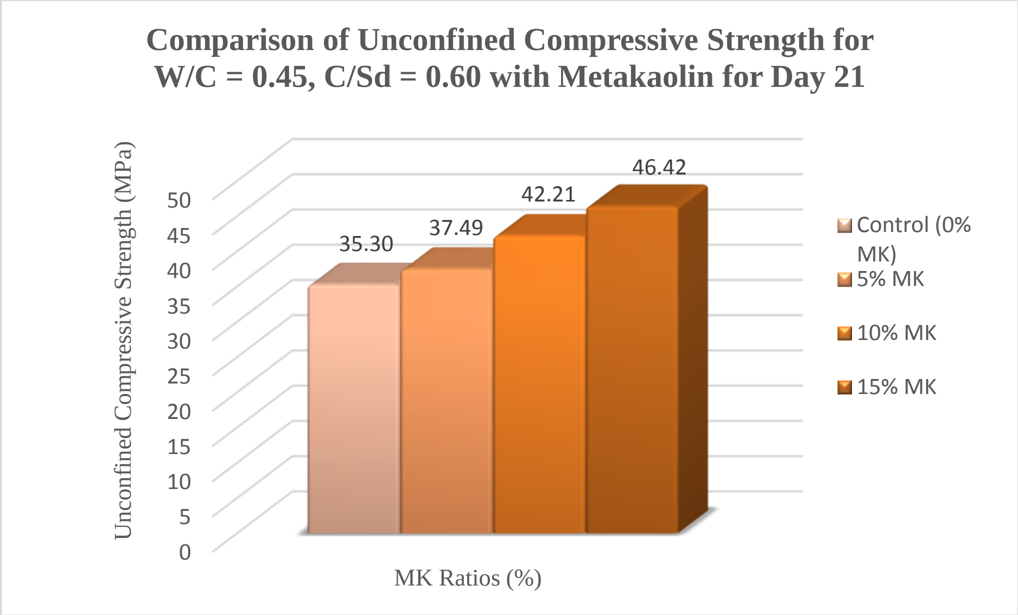

Figure 4.6: Comparison of Unconfined Compressive Strength for W/C = 0.45, C/Sd = 0.60 with Metakaolin for Day 21

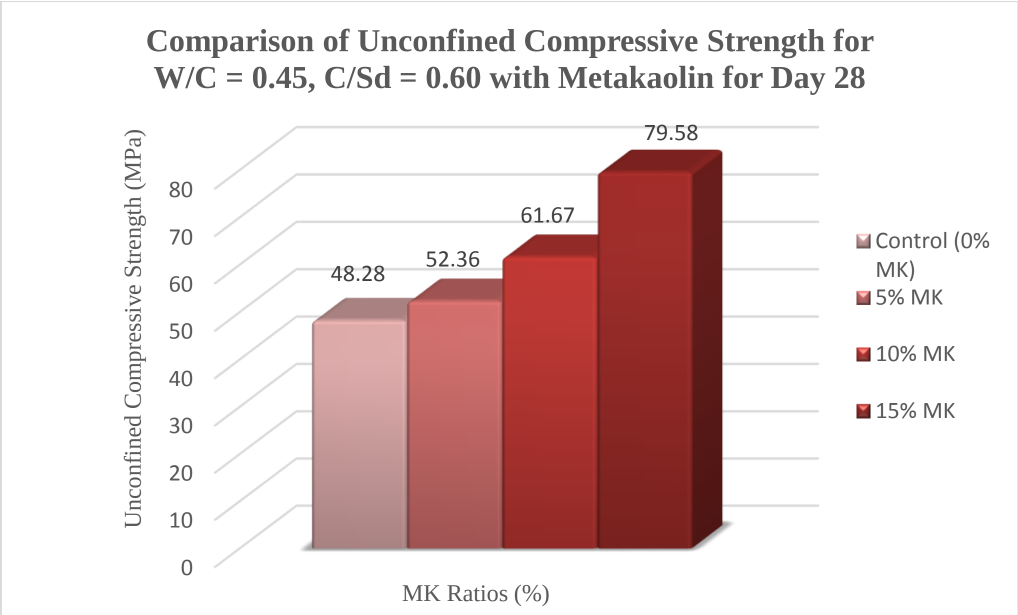

Figure 4.7: Comparison of Unconfined Compressive Strength for W/C = 0.45, C/Sd = 0.60 with Metakaolin for Day 28

Based on the charts above, the water to cement (W/C) and cement to sludge (C/Sd) ratios are kept constant, where the unconfined compressive strengths were studied based on the curing for days 7, 14, 21 and 28. The increase in sludge to binder ratio, generally caused the increase in the unconfined compressive strength of the solidified cubes. At C/B = 0, it was observed a rapid increase in unconfined compressive strength for day 7 and also 28. The highest unconfined compressive strength was given by 0.15 metakaolin on day 28 at 79.58 MPa as predicted from literature. The lowest amount of metakaolin, together with cement and sludge in the mixture gave the unconfined strength at 52.36 MPa. Based on the chart, it can be deduced that the highest cement to sludge ratio, 0.60 with highest amount of metakaolin, 0.15 produces the strongest cement matrix of 79.58 MPa compared to the other lower cement to sludge and sludge to binber ratios.

The U.S. EPA considers a stabilized material is satisfactory if it has UCS of 0.34 MPa or better. To further see the relationship between the cement, sludge, metakaolin as well as unconfined compressive strength development, a 3D surface plot was created using Microsoft Excel. Figure 4.8 depicts the relationship mentioned above. A clearer relationship of the unconfined compressive strength with curing period and cement to metakaolin ratios can be seen. The 3 colors of the surface plot depicts the strength range of the data; blue (0-20 MPa), red (20-40 MPa), green (40-60 MPa) and purple (60-80 MPa). As mentioned previously, the plots do clarify the previously mentioned findings for the change of strength according to the sludge and metakaolin. The higher sludge and metakaolin content increases the unconfined compressive strength of the samples.

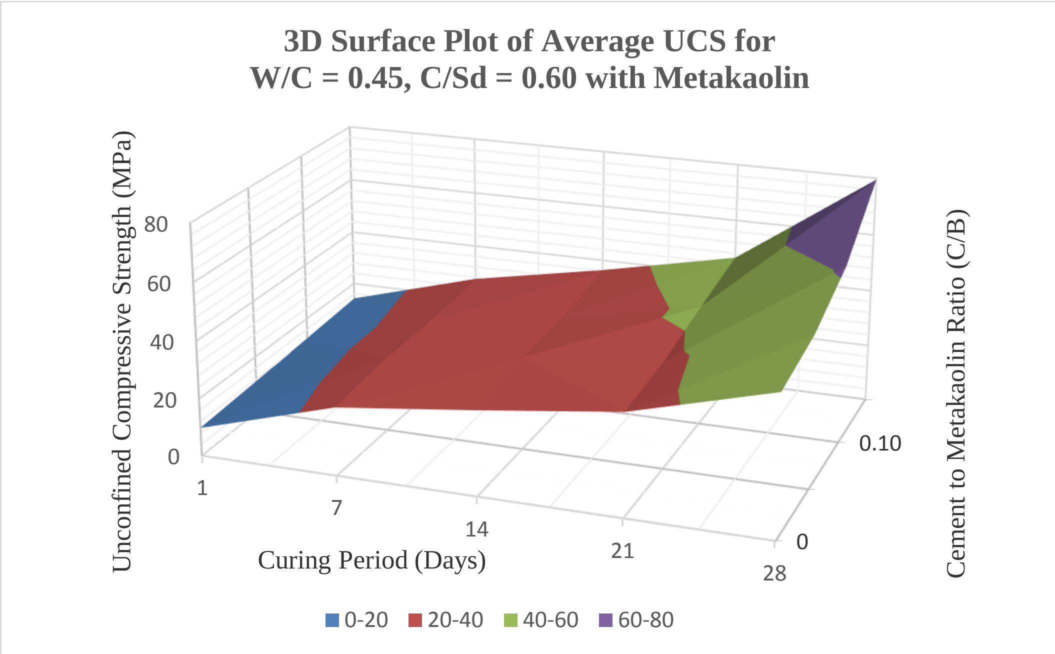

Figure 4.8: 3D Surface Plot for Average Unconfined Compressive Strength for W/C=0.45, C/Sd=0.60 with Metakaolin

4.7 Porosity

For the permeable porosity test, solidified cementitious matrix with the petroleum sludge waste and metakaolin will be analyzed for permeability. Matured samples after day 28, were crushed to size not less than 4 mm in diameter was taken and measured for its weight before being tested using mercury porosimeter. Not all sample undergone this procedure. Selected sample with distinctive difference in strength behavior was chosen based on the unconfined compressive strength test. The 4 chosen samples is as tabulated in the Tables 4.11 and 4.12 below.

Table 4.11: Porosity and Permeability Sample Data

Sample No.	Cement to Sludge Ratio (C/Sd)	Metakaolin Composition (%MK)	Water to Cement Ratio (W/C)	Mass (g)	Density (g/cm^3)
1	0.60	5%	0.45	0.73	2.52
2	0.60	10%	0.45	0.70	2.50
3	0.60	15%	0.45	0.72	2.52

Table 4.12: Porosity and Permeability Data

Sample	Without Compressibility		With Compressibility Correction	
	Accessible Porosity	Inaccessible Porosity	Accessible Porosity	Inaccessible Porosity
1	26.95	1.63	17.77	6.06
2	21.88	5.43	15.40	11.71
3	17.42	6.17	12.09	14.32

As depicted in the Figure 4.9, for C/Sd = 0.60 without compressibility correction, the accessible porosity increases with increase in metakaolin composition. The sample showed an increase in 25.6% of accessible porosity when the metakaolin composition increases from 5% to 10%. However, the result showed that the increase in accessible porosity is only 23.2% when metakaolin composition increases from 10% to 15%. In the segment of accessible porosity, it can be deduced that at low C/B ratio, the accessible porosity ratio is also low, whereas at high C/B ratio, the accessible porosity is the highest.

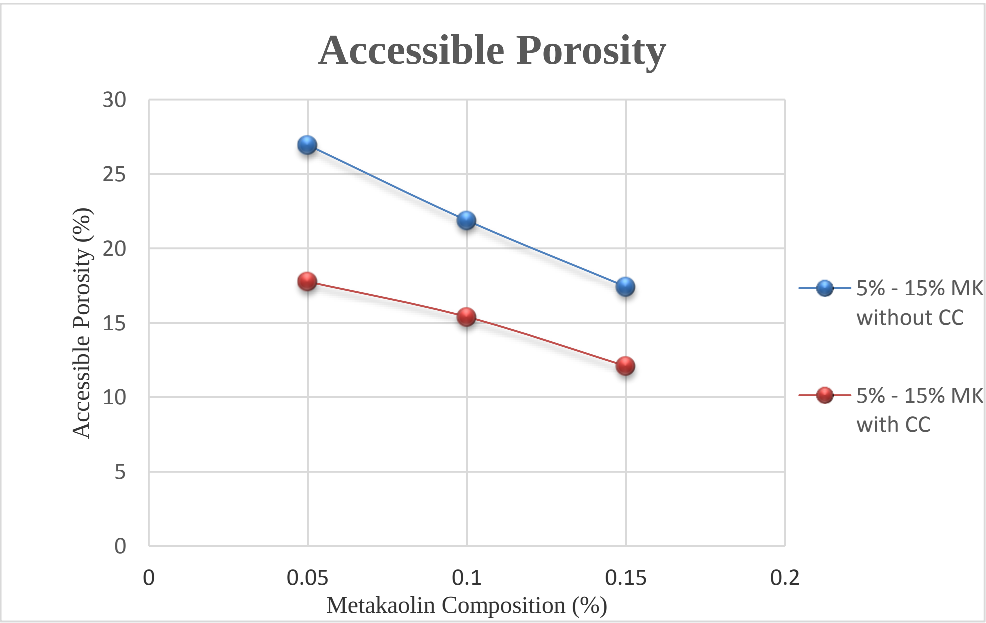

Figure 4.9: Comparison of Accessible Porosity with Metakaolin Composition

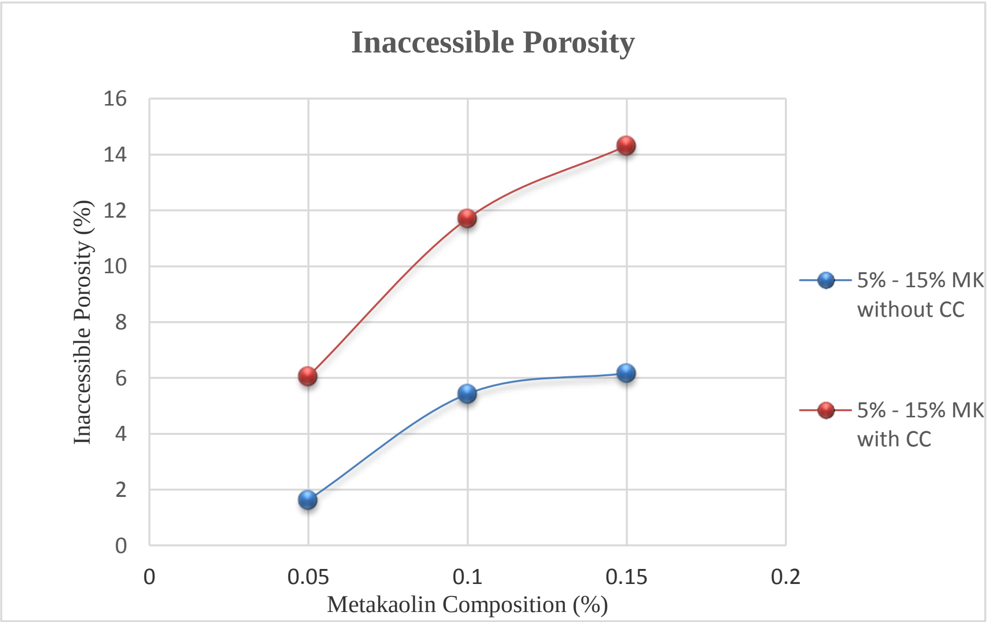

Figure 4.10: Comparison of Inaccessible Porosity with Metakaolin Composition

For the case of inaccessible porosity as shown in Figure 4.10, increase in metakaolin ratio from 5% to 10% with fixed W/C ratio of 0.45 and C/Sd ratio of 0.60 shows increase in inaccessible porosity. At low C/B ratio, the inaccessible porosity increases by 233% while an increase of 136% was observed in the high C/B ratio. At the same W/C ratio of 0.45 and C/Sd ratio of 0.60, low metakaolin composition showed an increase of 132% while the high metakaolin composition showed an increase of 223%. Higher cement and sludge ratio with high metakaolin composition showed a better increase in inaccessible porosity.

4.8 Permeability

Permeability is a measure of how easily fluid flow through the porous medium. Permeability is independent of fluid properties such as density and viscosity but dependent on the geometric properties of the sample itself such as porosity. Direct measurement of permeability is relatively costly and difficult to perform within a short period of time. In relation to permeability, Rose (1945) suggested a power-law relation as can be seen in Equation 10, where m is an exponent that is determined empirically. It was estimated that the m value is between 1.8 to 2 for consolidated sandstones (Archie, 1942).

For the permeability estimation for the S/S samples, m equal to 2 will be applied to investigate its relation to the changing composition of cement and metakaolin in this system.

$$Permeability. k \cong \phi^{m} \tag{11}$$

From the accessible porosity data of the selected optimized samples, using Equation 10, the permeability of the S/S were estimated and tabulated in Table 4.13.

Table 4.13: Estimated Permeability

Sample No.	Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Accessible Porosity with Compressibility Correction (CC), ϕ	Estimated Permeability (mD)
1	0.60	0.05	17.77	315.77
2	0.60	0.10	15.40	237.16
3	0.60	0.15	12.09	145.17

With estimation of permeability with m value equal to 2, the permeability property does not deviate further from its direct relationship with porosity. Similar pattern of changes were observed as porosity, where fixed W/C ratio of 0.45 and C/Sd ratio of 0.60 with increasing C/B ratio provides a higher porosity and in turn relates to increasing permeability. As such, the high W/C and C/Sd ratios with increasing C/B ratio provides a low porosity and ultimately decreasing permeability. In this context, the major objective of the technology is the reduction of the porosity and permeability of the S/S to reduce the contaminant leachability which in turn, favors the high C/Sd ratio which is 0.60 and the highest C/B ratio of 0.15 to provide the desired low porosity and permeability. The solidified sample strength is related to porosity as well as seen in Table 4.14 below.

Table 4.14: Unconfined Compressive Strength versus Porosity

Sample No.	Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Average Unconfined Compressive Strength, UCS (MPa) at Day 28	With Compressibility Correction (CC)
				Accessible Porosity
1	0.60	0.05	52.36	17.77
2	0.60	0.10	61.67	15.40
3	0.60	0.15	79.58	12.09

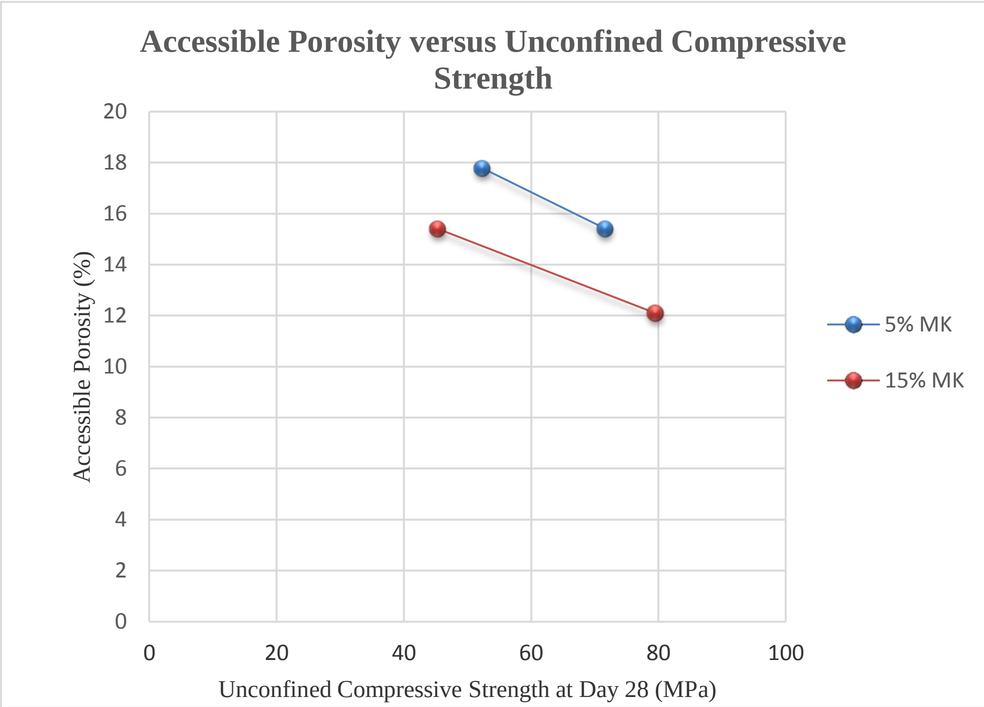

Figure 4.11: Accessible Porosity versus Unconfined Compressive Strength

From the Figure 4.11, a comparison was made between the fixed W/C and C/Sd ratios for an increase in C/B ratio. By referring to the 5 % metakaolin ratio line, as the ratio increases, the unconfined compressive strength increases, but it shows a decrease in the accessible porosity as can be seen in the chart. As for the 15% metakaolin ratio line, as the ratio increases, so does its unconfined compressive strength but the decrease was observed in its accessible porosity. The tabulated relationship between C/B ratios with UCS and accessible porosity are tabulated in Table 4.15.

Table 4.15: Comparisons of Binder Ratios with UCS and Accessible Porosity

Conditions	Unconfined Compressive	Accessible Porosity
C/B 5% MK	Increases	Decreases
C/B 10% MK	Increases	Decreases
C/B 15% MK	Increases	Decreases

4.9 Toxicity Characteristic Leaching Procedure (TCLP)

For this procedure, samples were tested before undergoing leaching procedure. TCLP 1311 procedure were followed as a standard outlined by USEPA. The extraction fluid used in this set of experiment would be acetic acid with pH within 2.88 ± 0.05. The extraction fluid was selected based on the preliminary test done for the selection of extraction under the TCLP 1311 procedures.

Based on the data obtained from the unconfined compressive strength, 5 samples were chosen to undergo this procedure. The 5 samples are the raw sludge, control sample without matakaolin and all samples of the C/B ratios of 0.05, 0.10 and 0.15 under the W/C = 0.45 and C/Sd = 0.60. The reason behind selecting these samples is due to the significant change in unconfined compressive strength observed from the lowest C/B ratio to the highest C/B ratio. The possible metals to be detected are copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), zinc (Zn), chromium (Cr), cadmium (Cd) and aluminium (Al). Prior to determining the concentration of the metals in the leachate, standard calibration curve be prepared by preparing standard solutions beforehand. The metal concentration in the leachate for TCLP has been tabulated in Table 4.16.

Table 4.16: Metal Concentration in Leachate for TCLP

Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Concentration (ppm)							
		Cu	Fe	Mn	Ni	Pb	Zn	Cr	Cd
Standard B		1.0	5.0	1.0	1.0	0.5	1.0	1.0	0.02
Raw Sludge		5.45	8.23	3.20	3.09	5.40	5.12	0.60	1.08
0.60	0.00	0.00	0.36	0.06	0.04	0.00	0.03	0.04	0.09
0.60	0.05	0.35	0.23	0.02	0.26	0.47	1.23	0.59	0.29
0.60	0.10	0.28	0.56	0.83	0.98	0.43	0.81	0.38	0.16
0.60	0.15	0.02	0.85	0.25	0.42	0.35	0.64	0.32	0.12

The readings were compared against the standard curve obtained from standard solutions ranged from 1, 2 and 4 ppm. Under Environmental Quality Act (EQA) 1974, 2 standards exist namely Standard A and B. Effluent that is discharged upstream of a water supply intake should meet Standard A, while effluent that is discharged downstream has to meet Standard B. The leachate falls under Standard B. The raw sludge showed a significantly high content of metals mainly iron and copper. All the metal content in the sludge exceeded the regulatory limit in Standard B outlined by EQA 1974 as can be seen in Table 4.19.

Higher C/B ratios were able to retain most metals in the solidified matrix of cement, petroleum sludge and metakaolin, in which lesser metals leached from cement into the solution. After being stabilized and solidified using OPC and matakaolin, almost all metals showed untraceable amount of metals from the hydrocarbon waste. The highest ratio of metakaolin shows the minimum amount of Cu while Al is expected to be the highest metal found because the main constituent in metakaolin is $Al_2Si_2O_7$. Based on the reading obtained in Table 4.16, it can be deduced that the leaching out of dissolved metal in the petroleum sludge waste are insignificantly low and below the regulated metals in industrial wastewater effluent of EQA 1974. The data obtained can be represented in the line graph as shown in Figure 4.12.

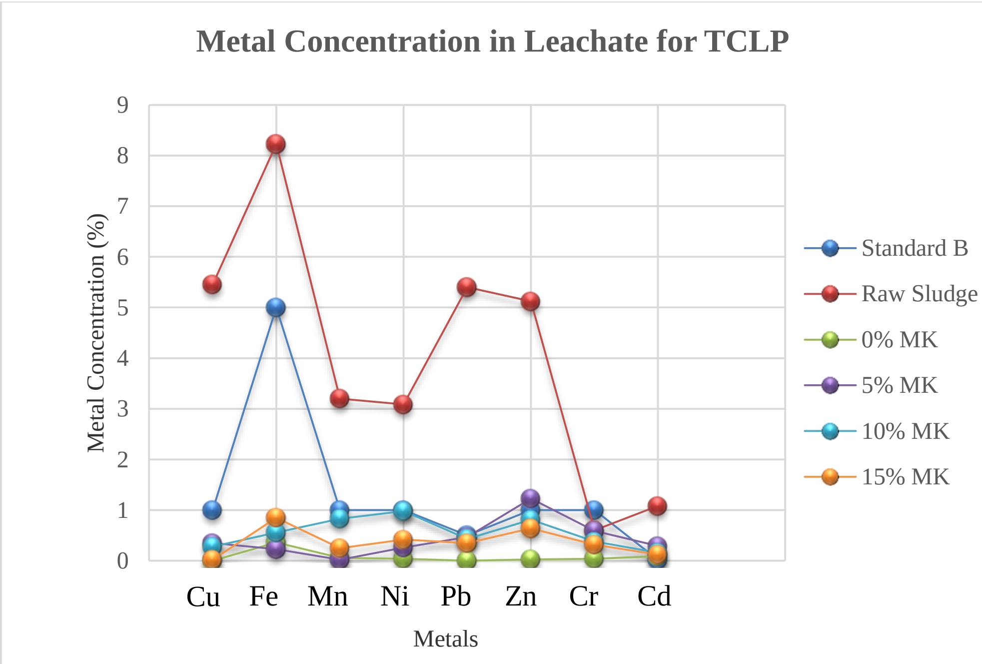

Figure 4.12: Metal Concentration in Leachate for TCLP

4.10 Surface Morphology

The surface morphology of the cementitious matrix of cement, petroleum sludge and metakaolin was studied using FESEM/EDX. The scanning electron microscopy (SEM) enables the particular sample to be examined visually from millimeters to micron meters. This is very useful to determine a specific topographical information as well as good physical and mechanical description of the microstructure of crystalline and amorphous materials, which cannot be detected by other techniques. On the other hand, non-crystalline, gel-like materials could be observed on the sample surface in the SEM images as shown in the Figures 4.13 to 4.21.

The EDX analysis indicated the presence of several elements such as C, O, Mg, Si, Ca, Si, Fe and others. The figures below show the results of FESEM/EDX carried out for the admixture metakaolin, 5% and 15% metakaolin with W/C=0.45 and C/Sd=0.60 ratios. As shown in the images, metakaolin appeared as flake-like plates, petroleum sludge as spongy cotton wool-like and cement appeared to be long needle-like structures. All of them had sizes only less than several microns in length. This is a possible indication that all the hydrated component in the matrix were amorphous. The appearance of metakaolin in the 15% sample appears to be more integrated with the cement and slugde as compared to the 5% sample. The 5% sample shows more of the needle-like structures of cement.

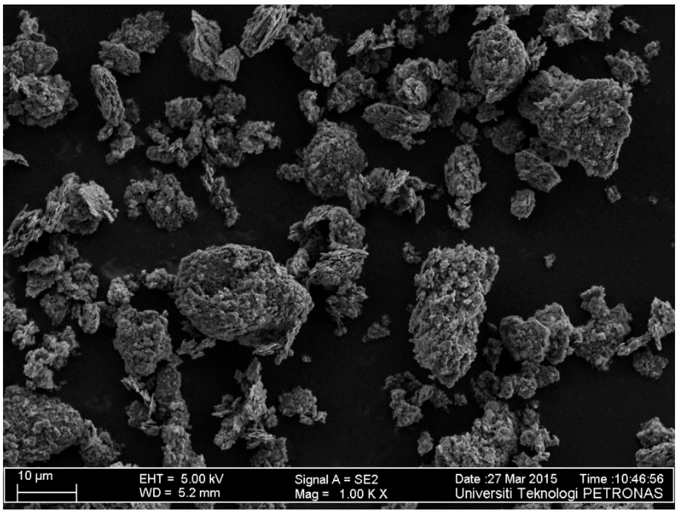

Figure 4.13: MK Sample at 1.00 K X magnification

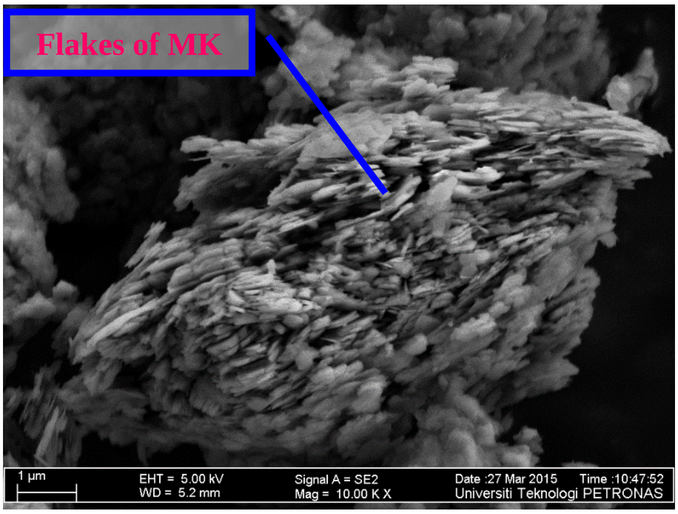

Figure 4.14: MK Sample at 10.00 K X magnification

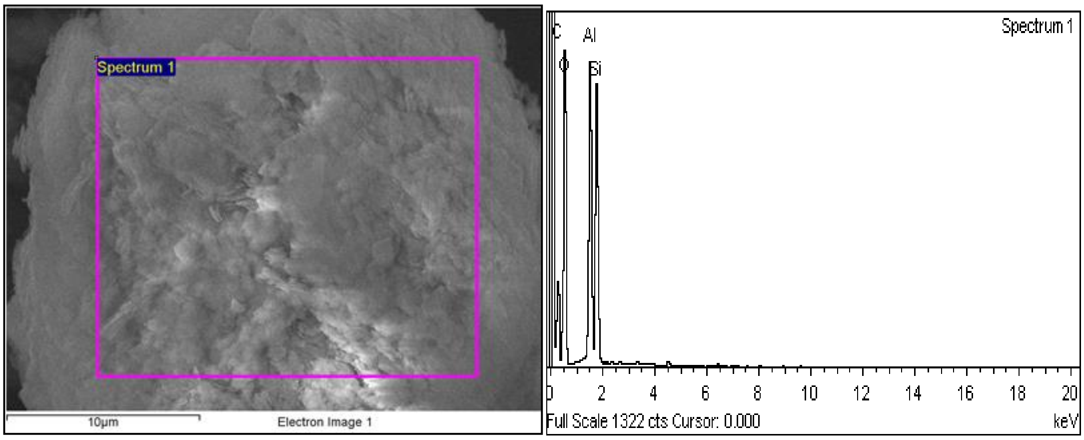

Figure 4.15: EDX of MK Sample

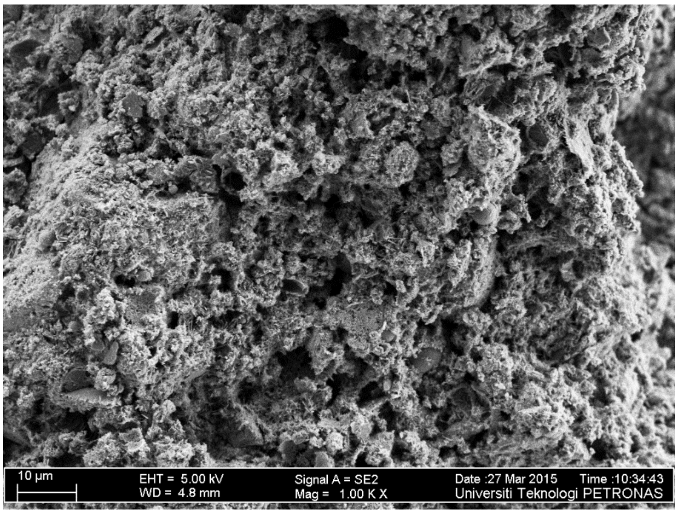

Figure 4.16: 5% MK at 1.00 K X magnification

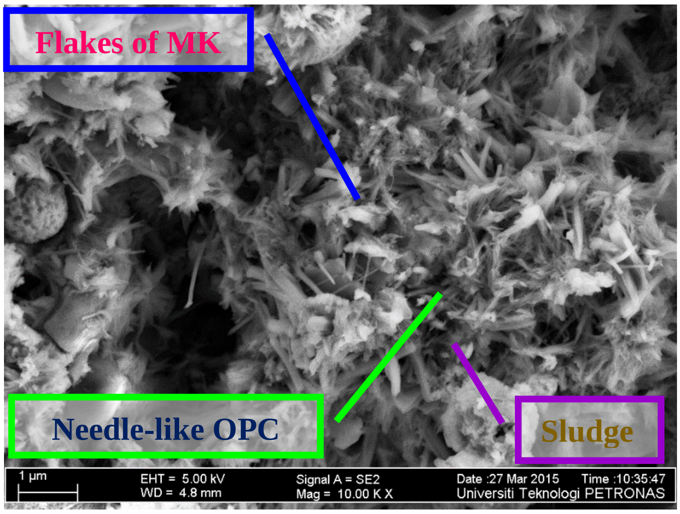

Figure 4.17: 5% MK at 10.00 K X magnification

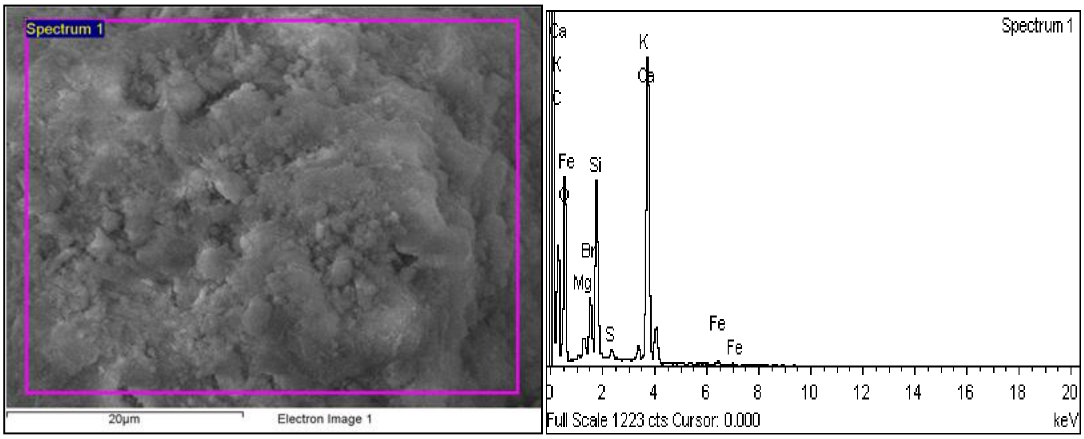

Figure 4.18: EDX of 5% Sample

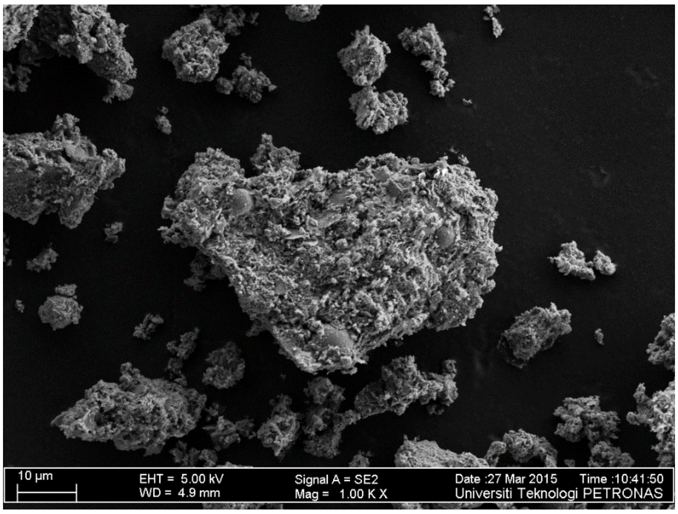

Figure 4.19: 15% MK at 1.00 X K magnification

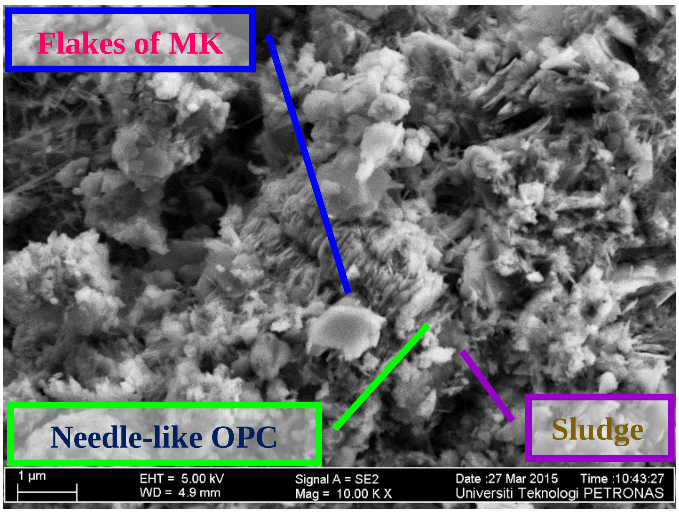

Figure 4.20: 15% MK at 10.00 K X magnification

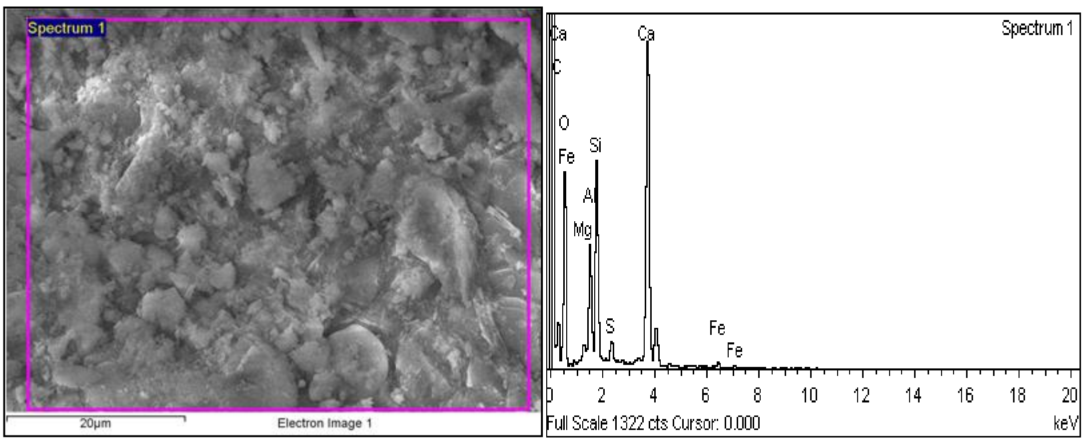

Figure 4.21: EDX for 15% Sample

The Table 4.17 shows the summary of the outcome of the EDX analysis. The all the samples, metakaolin, cement to binder ratio of 0.05 and 0.15 have the highest element of oxygen. Both 0.05 and 0.15 metakaolin content in the sample have the second highest calcium content with 22.94 wt% and 18.57 wt% respectively.

Table 4.17: EDX Results Summary

Elements	**Metakaolin, MK (wt %)**	**5% MK (wt %)**	**15% MK (wt %)**
Carbon, C	31.61	2.40	18.37
Oxygen, O	49.99	56.58	49.41
Magnesium, Mg	-	1.18	0.59
Aluminum, Al	8.91	-	4.07
Silicon, Si	9.48	9.00	7.23
Sulphur, S	-	0.46	0.94
Calcium, Ca	-	22.94	18.57
Iron, Fe	-	0.68	0.83
Potassium, K	-	0.88	-
Bromine, Br	-	5.90	-

4.11 X-Ray Diffraction (XRD) Study

XRD was used to study changes in the crystalline phases of the cement with and without metakaolin of cement to binder ratio of 0.15 after 28 days of curing. Type I Portland cement with the petroleum sludge, after hydration, was used as a control sample. The most prominent peaks in the control sample, Figure 4.26, were those of lead magnesium aluminium iron silicate oxide hydroxide. Calcium aluminum oxide ($CaO \cdot Al_2O_3$), an impurity compound found in cement, while the lead and magnesium comes from the petroleum sludge. For the cement to binder ratio of 0.15, Figure 4.26, there were various crystalline structures formed. The most prominent peaks were strontium lanthanum molybdenum oxide and yttrium tungsten oxide.

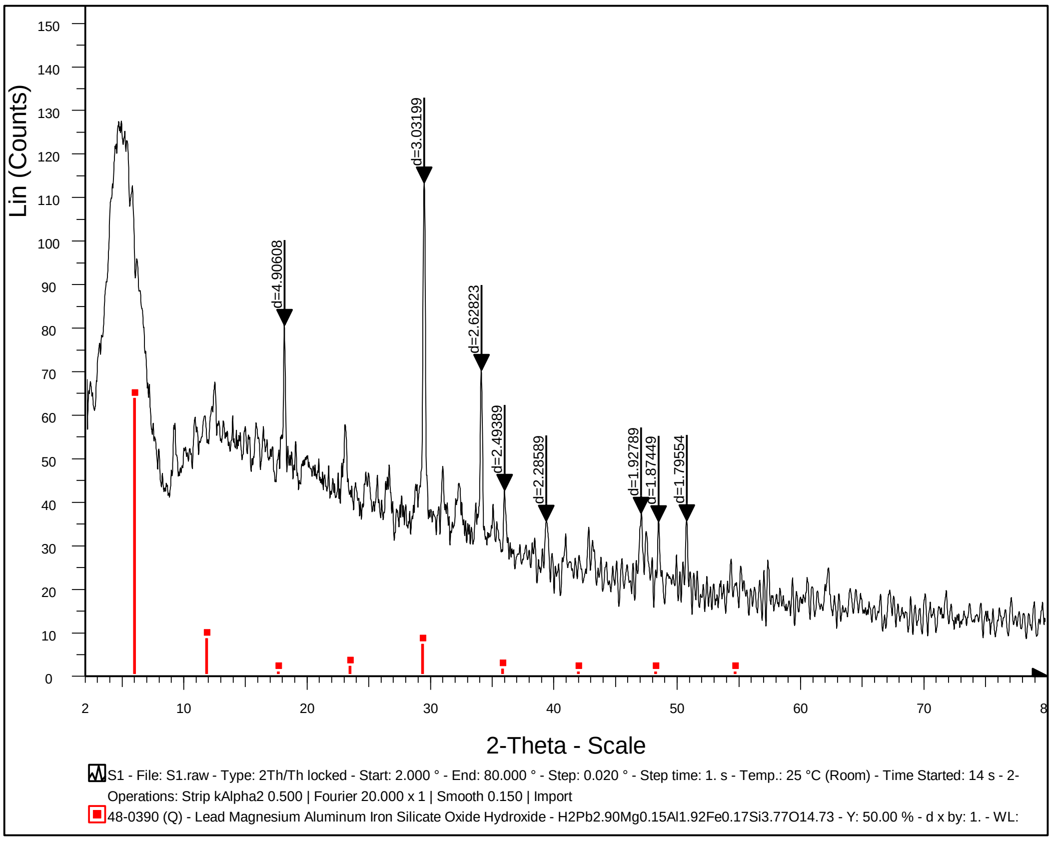

Figure 22: XRD Pattern of Control Sample of OPC and Petroleum Sludge

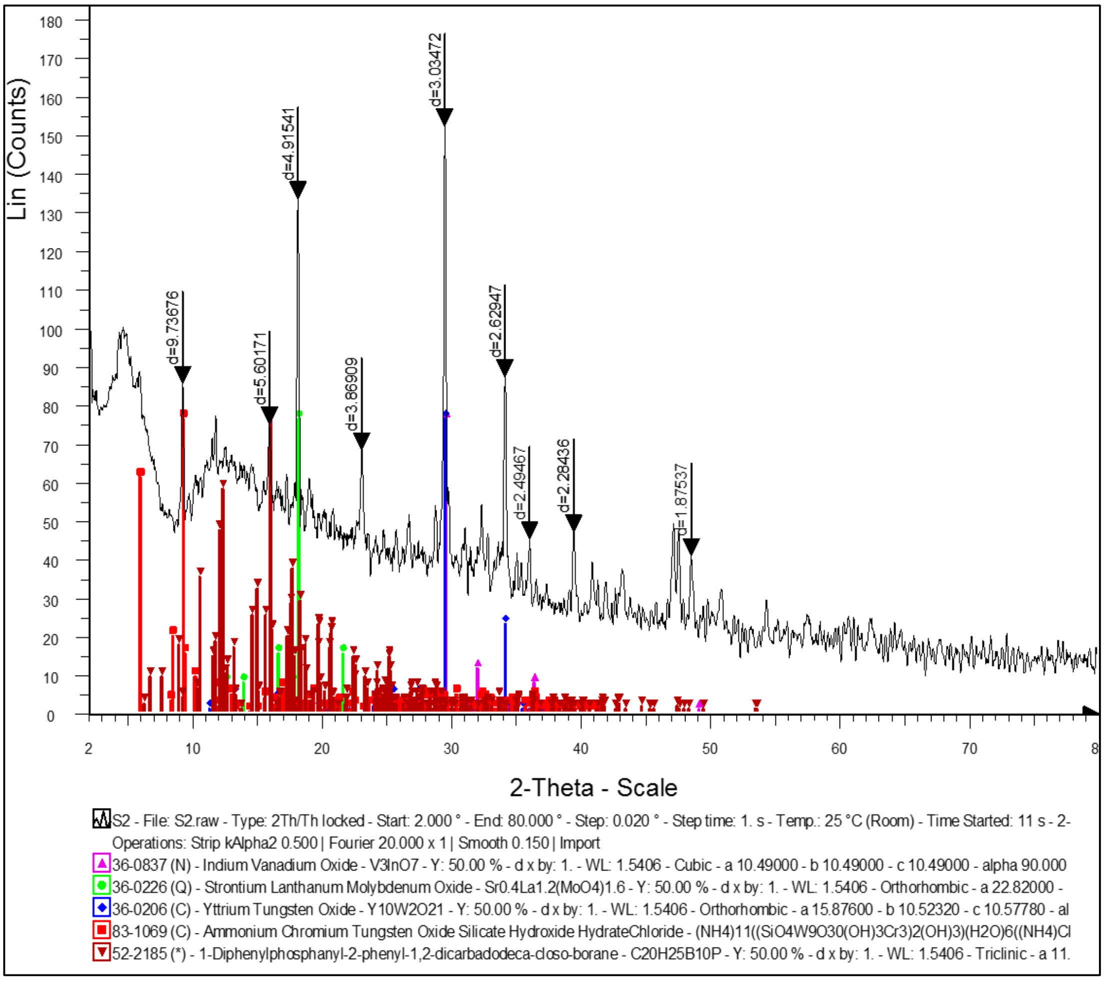

Figure 23: XRD Pattern of Cement to Metakaolin Ratio of 0.15

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From this study, it can be concluded that increase in the petroleum sludge waste ratio and metakaolin ratio increases the strength of the stabilized and solidified cement cubes. The highest C/Sd ratio of 0.60, with highest C/B ratio of 0.15 gives out the maximum strength of 79.58 MPa, highest strength compared to other C/ B ratio applied. Porosity was lowest at 12.09 when the W/C=0.45, C/Sd=0.60 and C/B at 0.15, which however increases rapidly as C/B decreases to 0.05. Metals content test proved the immobilization of selected metals with almost all metals almost undetectable after confined with cement together with metakaolin.

There were no distinct patterns or trends observed with increasing C/B ratio for metal leachability. All metal content tested for does not exceed the limit outlined under Standard B by EQA 1974. The surface morphology of the cementitious matrix of cement, petroleum sludge and metakaolin was studied using FESEM/EDX. The appearance of metakaolin in the 0.15 MK sample appears to be more integrated with the cement and sludge as compared to the 0.05 MK sample. The 0.05 sample shows more of the needle-like structures of cement. XRD was used to study changes in the crystalline phases of the cement with and without metakaolin of cement to binder ratio of 0.15, where there were prominent peaks showing various crystal formations in the samples.

The technology itself covers many aspects of environmental concerns, which carries the burden of undergoing multiple sets of tests and experimentation to further clarify or standardize the finding from this project. If given more time, more ratios can be researched on, and more tests can be conducted on the sample produced. Characterization of the samples can come from many angles, but due to the time constraint, the research ended with only few tests that is feasible within the time limit as well as provided budget. Add different ranges of additive, performing a lattice structure test, as well surface area would help to further understand the technology concept and its working principles.

REFERENCES

API (2010). Robust Summaries & Test Plan: Reclaimed Petroleum Hydrocarbons Category; Category Assessment Document. U. S. E. P. Agency. Washington, American Petroleum Institute: 60.

Aranda, C. B. A. (2008). Leaching Test Comparison for Solidified and Stabilized Contaminated Sediments. Faculty of Mathematics and Natural Sciences, University of Oslo. Environmental Geology and Geohazards: 99.

ASTM International, ASTM C109-91 Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimen), Cement, Lime Gypsum, vol. 04.01, 2005, pp.76-81.

Batchelor, B. (2006). "Overview of waste stabilization with cement." Waste Management 26(7): 689-698.

Bojes, H.K., and Pope, P.G. (2007). Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. Regulatory Toxicology and Pharmacology 47,288-295.

Bone, B. D. (2004). Review of scientific literature on the use of stabilisation/solidification for the treatment of contaminated soil, solid waste and sludges. E. A. UK. Bristol, Environent Agency: 343.

Bone, B. D. (2004). Guidance on the use of Stabilization/Solidification Technology for the Treatment of Contaminated Soil. E. A. UK, Environment Agency: 103.

Brace, W.F. (1980). Permeability of crystalline and argillaceous rocks. International Journal of Rock Mechanics and Mining Sciences and Geomechanics. Abstract. **17,** 241-251.

Chen, K., & Majewski, H. (1978). Disposal of heavy metal containing sludge wastes. *Disposal of Heavy Metal Containing Sludge Wastes*, *1*(1), 6-6.

Cloud, W.F. (1941). Effect of sand grin size distribution upon porosity and permeability. Oil Weekly. 103, 26.

Conner, J.R. and Hoeffner, S.L. (1998). A Critical Review of Stabilization/ Solidification Technology. Critical Reviews in Environmental Science and Technology 28 (4), 397-462

Cook, E. R. and B. Batchelor (1996). Chapter 4 Stabilization/solidification of hazardous wastes in soil matrices. Advances in Porous Media. M. Y. Corapcioglu, Elsevier. Volume 3: 307-359.

Davidovits, J., 1994. Properties of geopolymers cements. Proceedings First International Conference on Alkaline Cements and Concretes, 131-149.

Dell'Orso, M., Mangialardi, T., Paolini, A. E., & Piga, L. (2012). Evaluation of the leachability of heavy metals from cement-based materials. *J Hazard Mater, 227-228*, 1-8. doi: 10.1016/j.jhazmat.2012.04.017

Department of Environment, Environmental Quality Act (Sewage and Industrial Effluents) Regulations 1979. Third Schedule. Regulation 8(1), 8(2) and 8(3). Parameter Limit of Effluent of Standards A and B. Department of Environment, Ministry of Natural Resources and Environment Malaysia. 107.

Elizabeth, F. and John, C (1994). Evaluation of Solidification and Stabilization for Treating Contaminted Soils From The Frontier Hard Chrome Sites, Department of the Army: 279.

Hannak, P., and A.J. Liem. (1986). “Development of New Methods for Solid Waste Characterization.” In:International Seminar on the Solidification and Stabilization of Hazardous Wastes. Baton Rouge, Lousiana. April.

Holmes, T. T. (1991). A Comparison of Five Solidification/Stabilization Processes for Treatment of Municipal Waste Combustion Residues - Physical Testing. Studies in Environmental Science. H. A. v. d. S. J.J.J.M. Goumans and G. A. Th, Elsevier. Volume 48: 107-118.

Hu, G., et al. (2013). "Recent development in the treatment of oily sludge from petroleum industry: A review." Journal of Hazardous Materials 261(0): 470-490.

IPIECA (2010). Petroleum Refining Water/Wastewater Use and Management. R. W. M. T. Force. London, AECOM Inc.

Jeffery, L. M. (1995). The Application of Solidification/Stabilization to Waste Materials. Boca Raton, Florida, Lewis Publishers.

Karamalidis, A. K. and E. A. Voudrias (2007). "Cement-based stabilization/solidification of oil refinery sludge: Leaching behavior of alkanes and PAHs." Journal of Hazardous Materials 148(1–2): 122-135.

Larry, W. J. Interference Mechanism in Waste Stabilization/Solidification Processes. Environmental Laboratory, U.S. Army Engineer Waterways Experiment Station: 52.

Leonard, S. A. and J. A. Stegemann (2010). "Stabilization/solidification of petroleum drill cuttings: Leaching studies." Journal of Hazardous Materials 174(1–3): 484-491.

Luna Galiano, Y. (2011). "Stabilization/solidification of a municipal solid waste incineration residue using fly ash-based geopolymers." Journal of Hazardous Materials 185(1): 373-381.

Malviya, R. and R. Chaudhary (2006). "Factors affecting hazardous waste solidification/stabilization: A review." Journal of Hazardous Materials 137(1): 267-276.

Mamat, N. A. B. (2002). Stabilization/Solidification of Palm Oil Mill Effluent Sludge And A Pure Model Study Using Cementitious Technique. Institute of Postgradute Studies. Kuala Lumpur, Universiti of Malaya. Degree of Masters of Technology(Environmental Management): 243.

Pandey, B., Kinrade, S. D., & Catalan, L. J. (2012). Effects of carbonation on the leachability and compressive strength of cement-solidified and geopolymer-solidified synthetic metal wastes. *J Environ Manage, 101*, 59-67. doi: 10.1016/j.jenvman.2012.01.029

Qian, G., Sun, D. D., & Tay, J. H. (2003). Immobilization of mercury and zinc in an alkali-activated slag matrix. *J Hazard Mater, 101*(1), 65-77. doi: 10.1016/s0304-3894(03)00143-2

Roger, D. S. and S. Caijun (2005). Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes. D. S. Roger and S. Caijun. Boca Raton, Florida, CRC PRESS: 378.

Rose, H.E. (1945). An investigation into the laws of flows of fluids through bed of granular materials. Proceeding Institute of Mechanical Engineering and Applied Mechanics. **153**, 141.

Ruiz, M. C. and A. Irabien (2004). "Environmental behavior of cement-based stabilized foundry sludge products incorporating additives." Journal of Hazardous Materials 109(1–3): 45-52.

Saar, M.O. (1998). The relationship between permeability, porosity and mocrostructure in vesicular basalts. Department of Geological Sciences, University of Oregon. 2-41.

Shi, C. and A. Fernández-Jiménez (2006). "Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements." Journal of Hazardous Materials 137(3): 1656-1663.

Silva, M. A. R. (2011). "Environmental impact of industrial sludge stabilization/solidification products: Chemical or ecotoxicological hazard evaluation?" Journal of Hazardous Materials 192(3): 1108-1113.

Trussell, S. and R. D. Spence (1994). "A review of solidification/stabilization interferences." Waste Management 14(6): 507-519.

USEPA (1999). Solidification/Stabilization Resource Guide. U. S. E. P. Agency. Washington, Office of Solid Waste and Emergency Response: 91.

USEPA (1996). STABILIZATION/SOLIDIFICATION PROCESSES FOR MIXED WASTE. Washington, United States Environmental Protection Agency.

USEPA (2012). A Citizen's Guide to Solidification and Stabilization, USEPA.

Vale, J., et al. (1995). Stabilization/solidification of industrial inorganic wastes using coal flyashes from desulphurisation processes. Coal Science and Technology. J. A. Pajares and J. M. D. Tascón, Elsevier. Volume 24: 1955-1958.

Vandecasteele, C. (1997). ICP-MS, hydride generation-ICP-MS, and CZE for the study (analysis and speciation) of solidification/stabilisation of industrial waste containing Arsenic. Goumans and H. A. v. d. Sloot, Elsevier. Volume 71: 469-479.

Wiles, C. C. (1987). "A review of solidification/stabilization technology." Journal of Hazardous Materials 14(1): 5-21.

Wong, P.Z., Koplik, J. and Tomanic, J.P. (1984). Conductivity and permeability of rocks. Physical Revision B. **30**, 6606-6614.

Zain, A., Shaaban, M., & Mahmud, H. (2014). Leachability of Metal Ions in TCLP Leachate of Solidified Petroleum Sludge. *Key Engineering Materials,* 1094-1098. Retrieved December 14, 2014, from http://eprints.utp.edu.my/11227/1/AMR.917.123.pdf

Zain, A., Shaaban, M., & Mahmud, H. (2014). The Effect of Cement Replacement Materials to the Hydration of Petroleum Sludge in OPC. *Key Engineering Materials,* 385-389. Retrieved December 14, 2014, from https://www.academia.edu/

APPENDICES

APPENDIX I SAMPLE PREPARATION & MIXING OF SAMPLE

Figure A.1: Preparation of Metakaolin at 700^{0}C for 4 hours

Figure A.2: Cement, Sludge and Metakaolin after Mixing

APPENDIX II SAMPLE MOULDING & TESTING

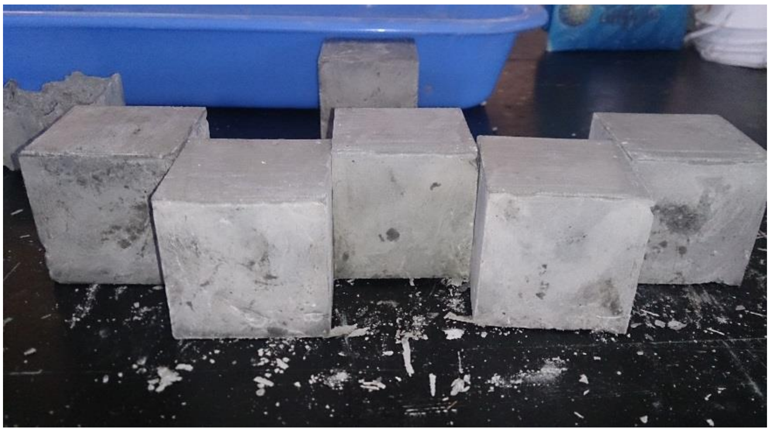

Figure A.3: Casting of mixture in 5cm x 5cm x 5cm moulds

Figure A.4: Unconfined Compressive Strength Test on Sample

APPENDIX III MIXING CALCULATION FOR (W/C)

ratio	ratio	ratio	KG	KG	m^3	KG	KG	m^3	KG	m^3	m^3	ratio	KG	KG	KG	KG	KG	KG
C/S_d	W/C	C/B	S raw	S dry	S volume	C	C used	C volume	B used	B volume	total	needed	C real	S real	B real	W real	W in S	W add
0	0.35	0	0	0	0	1	1	0.0003	0	0	0.0003	0.1699	5.8875	0	0	2.0606	0	2.0606
0	0.40	0	0	0	0	1	1	0.0003	0	0	0.0003	0.1699	5.8875	0	0	2.3550	0	2.3550
0	0.45	0	0	0	0	1	1	0.0003	0	0	0.0003	0.1699	5.8875	0	0	2.6494	0	2.6494

Appendix II: Mixing Calculation for Different Water to Cement Ratio (W/C)

APPENDIX IV MIXING CALCULATIONS FOR (C/Sd)

ratio	ratio	ratio	KG	KG	m^3	KG	KG	m^3	KG	m^3	m^3	ratio	KG	KG	KG	KG	KG	KG
C/S_d	W/C	C/B	S raw	S dry	S volume	C	C used	C volume	B used	B volume	total	needed	C real	S real	B real	W real	W in S	W add
60	0.45	0	11.6089	1	0.0114	40	40	0.0127	0	0	0.0241	12.8563	3.1113	0.9030	0	1.0890	0.8252	0.2638
60	0.45	0	11.6089	1	0.0114	50	50	0.0159	0	0	0.0273	14.5548	3.4353	0.7976	0	1.2024	0.7289	0.4735
60	0.45	0	11.6089	1	0.0114	60	60	0.0191	0	0	0.0305	16.2533	3.6916	0.7142	0	1.2920	0.6527	0.6393

Appendix III: Mixing Calculation for Same Water to Cement Ratio (W/C) = 0.45 and Different Cement to Sludge Ratio

APPENDIX V MIXING CALCULATION FOR (C/B)

ratio	ratio	ratio	KG	KG	m^3	KG	KG	m^3	KG	m^3	m^3	ratio	KG	KG	KG	KG
C/S_d	W/C	C/B	S raw	S dry	S volume	C	C used	C volume	B used	B volume	total	needed	C real	S real	B real	W add
60	0.45	0	3.9657	1	0.0035	60	60	0.0191	0	0.0000	0.0226	12.0524	4.9782	0.3290	0.0000	1.9941
60	0.45	0.05	3.9657	1	0.0035	60	57	0.0182	3	0.0012	0.0228	12.1608	4.6872	0.3261	0.2467	1.8654
60	0.45	0.1	3.9657	1	0.0035	60	54	0.0172	6	0.0023	0.0230	12.2692	4.4013	0.3232	0.4890	1.7388
60	0.45	0.15	3.9657	1	0.0035	60	51	0.0162	9	0.0035	0.0232	12.3776	4.1203	0.3204	0.7271	1.6146

Appendix VI: Mixing Calculation for Cement to Sludge Ratio (C/Sd) = 60 with Metakaolin