Admixture Effect on the Porosity, Permeability and Leachability of Immobilized Hydrocarbon Waste

By

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13078

Dissertation submitted in partial fulfilment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical)

May 2014

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CERTIFICATION OF APPROVAL

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

Approved by,

____

(Dr Asna binti Mohd Zain)

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TRONOH, PERAK
MAY 2014

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.

(Harishinan A/L Nadrajah)

ABSTRACT

This research studies the waste management of residual hydrocarbon waste that can be retrieved from the wastewater stream in a petroleum refinery complex by the application of a technique known as Solidification and Stabilization (S/S). 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 objective is to optimize waste to cement and admixture effect (fly ash) ratio based on the unconfined compressive strength as the main criteria. The performance of the S/S is measured through leaching analysis to determine leachability of metal in the leachate, porosity and permeability properties of the stabilized waste with the unconfined compressive strength and its leaching behaviour. It was found that the lowest water to cement ratio, 0.35 gives out the largest unconfined compressive strength of 66.17 MPa. The presence of sludge and fly ash showed that the highest cement to sludge ratio of 60 with highest amount of fly ash of 15% produces the strongest cement matrix of strength of 39.75 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 and total oil grease content in the leachate were relatively low and below the regulated metals content and total oil grease content in wastewater as outlined in EQA 1974.

ACKNOWLEDGEMENT

In the name of God, I thank Him 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. I thank God for sending such wonderful being my supervisor for my final year project. For all the knowledge that she did not felt stingy to share with her fellow student, it has been a remarkable journey 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.

As for the remarkable coordinator, Dr Abrar Inayat, I would personally thank him for providing support from time to time and accommodate to the students need. Without the complete guidelines and seminars on matters regarding the final year projects, the student might have found it difficult to handle things. Thanks to the coordinator quick thinking and full support, I was able to complete the project within the time frame as well as designated formats. A special gratitude to Ms Azriha Anuar for her assistance on the Atomic Absorption Spectrometry, Mr Shahrul, for the Compression Test Machined, as well as Mr Saharuddin for the chemicals and equipments provided throughout the project.

Who I am now if due to my parents, and I believe this report is dedicated to them, signifying the end of the remarkable journey in my life, and I thank them for being there with me, supportive and encouraging through my ups and downs and lastly in completing my final year project.

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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 behaviour which results in better outcome. However, the application of admixtures under this technology is still under study. Fly ash is generally applied as a replacement material for binder as it exhibit similar behaviour as a cementing material (Roger and Caijun 2005). Generally, fly ash mixed with Portland cement has many advantages including increase in viscosity, preventing phase separation, acting as pozzolan, binding additional water, decreasing the pore pH, adsorbing metal ions, and sometimes results in retarding the setting time of the cement (Trussell and Spence 1994). The application of fly ash 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 fly ash might be altered which may result in better or underperforming S/S cement matrix.

1.2 Problem Statement

Hydrocarbon waste which originates from crude oil refineries are classified under the nonspecific source wastes, which is called as F list wastes specified under USEPA. When considering the application of this S/S technology, there are few factors that must be taken into considerations. Among the important ones is the interference of the organic compound with the cement hydration, including setting time, strength development and durability as well as the purpose of S/S technology which is the immobilization of contaminants. Generally, not all waste is compatible with the cement hydration which eventually will result in certain critical goal not being achieved by the cement based matrix. The alteration in the setting time may results in the matrix losing its plasticity immediately upon mixing. 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 behaviour may prove the technology not suitable for hydrocarbon based waste.

1.3 Objectives

1. To study the effects of the absence and presence of fly ash on the porosity, permeability, leachability and unconfined compressive strength of the immobilized HC waste.
2. To study the effect of cement to fly ash ratio, C/B, cement to HC waste ratio, C/Sd and water to cement ratio, W/C towards the porosity, permeability, leaching and unconfined compressive strength behaviour.
3. The study the leachability of metals and oil and grease content from the S/S waste leachate.
4. To investigate the optimize composition of the solidified cement based matrix with immobilized HC waste that fulfils the standard requirement.

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 United States Environmental Protection Agency.
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 and organic release from cement based matrix.

8. Quality assurance and quality control (QA/QC) for the solidification and stabilization technology.

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 pre treatments 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. 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 Admixtures

Admixtures are ingredients other than water, aggregates, hydraulic cement, and fibers that are added to the concrete batch immediately before or during mixing (Ruiz and 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. Roughly 80% of the concrete are produced so to increase its workability and feasibility. Based on a survey conducted by the National Ready Mix Concrete Association, fly ash is used in 39% of all ready-mixed concrete, while water-reducer admixture were used in at least 70% of the concrete (Aranda 2008). Depends on the chemical composition of these admixtures, they serve respective purposes based on the client's requirement. According to US Federal Highway Administration, two basic types of admixtures are available: chemical and mineral.

Fly ash is categorized under mineral admixtures. Fly ash is defined in Cement and Concrete Terminology (ACI Committee 116) as "the finely divided residue resulting from the combustion of ground or powdered coal, which is transported from the firebox through the boiler by flue gases." Fly ash is generated by combustion of coal which is usually obtained from coal-fired electric generating plants. Ash which does not fly with the flue gas from the combustion is known as bottom ash. Two classifications of fly ash are produced, according to the type of coal used. Class C fly ash is generated via combustion of lignite or in certain cases, sub bituminous coal. Anthracite and bituminous coal on the other hand are what Class F fly ash is made up of.

CHAPTER 3

METHODOLOGY

3.1 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.

3.1.1 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 Equation 1 and 2.

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

$$= \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4℃} = \frac{S-W}{R-W} \times F \quad (1)$$

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

$$= \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4℃} = \frac{(P-W)}{(R-W)-(Q-P)} \times F \quad (2)$$

Based on the temperature, T measured, derived the value of F from the tabulated temperature correction factor shown in Table 1.

Table 3.1 Temperature Correction Factor, F

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

3.1.2 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 3.

$$Moisture\ Content\ (\%) = \frac{(D - C) \times 100}{C - E} \quad (3)$$

3.1.3 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 dessicator 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 dessicator 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 Equation 4, 5 and 6 accordingly.

$$\%\ total\ solids = \frac{(A - B) \times 100}{C - B} \tag{4}$$

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

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

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

3.1.4 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.

3.1.5 Total Oil and Grease Analysis (TOG)

The analysis is to measure certain constituents that may influence leachate. Aerobic and anaerobic biological processes might be disrupted with the presence of excessive amount of waste thus reducing the efficiency of the wastewater treatment itself. “Oil and grease” is a conventional pollutant under 40 CFR 401.16 and generally refers to substances, including biological lipids and mineral hydrocarbons that have similar physical characteristics and common solubility in an organic extracting solvent. According to U.S. EP SW-846 Method 9071b, this procedure helps to examine the total content of oil and grease in a sample. This analysis is crucial as oil and grease interfere with cement or pozzolan-based S/S treatment. This test must be conducted on the hydrocarbon waste as well as the leachate for ensuring the S/S technology does aids in stabilizing and immobilizing the hydrocarbon waste in the cement based matrix.

3.1.6 Loss on Ignition (LOI)

Loss on ignition purpose is to provide a rough estimation on the percentage of organic content of the sediment. At high temperature, this procedure oxidizes organic content of the sample, thus determining the amount of mass lost due to the ignition. In moisture content procedure, water removed from the hydrocarbon sample represents only one part of total moisture, known as hygroscopic water. That moisture is made up of the water adsorption on the surface of solids, the water of capillarity and swelling as well as the hygrometrical water of the gas fraction of the soil which was mentioned in the Handbook of Soil Analysis. To further remove water beyond hygroscopic water, this measurement will elevate the temperature to a certain extent, where most moisture and even organic content will be removed via oxidation. For this research purpose, loss on ignition of cement and fly ash were measured. If the water content represents less than 5 % of the total mass of the sample, then it could be considered negligible from including in the calculation of water required to be added in the cement mixture. The procedure is as per below :

1. Place empty crucible in the furnace at 550 ^oC for 30 minutes. Cool the crucible in the dessicator at ambient temperature and weigh the crucible to the nearest 1 mg. Record the mass as A.
2. Add roughly 0.5 to 5 g of sample into the crucible and weigh the mass of the crucible plus sample. Record the weight as B.
3. Heat the furnace up to 105 ^oC. Place the sample + crucible into the furnace and leave it for 24 hours. Cool the crucible in the dessicator at ambient temperature and weigh the crucible to the nearest 1 mg. Once done, weigh the sample + crucible, and record it as C.
4. Heat up the furnace till it reaches 550 ^oC. Place the sample from procedure 3 into the furnace at 550 ^oC for 4 hours. Cool the crucible in the dessicator at ambient temperature and weigh the crucible to the nearest 1 mg. Once done. Weight the sample + crucible, and record it as D.

The loss of ignition at 550 ^oC is calculated as per the formula shown in Equation 7.

$$Loss\ on\ Ignition\ (\%) = \frac{(C - D) \times 100}{B - A} \tag{7}$$

where :

A = weight of dried crucible, g

B = weight of dried crucible + sample, g

C = weight of residue + crucible at 105 ^oC, g

D = weight of residue + crucible at 550 ^oC, g

3.2 S/S Evaluation

3.2.1 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.

3.2.2 Leaching Test

This test is used to evaluate the leaching of metals, volatile and semivolatile 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 behaviour of the solidified waste. The simulation of the leaching behaviour 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.

3.2.3 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.

3.3 Gantt Chart and Key Milestones

The process flow for the whole project is as depicted below with the key milestones being highlighted as the important parameter for both FYP I and FYP II. The feasibility of the project to be done within the provided looks satisfactory provided the process takes place as planned below.

Final Year Project Gantt Chart														
ACTIVITIES	FYP I													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Title Selection	■	■												
Literature Review Analysis and Project Planning			■	■										
Preliminary Experimentation					■	■	■	■	■	■	■	■	■	■
i. CharacterizationTest for HC Sludge, Binder and Fly Ash					■	■	■	■	■	■	■	■	■	■
ii. Mixing and Moulding Cement Sample					■	■	■	■	■	■	■	■	■	■
iii. Curing (28 days)					■	■	■	■	■	■	■	■	■	■
Extended Proposal Submission							●							
Oral Proposal Defence Presentation								●						
Experimentation Continuation and Interim Report Preparation									■	■	■	■		
Interim Report First Draft Submission (9 April)													●	
Interim Report Final Draft Submission(21 April)														●

FIGURE 3.1 Final Year Project I Gantt Chart

Final Year Project Gantt Chart														
ACTIVITIES	FYP II													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Experimentation Continuation and Analysis	■	■	■	■	■	■	■	■						
i. Cement Based Matrix Test	■	■	■	■	■	■	■	■						
ii. Compressive Strength Test	■	■	■	■	■	■	■	■						
iii. Permeability & Porosity Test	■	■	■	■	■	■	■	■						
iv. Leaching and Leachate Analysis	■	■	■	■	■	■	■	■						
Submission of Progress Report								■						
Results and Discussion Summarization									■	■				
Pre-SEDEX											●			
Draft Report Submission												■		
First Dissertation Submission (Softbound)													■	
Technical Paper Submission													●	
Oral Presentation														●

FIGURE 3.2 Final Year Project II Gantt Chart

● Key Milestones

■ Process

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 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 8 and the calculated value as per tabulated in Table 4.1.

$$Specific\ Gravity_{\frac{T}{4}°C}$$
$$= \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4\ °C} = \frac{(S-W)}{(R-W)} \times F \qquad (8)$$

Table 4.1 Specific Gravity

Specific Gravity	Hydrocarbon Waste		
	1	**2**	**3**
Temperature (^{o}C)	25.00	25.00	25.00
Mass of Empty Container (g), **W**	109.70	110.85	109.31
Mass of Empty Container + Sludge (wet) (g), **S**	120.16	121.14	119.70
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	**1.02**		

4.2 Total Oil and Grease (TOG)

The TOG was measured using the InfraCal TOG/TPH Analyzer. Referring to the previously mentioned procedure, a sample size of 10 mL was taken, combining a mixture of n-hexane and the sample. The sample was vigorously shaken for 2 minutes before the clear top layer of the mixture was extracted to measure the TOG. The trials were repeated for 3 times before taking the average value for the sample TOG as shown in Table 4.2.

Table 4.2 Total Oil and Grease

Total Oil Grease (TOG)	Hydrocarbon Waste		
	1	2	3
Concentration (ppm)	61.4	55.5	58.3
Average TOG (ppm)	**58.4**		

4.3 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 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. The calculated moisture content is as shown in Table 4.3 using Equation 9.

$$Moisture\ Content = \frac{wet\ weight - dry\ weight}{wet\ weight} \times 100 = \frac{(C-B)}{B} \times 100 \quad (9)$$

Table 4.3 Moisture Content

Moisture Content (%)	Hydrocarbon Waste		
	1	2	3
Mass of Empty Container (g)	109.72	110.86	109.31
Mass of Empty Container + Sludge (wet) (g)	114.83	115.85	114.31
Mass of Sludge (wet) (g), C	5.11	4.99	5.00
Mass of Empty Container + Sludge (dry) (g)	114.79	115.80	114.27
Mass of Sludge (dry) (g), B	0.05	0.04	0.05
Moisture Content (%)	92.31	90.03	91.82
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.

4.4 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 4.4.

Table 4.4 Total, Fixed & Volatile Solid

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) (g)		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**		

4.5 Loss on Ignition (LOI)

Based on the procedures mentioned previously, the mass of sample lost through ignition at 550 ^{o}C is as tabulated in Table 4.5 and 4.6 for cement and fly ash accordingly. The result showed a typically small amount of loss of mass, which in this research is considered as negligible to be considered in the cement mixture calculation. The presentable amount of water in both samples is insignificant compared to the moisture content of the hydrocarbon waste sample.

Table 4.5 Loss on Ignition (Cement)

Loss on Ignition (%)	Cement		
	1	2	3
Mass of Empty Crucible, A (g)	82.86	83.97	86.50
Mass of Empty Crucible + Sample, B (g)	87.23	88.41	90.91
Mass of Sample (g)	4.38	4.44	4.41
Mass of Residue + Crucible at 105 ^oC, C(g)	87.20	88.39	90.90
Mass of Residue + Crucible at 550 ^oC, D (g)	87.15	88.33	90.85
Loss on Ignition (%)	1.26	1.29	1.23
Average Loss on Ignition (%)	**1.26**		

Table 4.6 Loss on Ignition (Fly Ash)

Loss on Ignition (%)	Fly Ash		
	1	2	3
Mass of Empty Crucible, A (g)	82.86	83.97	86.54
Mass of Empty Crucible + Sample, B (g)	87.42	88.46	91.04
Mass of Sample (g)	4.57	4.49	4.50
Mass of Residue + Crucible at 105 ^oC, C(g)	87.39	88.44	91.00
Mass of Residue + Crucible at 550 ^oC, D (g)	87.30	88.35	90.89
Loss on Ignition (%)	2.03	1.99	2.23
Average Loss on Ignition (%)	**2.09**		

4.6 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 Fly Ash	= 2634.1 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 fly ash, the mass of cement reduced according to the percentage of fly ash added. For example :

Percentage of Fly Ash : 15 %

Mass of Fly Ash 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, fly ash 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 Fly Ash	= 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

= 13.056

Based on the ratio calculated above, the real mass of cement, fly ash and raw sludge required for mixing 15 cubic moulds of cement block can be calculated as shown below:

Mass of Cement Required	= 34 kg / 13.056	= 2.6042 kg
Mass of Fly Ash 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 0.913859

= 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 4.7.

Table 4.7 Mass for C/Sd = 40 and C/W = 0.45

Component	Mass
Cement	2.6042
Raw Sludge	0.8892
Fly Ash	0.4596
Water	0.3756

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 Table 4.8, 4.9 and 4.10. The complete calculation for all the selected ratios is included in Appendices. The calculation was made by using Microsoft Excel spreadsheet. Once the mixing calculation is completed, the next thing to look into is the mixing procedure for the mixture.

Table 4.8 Proposed Set of Ratios for Cement + Water

Water to Cement Ratio
0.35
0.40
0.45

Table 4.9 Proposed Set of Ratios for Cement + Water + Waste Sludge

Cement to Sludge Ratio (C/Sd)	Water to Cement Ratio
40	0.35
50	0.35
60	0.35

Table 4.10 Proposed Set of Ratios for Cement + Water + Waste Sludge + Fly Ash

Cement to Sludge Ratio (C/Sd)	Fly Ash Composition (%F.A.)	Water to Cement Ratio (W/C)
40	5%	0.45
	10%	
	15%	
50	5%	0.45
	10%	
	15%	
60	5%	0.45
	10%	
	15%	

4.7 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 fly ash. 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 caste 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 fly ash 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.

4.8 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, 3, 7, 14 and 28. The measured unconfined compressive strength was taken according to a planned schedule, which can be seen in Appendix VII. 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.

4.8.1 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 waste sludge and fly ash.

Table 4.11 Unconfined Compressive Strength for W/C Ratios

Water to Cement Ratio (W/C)	Unconfined Compressive Strength (UCS) Average UCS (MPa)				
	Day 1	Day 3	Day 7	Day 14	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

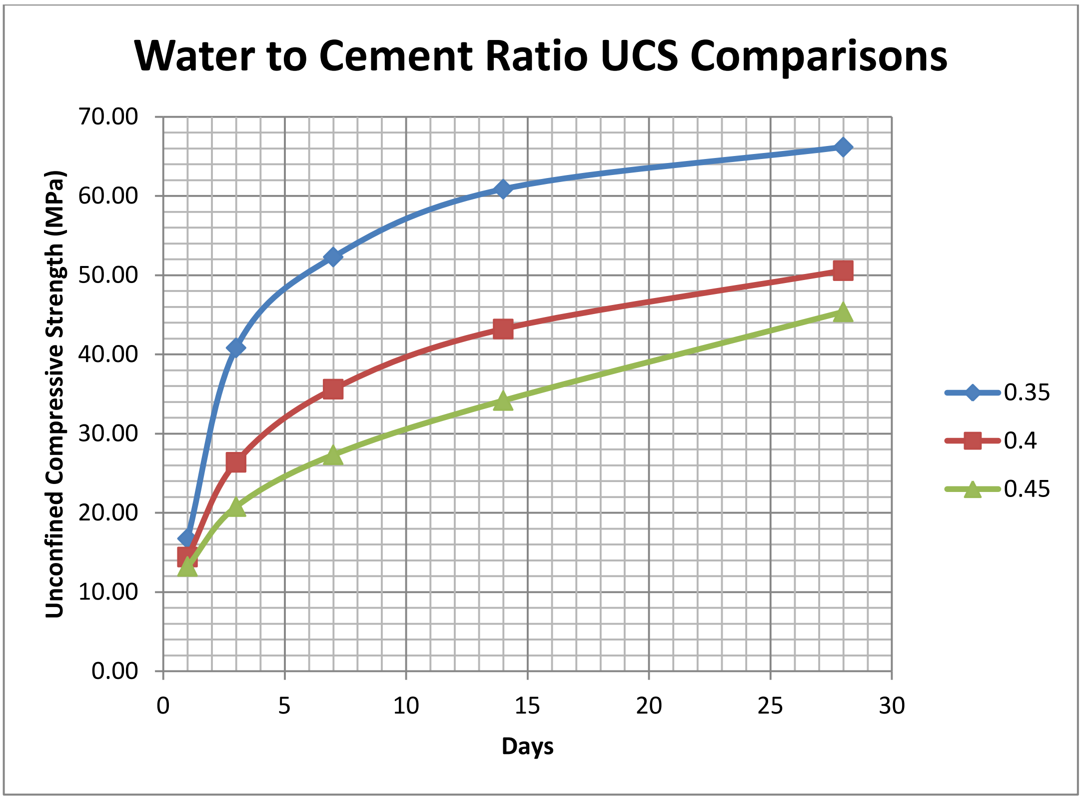

FIGURE 4.1 Water to Cement Ratios UCS Comparison

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 0.35 as it exhibits the highest unconfined compressive strength as can be observed in Figure 4.1.

4.8.2 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 fly ash. 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 4.12 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	0.35	13.94	32.01	36.73	41.46	45.78
50	0.35	16.61	34.61	36.71	41.26	46.29
60	0.35	19.19	35.33	38.28	41.24	46.43

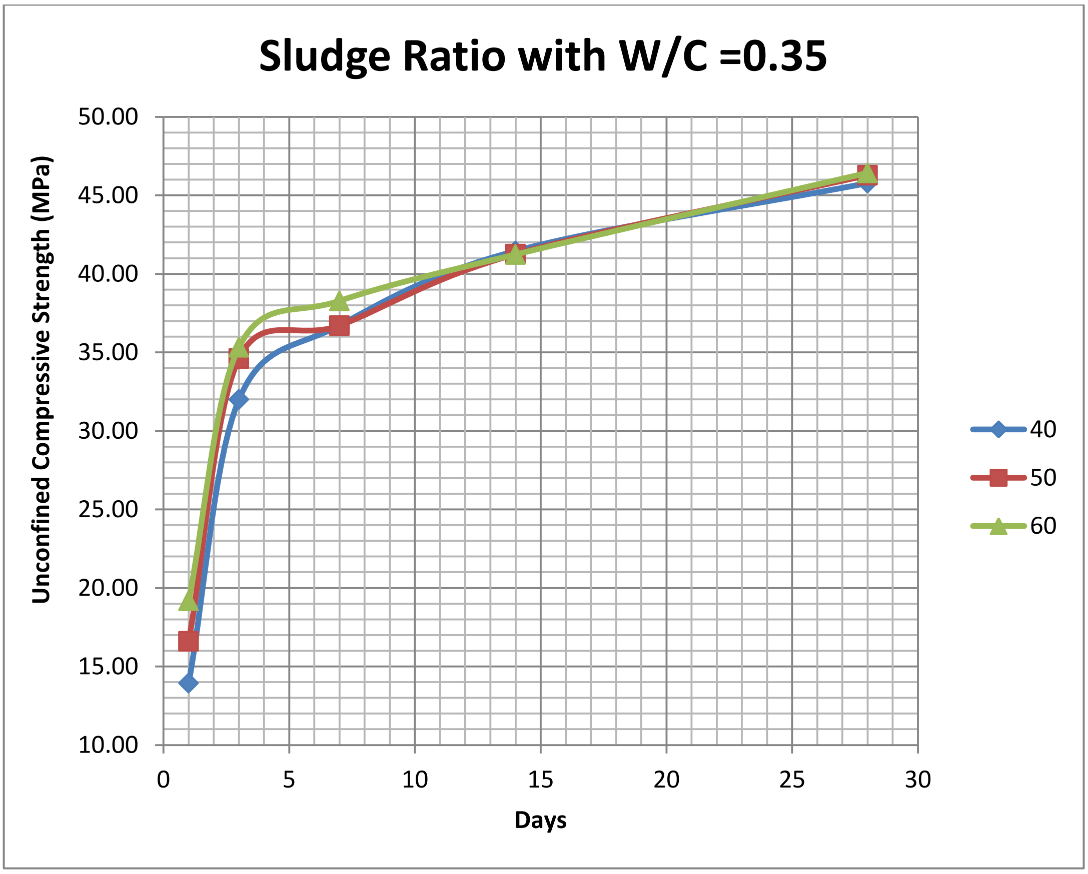

FIGURE 4.2 Cement to Sludge UCS Comparison

Based on Figure 4.2 above, it can be seen that the strength development for the samples almost shows similar behaviour 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, since the graph was indecisive, it was decided to carry out all 3 cement to sludge ratios together with the fly ash, to get a better picture on the difference on unconfined compressive when added together with an additive which is fly ash.

4.8.3 Cement to Binder Ratio Unconfined Compressive Strength Development

Fly ash 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, fly ash 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 all 3 cement to sludge ratios due to indecisive in the unconfined compressive strength, the detailed calculations for all the ratios mentioned can be seen in Appendix IV, V and VI.

In the process of adding fly ash 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 fly ash 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 4.13 shows the tabulated values for all samples mixed with the presence of both petroleum waste sludge as well as fly ash. From the data obtained, graphs were plotted to depict the relationship between the unconfined compressive strength development as well as the sludge and fly ash compositions. To begin with, comparison on the matured sample was analyzed as can be seen in Table 4.13.

Table 4.13 Unconfined Compressive Strength for C/B Ratios with W/C = 0.45

Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Water to Cement Ratio (W/C)	Days				
			1	3	7	14	28
			Average Unconfined Compressive Strength (MPa)				
40	0.05	0.45	10.83	17.53	24.72	28.29	39.34
40	0.10	0.45	13.07	18.74	25.78	30.81	37.88
40	0.15	0.45	15.80	22.10	25.98	34.80	35.73
50	0.05	0.45	9.43	14.63	21.80	29.03	38.44
50	0.10	0.45	10.00	18.00	27.65	32.32	35.02
50	0.15	0.45	10.30	23.10	28.61	31.18	33.66
60	0.05	0.45	7.00	19.12	28.98	30.20	34.13
60	0.10	0.45	8.90	25.33	27.56	29.39	34.58
60	0.15	0.45	10.51	26.53	28.75	32.25	39.75

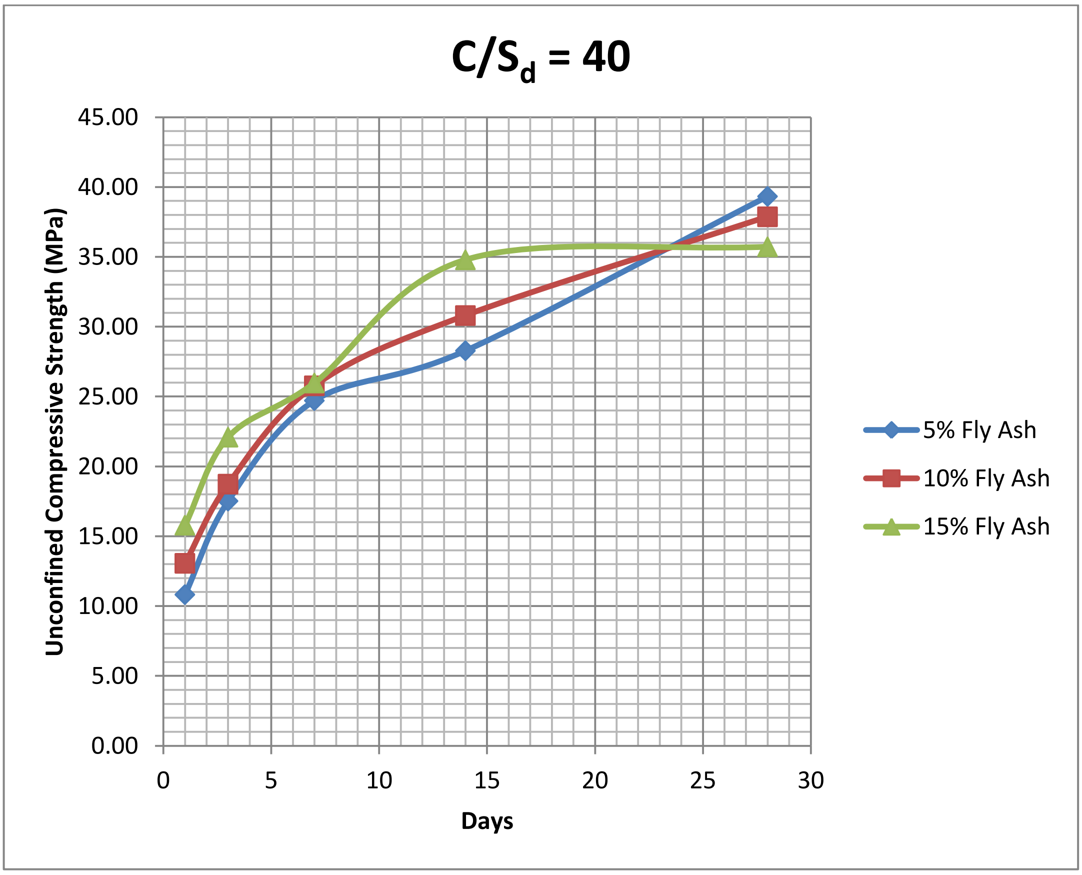

FIGURE 4.3 Unconfined Compressive Strength Development for C/Sd = 40

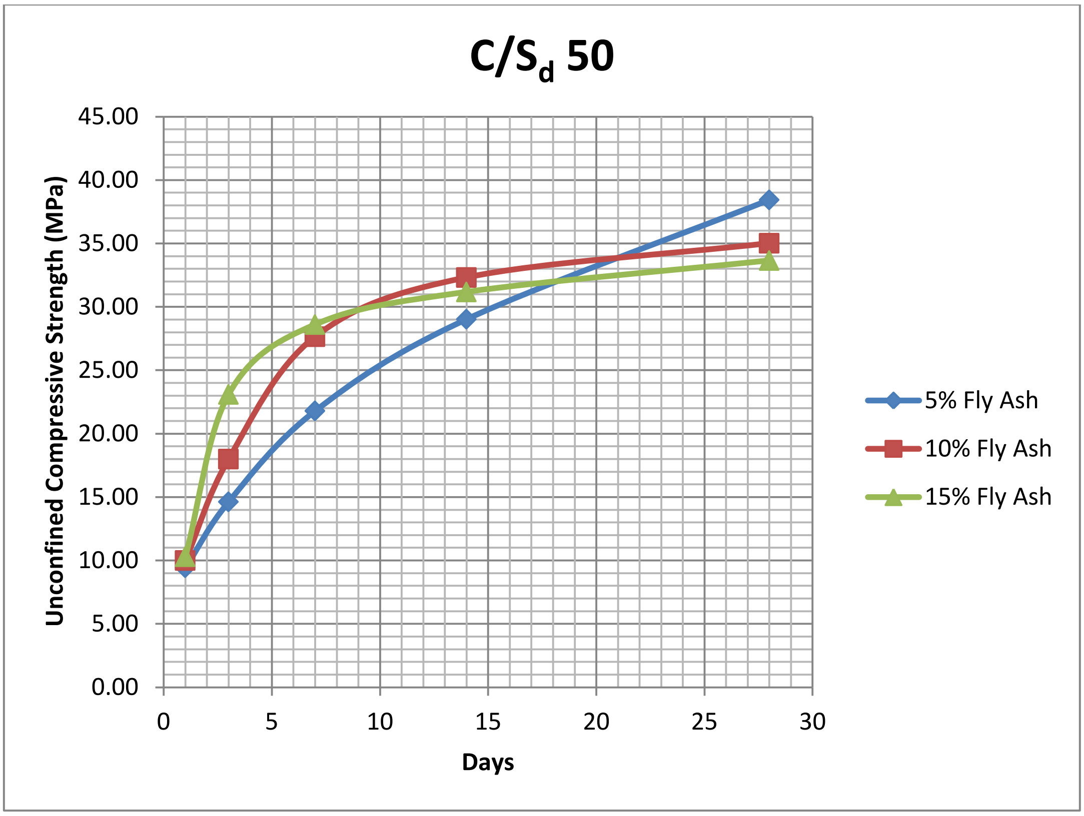

FIGURE 4.4 Unconfined Compressive Strength Development for C/Sd = 50

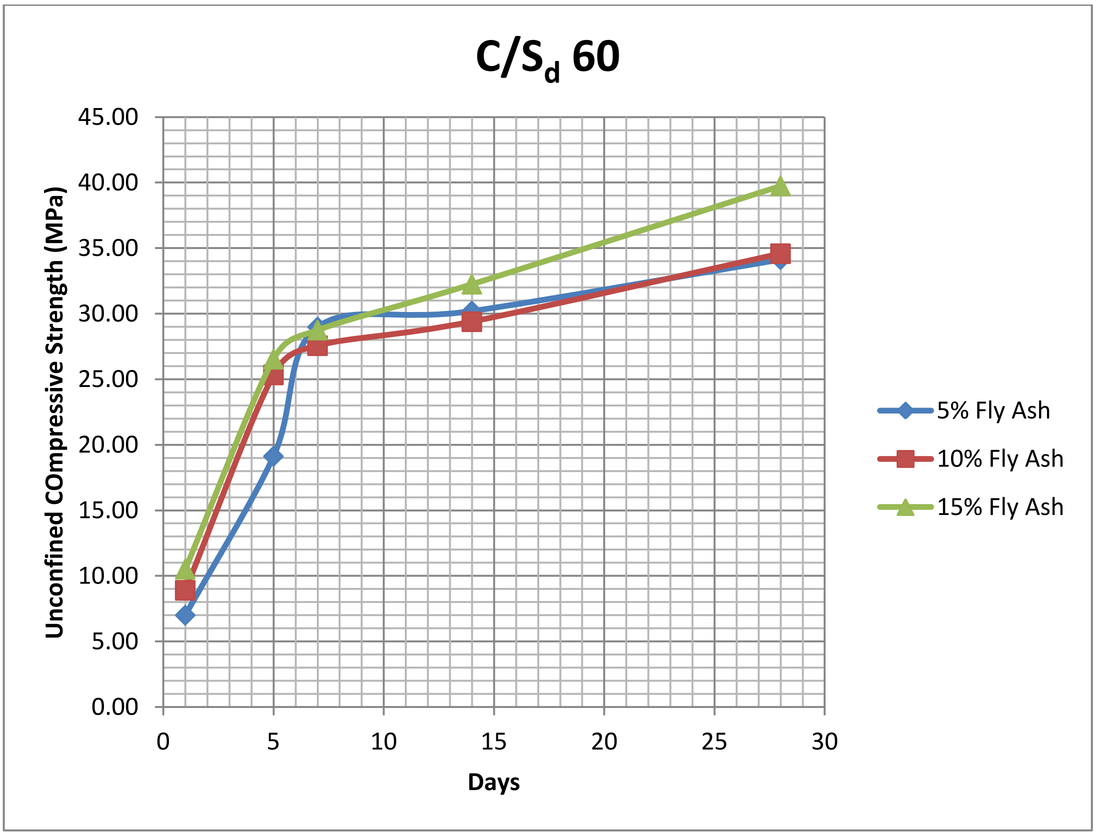

FIGURE 4.5 Unconfined Compressive Strength Development for C/Sd = 60

Figure 4.3, 4.4 and 4.5 shows the comparison between the same sludge ratio but different fly ash content. All 3 charts shows the same initial unconfined compressive strength development however it differs at the end for the highest cement to sludge ratio, C/Sd = 60. The unconfined compressive strength increases steadily for C/Sd = 60 until the end for all composition of fly ash with 15% fly ash ratio showing the highest strength achieved. For C/Sd = 60, the unconfined compressive strength increases as the composition of the fly ash increases. However, for C/Sd = 40 and C/Sd = 50, the strength increases with decrease in the composition of fly ash. Figure 4.6 shows the relationship of the composition of fly ash and unconfined compressive strength of the fully matured samples.

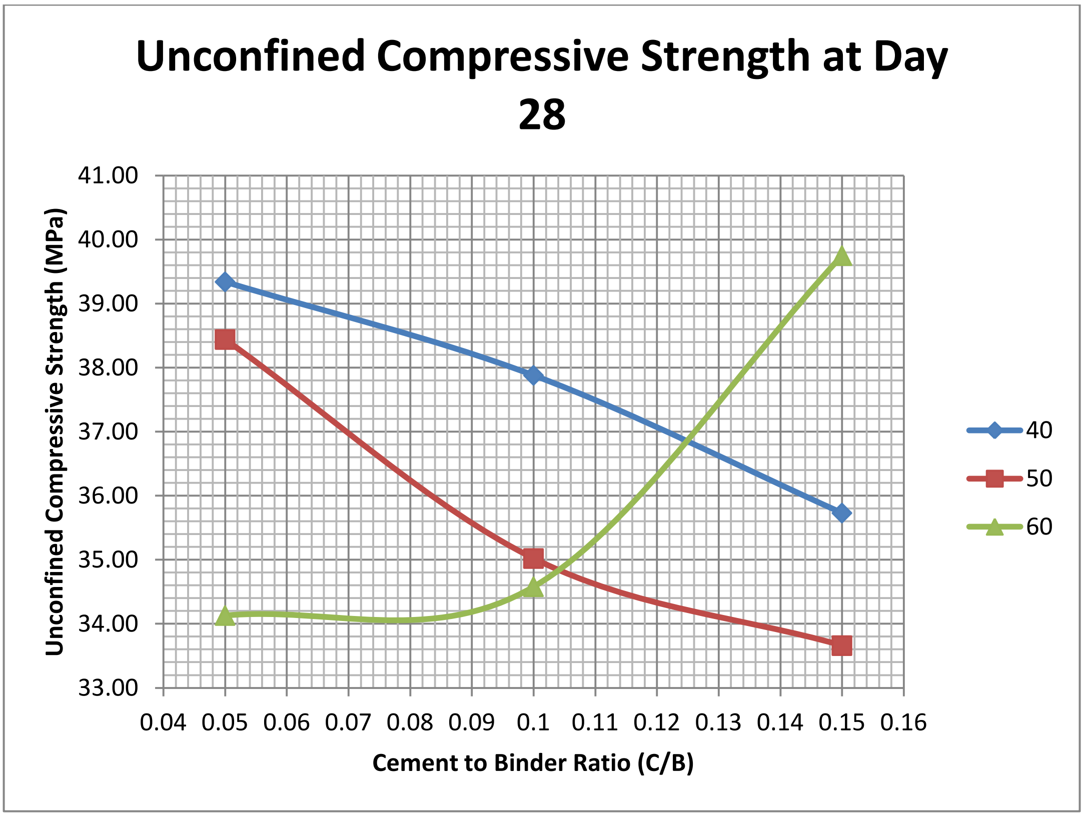

FIGURE 4.6 Matured Sample Comparisons for Different C/B Ratio

Based on the chart above, as the cement to sludge(C/Sd) ratio increases, the unconfined compressive strength took reversal behaviour of increasing strength as increasing fly ash amount is observed. At the lowest C/Sd ratio, the graph showed a decrease in unconfined compressive strength as the increase in fly ash amount in the sample. The increase in cement to sludge ratio, C/Sd = 50, observed a rapid decrease in unconfined compressive strength as the increase in the amount of fly ash in the samples. Both ratios, C/Sd = 40 and C/Sd = 50 showed a high value in unconfined compressive strength with the lowest amount of fly ash in the mixture which is not the case for C/Sd = 60. For C/Sd = 60 samples, it develop a low unconfined strength at low amount of fly ash which in turn producing the highest strength in the presence of high amount of fly ash in the mixture. Based on the chart, it can be deduced that the highest cement to sludge ratio, 60 with high amount of fly ash, 15% produces the strongest cement matrix of 39.75 MPa compared to the other lower cement to sludge ratio. 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 sludge, fly ash as well as unconfined compressive strength development, a 3D surface plot was created using Microsoft Excel. Figure 4.7, 4.8, and 4.9 depicts the relationship mentioned above. 3 colours of the surface plot depicts the strength range of the data; blue (0-9.9), red (10-19.9 MPa), green (20-29.9 MPa) and violet (30-39.9 MPa). As mentioned previously, the plots do clarify the previously mentioned findings for the change of strength according to the sludge and fly ash. The higher sludge and fly ash content increases the unconfined compressive strength of the samples.

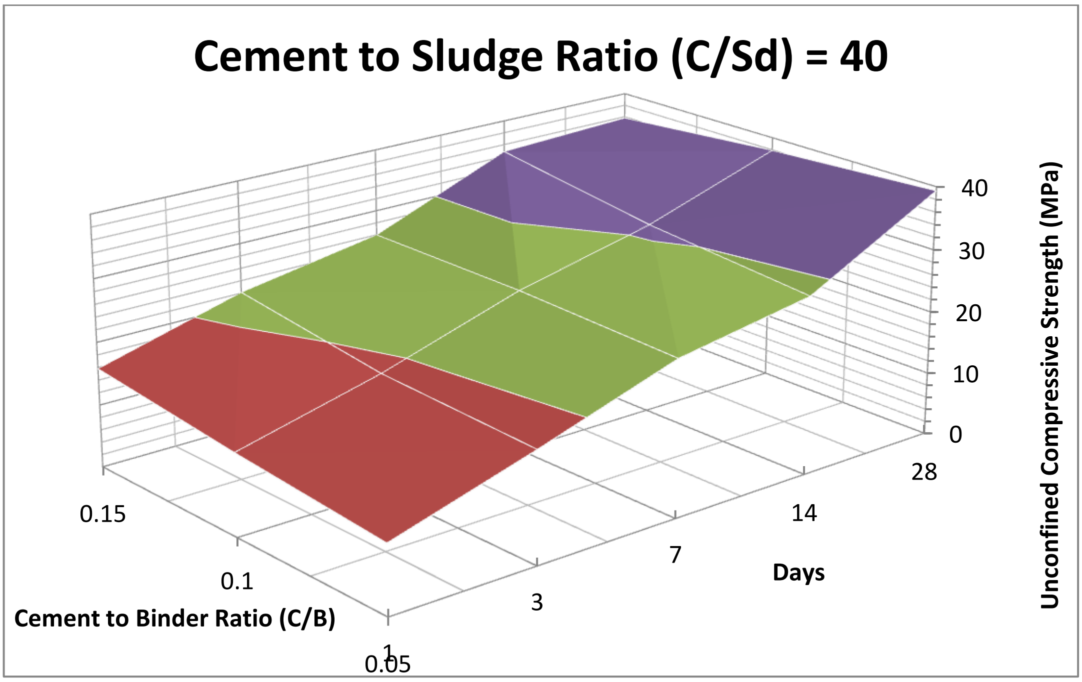

FIGURE 4.7 Unconfined Compressive Strength Development for C/Sd = 40

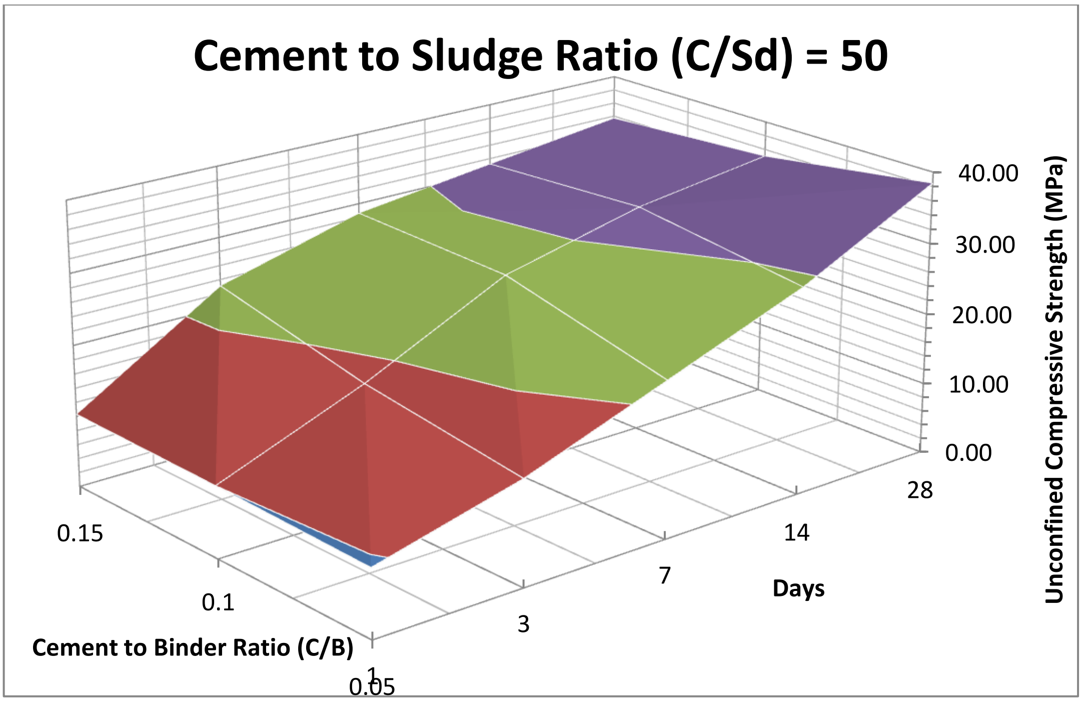

FIGURE 4.8 Unconfined Compressive Strength Development for C/Sd = 50

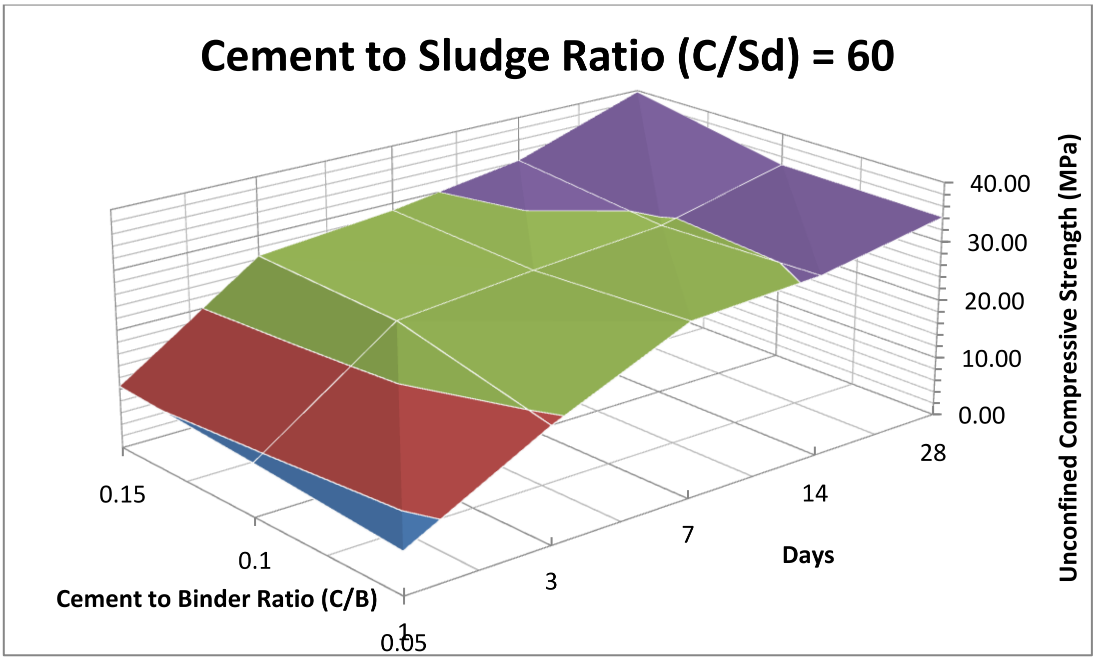

FIGURE 4.9 Unconfined Compressive Strength Development for C/Sd = 60

4.9 Porosity and Permeability

For the porosity and permeability test, samples mixed with the waste petroleum sludge and fly ash will be analyzed for porosity and permeability. Matured crushed samples, with 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 behaviour was chosen based on the unconfined compressive strength test. The 4 chosen samples are as tabulated in Table 4.14 and 4.15.

Table 4.14 Porosity and Permeability Sample Data

Sample No.	Cement to Sludge Ratio (C/Sd)	Fly Ash Composition (%F.A.)	Water to Cement Ratio (W/C)	Mass (g)	Density (g/cm^3)
1	40	5%	0.45	0.76	2.42
2		15%		0.60	2.40
3	60	5%	0.45	0.62	2.42
4		15%		0.71	2.44

Table 4.15 Porosity and Permeability Data

Sample	Without Compressibility Correction (CC)		With Compressibility Correction (CC)	
	Accessible Porosity	Inaccessible Porosity	Accessible Porosity	Inaccessible Porosity
1	16.22	1.93	12.09	6.06
2	20.18	6.93	15.40	11.71
3	16.95	4.14	13.77	7.32
4	16.58	17.54	12.26	21.72

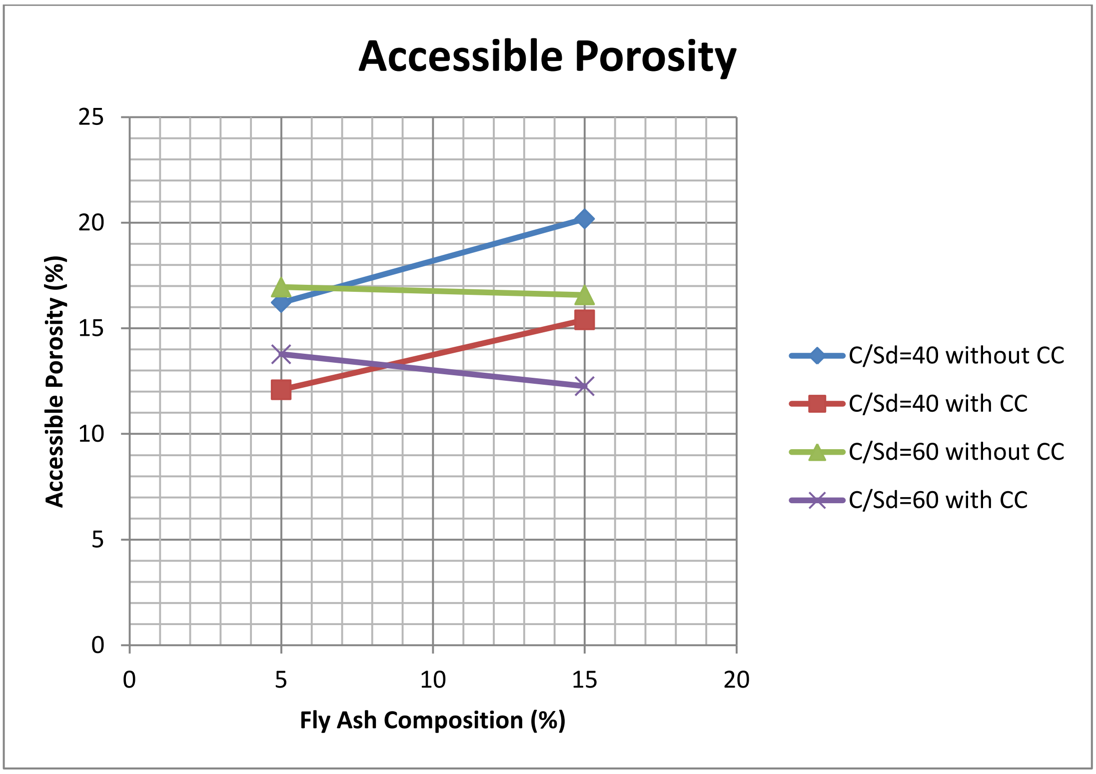

FIGURE 4.10 Comparison of Accessible Porosity with Fly Ash Composition

4.9.1 Without Compressibility Correction (CC)

As depicted in the Figure 4.10, for C/Sd = 40 without compressibility correction, the accessible porosity decreases with increase in fly ash composition. The sample showed an increase in 24% of accessible porosity when the fly ash composition increases from 5% to 15%. However, the result showed otherwise for sample with the higher C/Sd ratio. For C/Sd = 60 samples, the accessible porosity decreases by 2% as the fly ash composition increases from 5% to 15%. At 5% C/B to ratio, the increase in C/Sd ratio does not produce a significant change in the accessible porosity of the samples. At high C/B ratio which is 15%, the sample showed a reduction of 18% in accessible porosity.

In the segment of accessible porosity, it can be deduced that at low C/Sd ratio, the accessible ratio increases sharply with increase in the fly ash composition but decreases marginally at higher C/Sd ratio. As for the binder relationship, it showed an inverse behaviour where for the same fly ash composition, at low fly ash composition, increase in C/Sd ratio showed marginal increase but at high fly ash composition, rapid decrease was observed in the accessible porosity.

For the case of inaccessible porosity as shown in Figure 4.11, both increase in C/Sd ratio and C/B shows increase in inaccessible porosity. At low fly C/Sd ratio, the inaccessible porosity increases by 259% while an increase of 324% was observed in the high C/Sd ratio when the composition of fly ash increases from 5% to 15%. At the same fly ash composition, low fly ash composition showed an increase of 115% while the high fly ash composition showed an increase of 153% when the C/Sd ratio increases from 40 to 60. Higher sludge ratio with high fly ash composition showed a better increase in inaccessible porosity with increasing C/Sd ratio.

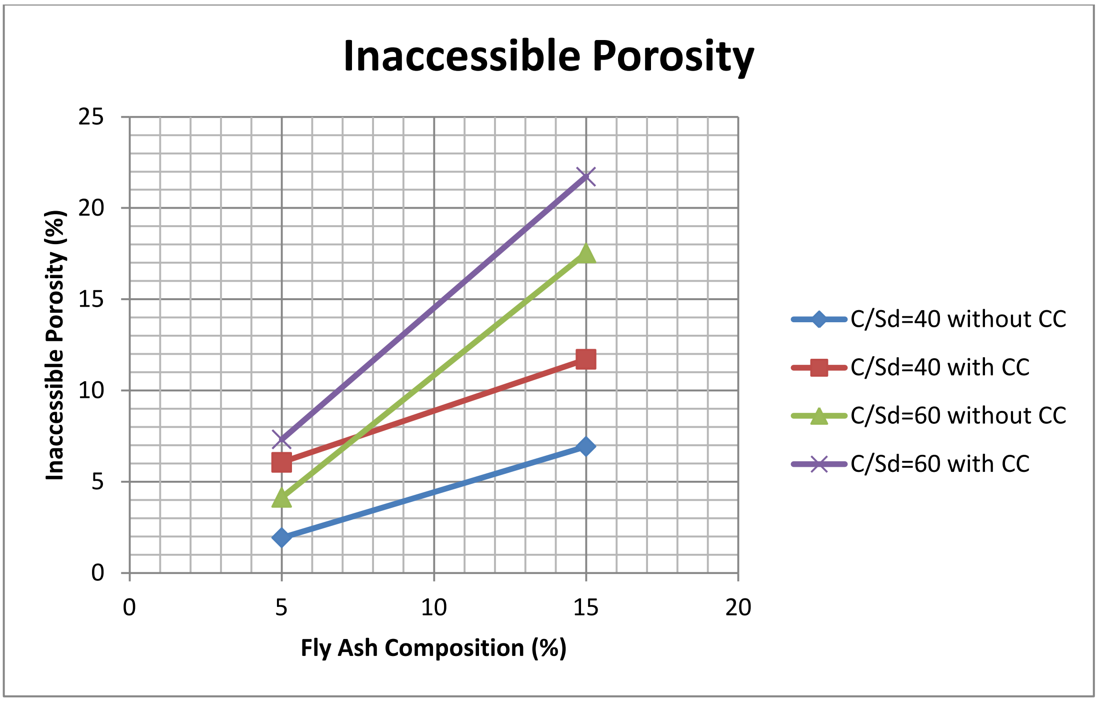

FIGURE 4.11 Comparison of Inaccessible Porosity with Fly Ash Composition

4.9.2 With Compressibility Correction (CC)

For accessible porosity, similar behaviour was observed as previously mentioned in the without the compressibility correction segment. For both C/Sd ratio and fly ash ratio, the accessible porosity showed a lower reading compared to the one without compressibility correction. Within the same C/Sd ratio, a decrease in 27% was observed for C/Sd = 40 while 11% decrease was observed for C/Sd = 60 as the fly ash composition increases from 5% to 15%. Low C/Sd ratio showed a rapid decrease in accessible porosity compared to high C/Sd ratio as fly ash composition increases. In the case of similar fly ash ratio, the result showed an increase in accessible porosity as C/Sd ratio increases for fly ash composition 5%. However, a decrease in accessible porosity was observed as high fly ash composition was tested with for porosity with increase in C/Sd ratio.

For accessible porosity with compressibility correction, it can be deduced that at low C/Sd ratio, the accessible ratio increases sharply with increase in the fly ash composition but decreases marginally at higher C/Sd ratio. As for the binder relationship, it showed an inverse behaviour where for the same fly ash composition, at low fly ash composition, increase in C/Sd ratio showed marginal increase but at high fly ash composition, rapid decrease was observed in the accessible porosity.

When the compressibility correction is considered, similar behaviour was observed for the inaccessible porosity of the samples. For the same C/Sd ratio, an increase in 93% was observed for C/Sd = 40 while increase in 196% was observed for C/Sd = 60 as the fly ash composition increases from 5% to 15%. For the similar fly ash composition, the increase observed for 5% fly ash composition was 21% while 86% was observed for 15% fly ash composition as the C/Sd ratio increases from 40 to 60. Overall, similar deduction can be made as mentioned previously in the without the compressibility segment which is higher sludge ratio with high fly ash composition showed a better increase in inaccessible porosity with increasing C/Sd ratio.

Permeability is a measure of how easily fluid flow through the porous medium. Permeability is independent of fluid properties such as density and viscosity and dependant 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 rocks, Brace (1977) and Wong et al (1984) estimated that m is equal to 2. 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 fly ash in this system.

$$Permeability, k \cong \emptyset^{m} \quad (10)$$

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 4.16.

Table 4.16 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	40	0.05	12.09	146.17
2	40	0.15	15.40	237.16
3	60	0.05	13.77	189.61
4	60	0.15	12.26	150.31

With estimation as such m is 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 low C/Sd with increasing C/B ratio provides a higher porosity and in turn relates to increasing permeability. As such, the high C/Sd ratio 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, favour the high C/Sd ratio which is 60 and the highest C/B ratio of 1 15% to provide the desired low porosity and permeability. The solidified sample strength is also related to the porosity as well as be seen in Table 4.17.

Table 4.17 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	40	0.05	39.34	12.09
2	40	0.15	35.73	15.4
3	60	0.05	34.13	13.77
4	60	0.15	39.75	12.26

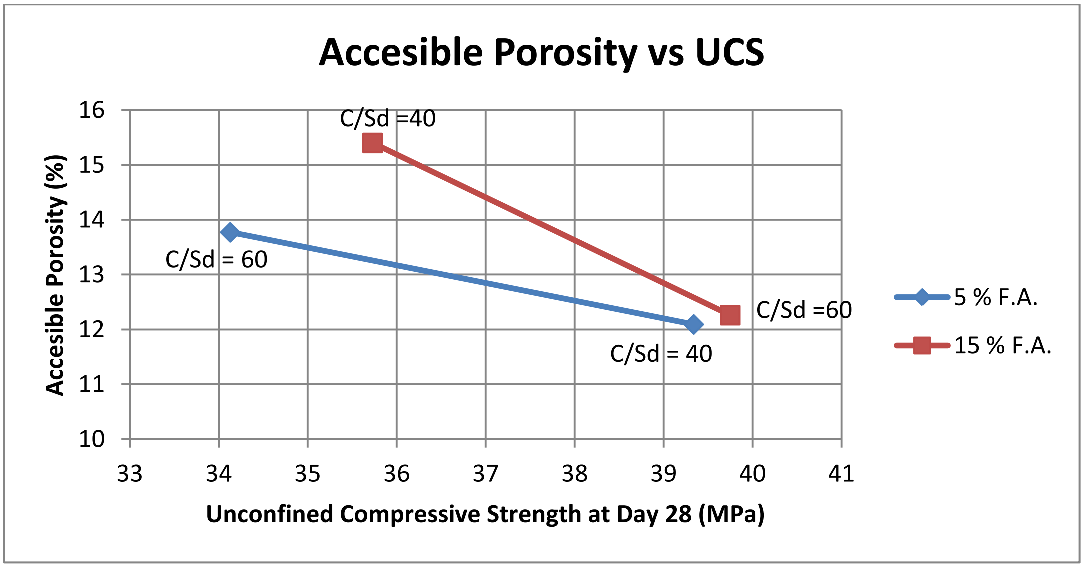

FIGURE 4.12 Comparisons of Accessible Porosity and Fly Ash Composition with Unconfined Compressive Strength (UCS)

From the Figure 4.12, a comparison was made between the similar C/B ratio for an increase in C/Sd ratio. By referring to the 5 % fly ash ratio line, as the C/Sd ratio increases, the unconfined compressive strength decreases, but it shows an increase in the accessible porosity as can be seen in the chart. As for the 15% fly ash ratio line, as the C/Sd ratio increases, so does its unconfined compressive strength but the decrease was observed in its accessible porosity. Referring to the C/Sd = 40 points in the chart, as the fly ash composition increases, the unconfined compressive strength decreases, with increasing accessible porosity. However, referring to the C/Sd = 60 points in the chart, the increase in fly ash composition increases the unconfined compressive strength with decreasing accessible porosity. The tabulated relationship between C/Sd and C/B ratios with UCS were tabulated in Table 4.18.

Table 4.18 Compiled Comparisons

Conditions	Unconfined Compressive Strength	Accessible Porosity
Increase in C/Sd Ratio at 5% C/B Ratio	Decreases	Increases
Increase in C/Sd Ratio at 15% C/B Ratio	Increases	Decreases
Increase in C/B Ratio at C/Sd = 40	Decreases	Increases
Increase in C/B Ratio at C/Sd = 60	Increases	Decreases

4.10 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. Refer to Appendix VIII for the flowchart of the whole process. 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, 6 samples were chosen to undergo this procedure. The 6 samples are all samples under the C/Sd = 40 and C/Sd = 60 ratios. The reason behind selecting these samples is due to the significant change in unconfined compressive strength observed from the lowest C/Sd ratio to the highest C/Sd ratio. The possible metals to be detected are zinc (Zn), manganese (Mn), lead (Pb), chromium (Cr), copper (Cu), nickel (Ni), and iron (Fe). Prior to determining the concentration of the metals in the leachate, standard calibration curve be prepared by preparing standard solutions beforehand.

Table 4.19 Metal Content Result

Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B)	Concentration (ppm)						
		Fe	**Ni**	**Pb**	**Mn**	**Cu**	**Cr**	**Zn**
Standard B		**5.00**	**1.00**	**0.50**	**1.00**	**1.00**	**1.00**	**1.00**
Raw Sludge		5.09	2.09	2.93	2.05	3.15	0.45	4.07
40	0.05	0.04	ND	ND	ND	0	ND	ND
40	0.10	0.04	ND	ND	ND	0	ND	ND
40	0.15	0.04	ND	ND	ND	0	ND	ND
60	0.05	0.04	ND	ND	ND	ND	ND	ND
60	0.10	0.04	ND	ND	ND	0	ND	ND
60	0.15	0.04	ND	ND	ND	0	ND	ND

Note: ND is abbreviation for Not Detectable.

The readings were obtained 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 zinc. 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. However, after being stabilized and solidified using OPC and fly ash, almost all metals showed untraceable amount of metals from the hydrocarbon waste. Based on the reading obtained in Table 4.19, it can be deduced that the leaching out of dissolved metal in the hydrocarbon waste are insignificantly low and below the regulated metals in industrial wastewater effluent of EQA 1974.

4.11 Oil and Grease in Leachate

Oil and grease content for the leachate were analyzed and compared with the sludge content oil and grease content. The lowest C/Sd ratio was selected to detect the total oil and grease content because the lowest C/Sd ratio contains the highest amount of hydrocarbon waste sludge which are 898.40 g, 893.90 g and 889.40 g for each C/B ratio of 5%, 10% and 15% respectively as compared to other sludge ratios as can be seen in Appendix IV, V and VI.

Table 4.20 Leachate Total Oil Grease

Cement to Sludge Ratio (C/Sd)	Cement to Binder Ratio (C/B), %	Total Oil Grease (TOG), ppm
Standard B		**10.0**
Raw Sludge		58.4
40	5	5.5
40	10	4.0
40	15	0.8

Referring to Table 4.20, compared to the initial Total Oil and Grease (TOG) in the raw sludge sample, the leachate showed a low content of TOG after bring solidified and stabilized with cement and fly ash. As per outlined in Standard B, EQA 1974, TOG is limited to 10 ppm, in which the raw sludge must be treated before being released to the environment due to the high content of oil and grease in the waste itself. However, the leachate from the S/S showed a significantly low quantity of oil and grease which allows it to be safely discharged to the environment. The S/S hydrocarbon waste using fly ash as an additive proved to help reduce the oil and grease discharge level which allows it to be safely disposed to the environment without concerning the harmful effect of the hydrocarbon waste sludge.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

From this study, it can be concluded that increase in the waste hydrcarbon sludge ratio and fly ash ratio increases the strength of the stabilized and solidified cement cubes. The highest C/Sd ratio of 60, with highest C/B ratio of 15% gives out the maximum strength of 39.75 MPa, highest strength compared to other C/Sd and C/B ratio applied. 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. Metals content test proved the immobilization of selected metals with almost all metals almost undetectable after confined with cement together with fly ash. No patterns or trend observed with increasing C/Sd or C/B ratio for metal leachability. All metal content tested for does not exceed the limit outlined under Standard B by EQA 1974. Total oil and grease showed a drop in oil and grease content from 58.4 ppm to less than 10 ppm in the leachate analyzed compared to the raw sludge. The increase in fly ash composition results in the decrease in the oil and grease content in the leachate and abides the standard regulation limit outlined by EQA 1974 which is 10 ppm.

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.

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APPENDICES

APPENDIX I

Hazardous Waste Generated By Generic Processes ("F" List) *(continued)*		
EPA Waste No.	**Hazardous waste**	**Hazard code**
F037	Petroleum refinery primary oil/water/ solids separation sludge – Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oily cooling wastewaters from petroleum refineries. Such sludges include, but are not limited to, those generated in: oil/water solids separators; tanks and impoundments; ditches and other conveyances; sumps; and stormwater units receiving dry weather flow. Sludge generated in stormwater units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges generated in aggressive biological treatment units as defined in RCRA Section 261.31(b)(2) (including sludges generated in 1 or more additional units after wastewaters have been treated in aggressive biological treatment units) and K051 wastes are not included in this listing.	(T)
F038	Petroleum refinery secondary (emulsified) oil/water/solids separation sludge – Any sludge and/or float generated from the physical and/or chemical separation of oil/water/solids in process wastewaters and oily cooling wastewaters from petroleum refineries. Such wastes include, but are not limited to, all sludges and floats generated in: induced air flotation (IAF) units, tanks and impoundments, and all sludges generated in dissolved air flotation (DAF) units. Sludges generated in storm water units that do not receive dry weather flow, sludges generated from non-contact once-through cooling waters segregated for treatment from other process or oily cooling waters, sludges and floats generated in aggressive biological treatment units as defined in RCRA Section 261.31(b)(2) (including sludges and floats generated in 1 or more additional units after wastewaters have been treated in aggressive biological treatment units) and F037, K048, and K051 wastes are not included in this listing.	

Hazardous Waste Generated By Generic Processes ("F" List) *(continued)*		
EPA Waste No.	**Hazardous waste**	**Hazard code**
F039	Leachate (liquids that have percolated through land disposed wastes) resulting from the disposal of more than 1 restricted waste classified as hazardous under Subpart D (Leachate resulting from the disposal of 1 or more of the following EPA hazardous wastes and no other hazardous wastes retains its EPA hazardous waste number(s): F020, F021, F022, F026, F027, and/or F028).	(T)

Notes:

* (I,T) should be used to specify mixtures containing ignitable and toxic constituents.

- For the purposes of the F037 and F038 listings, oil/water/solids is defined as oil and/or water and/or solids.
- For the purposes of the F037 and F038 listings, aggressive biological treatment units are defined as units that employ 1 of the following 4 treatment methods: activated sludge; trickling filter; rotating biological contactor for the continuous accelerated biological oxidation of wastewaters; or high-rate aeration. High-rate aeration is a system of surface impoundments or tanks in which intense mechanical aeration is used to completely mix the wastes and enhance biological activity. High-rate aeration units employ a minimum of 6 horsepower per million gallons of treatment volume, and either the hydraulic retention time of the unit is no longer than 5 days, or the hydraulic retention time is no longer than 30 days and the unit does not generate a sludge that is a hazardous waste by the toxicity characteristic. Generators and TSD facilities have the burden of proving that their sludges are exempt from listing as F037 and F038 wastes under this definition. Generators and TSD facilities must maintain, in their operating or other onsite records, documents and data sufficient to prove that the unit is an aggressive biological treatment unit and the sludges sought to be exempted were actually generated in the aggressive biological treatment unit.

APPENDIX II

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 III

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
40	0.35	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
50	0.35	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	0.35	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) = 0.35 and Different Cement to Sludge Ratio

APPENDIX IV

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
40	0.45	0.05	11.6089	1	0.0114	40	38	0.0121	2	0.0008	0.0242	12.9215	2.9408	0.8984	0.1548	1.3234	0.8210	0.5024
40	0.45	0.1	11.6089	1	0.0114	40	36	0.0115	4	0.0015	0.0244	12.9867	2.7721	0.8939	0.3080	1.2474	0.8169	0.4305
40	0.45	0.15	11.6089	1	0.0114	40	34	0.0108	6	0.0023	0.0245	13.0520	2.6050	0.8894	0.4597	1.1722	0.8128	0.3594

Appendix IV : Mixing Calculation for Cement to Sludge Ratio (C/Sd) = 40

APPENDIX V

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
50	0.45	0.05	11.6089	1	0.0114	50	47.5	0.0151	2.5	0.0009	0.0274	14.6363	3.2453	0.7932	0.1708	1.4604	0.7248	0.7356
50	0.45	0.1	11.6089	1	0.0114	50	45	0.0143	5	0.0019	0.0276	14.7179	3.0575	0.7888	0.3397	1.3759	0.7208	0.6551
50	0.45	0.15	11.6089	1	0.0114	50	42.5	0.0135	7.5	0.0028	0.0277	14.7994	2.8717	0.7844	0.5068	1.2923	0.7168	0.5754

Appendix V : Mixing Calculation for Cement to Sludge Ratio (C/Sd) = 50

APPENDIX VI

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	0.05	11.6089	1	0.0114	60	57	0.0182	3	0.0011	0.0307	16.3512	3.4860	0.7100	0.1835	1.5687	0.6488	0.9199
60	0.45	0.1	11.6089	1	0.0114	60	54	0.0172	6	0.0023	0.0308	16.4490	3.2829	0.7057	0.3648	1.4773	0.6450	0.8323
60	0.45	0.15	11.6089	1	0.0114	60	51	0.0162	9	0.0034	0.0310	16.5469	3.0822	0.7016	0.5439	1.3870	0.6411	0.7458

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

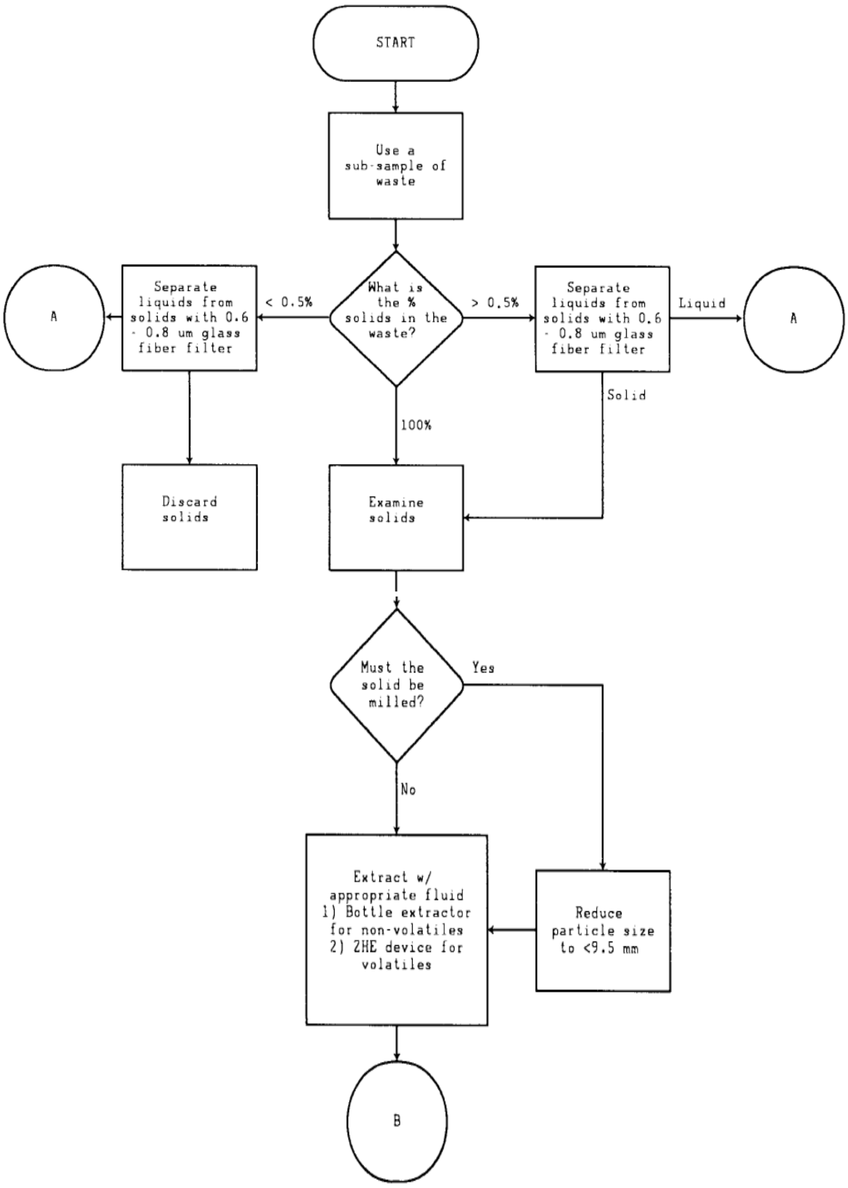
APPENDIX VII

Appendix VII : Images for Cement Mix C/Sd = 40, W/C = 0.35 and C/B = 0.05

APPENDIX VIII

METHOD 1311

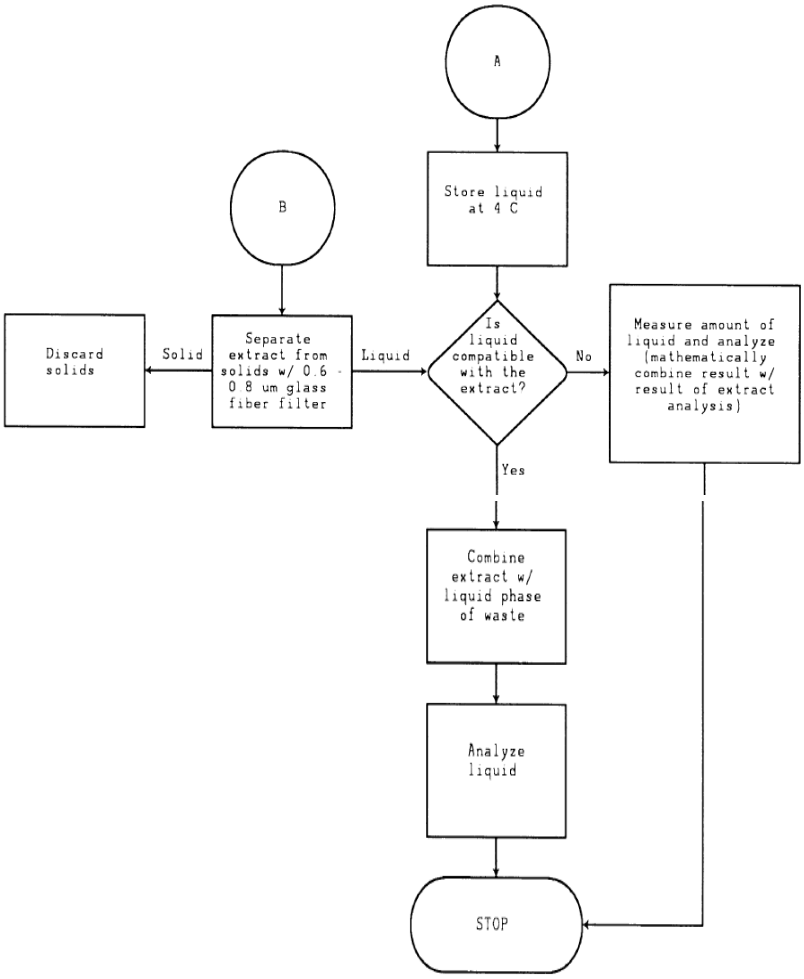
TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



APPENDIX VIII (CONTINUED)

METHOD 1311 (CONTINUED)

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE



APPENDIX IX : CEMENT CASTING AND UCS SCHEDULE

Water to Cement Ratio (W/C)	Casting	1	3	7	14	28
0.35	25/3/2014	26/3/2014	28/3/2014	1/4/2014	8/4/2014	22/4/2014
0.40	26/3/2014	27/3/2014	29/3/2014	2/4/2014	9/4/2014	23/4/2014
0.45	27/3/2014	28/3/2014	30/3/2014	3/4/2014	10/4/2014	24/4/2014

Schedule for Water to Cement Ratio Mixing and UCS Test

Cement to Sludge Ratio (C/S_d)	Water to Cement Ratio (W/C)	Casting	1	3	7	14	28
40	0.35	28/4/2014	29/4/2014	1/5/2014	5/5/2014	12/5/2014	26/5/2014
50	0.35	29/4/2014	30/4/2014	2/5/2014	6/5/2014	13/5/2014	27/5/2014
60	0.35	30/4/2014	1/5/2014	3/5/2014	7/5/2014	14/5/2014	28/5/2014

Schedule for Cement to Sludge Ratio Mixing and UCS Test

Cement to Sludge Ratio (C/S_d)	Water to Cement Ratio (W/C)	Cement to Binder Ratio (C/B)	Casting	1	3	7	14	28
40	0.45	0.05	29/5/2014	30/5/2014	1/6/2014	5/6/2014	12/6/2014	26/6/2014
40	0.45	0.10	30/5/2014	31/5/2014	2/6/2014	6/6/2014	13/6/2014	27/6/2014
40	0.45	0.15	2/6/2014	3/6/2014	5/6/2014	9/6/2014	16/6/2014	30/6/2014
50	0.45	0.05	3/6/2014	4/6/2014	6/6/2014	10/6/2014	17/6/2014	1/7/2014
50	0.45	0.10	4/6/2014	5/6/2014	7/6/2014	11/6/2014	18/6/2014	2/7/2014
50	0.45	0.15	5/6/2014	6/6/2014	8/6/2014	12/6/2014	19/6/2014	3/7/2014
60	0.45	0.05	6/6/2014	7/6/2014	9/6/2014	13/6/2014	20/6/2014	4/7/2014
60	0.45	0.10	9/6/2014	10/6/2014	12/6/2014	16/6/2014	23/6/2014	6/7/2014
60	0.45	0.15	10/6/2014	11/6/2014	13/6/2014	17/6/2014	24/6/2014	7/7/2014

Schedule for Cement to Binder Ratio Mixing and UCS Test

APPENDIX X : ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS, 1979

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT, 1974

ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS, 1979

(Regulation 8 (1), 8 (2), 8 (3)]

PARAMETER LIMITS OF EFFLUENT OF STANDARDS A AND B

Parameter	*Unit*	*Standard*	
		A	*B*
(1)	(2)	(3)	(4)
(i) Temperature	°C	40	40
(ii) pH Value	–	6.0-9.0	5.5-9.0
(iii) BOD_5 at 20°C	mg/1	20	50
(iv) COD	mg/1	50	100
(v) Suspended Solids	mg/1	50	100
(vi) Mercury	mg/1	0.005	0.05
(vii) Cadmium	mg/1	0.01	0.02
(viii) Chromium, Hexavalent	mg/1	0.05	0.05
(ix) Arsenic	mg/1	0.05	0.10
(x) Cyanide	mg/1	0.05	0.10
(xi) Lead	mg/1	0.10	0.5
(xii) Chromium, Trivalent	mg/1	0.20	1.0
(xiii) Copper	mg/1	0.20	1.0
(xiv) Manganese	mg/1	0.20	1.0
(xv) Nickel	mg/1	0.20	1.0
(xvi) Tin	mg/1	0.20	1.0
(xvii) Zinc	mg/1	1.0	1.0
(xviii) Boron	mg/1	1.0	4.0
(xix) Iron (Fe)	mg/1	1.0	5.0
(xx) Phenol	mg/1	0.001	1.0
(xxi) Free Chlorine	mg/1	1.0	2.0
(xxii) Sulphide	mg/1	0.50	0.50
(xxiii) Oil and Grease	mg/1	Not Detectable	10.0