Leachability and Permeability of Immobilized Waste in Activated Carbon Cement Binder

by

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

____

(Dr. Asna Bt Mohd Zain)

Universiti Teknologi PETRONAS
Bandar Seri Iskandar, Perak
January 2015

CERTIFICATE 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.

(Franzeene Nadia A/P Rajasegaran)

ABSTRACT

This research studies the waste management of residual petroleum sludge waste that can be retrieved from after the de-cantering 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 waste to chemically stabilize it, thus, preventing from external chemical reaction with the environment. The objective is to optimize waste to cement and introduce an admixture (activated carbon) 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 water to cement ratio, 0.45, cement to sludge ratio, 60 and cement to binder ratio 0.15 gives out the largest unconfined compressive strength of 43.75 MPa compared to the other lower cement to binder ratio. Porosity showed an increase of 31% as 15% activated carbon was added. The metals content in the leachate were relatively low and below the regulated metals content in sludge disposal as outlined in Standard B of EQA 1974.

ACKNOWLEDGEMENT

In the name of God, I thank Him for the courage and patience He provided me to see through to the end of my Final Year Project. For without His blessings, the work might not have been completed.

I convey my endless gratitude and appraisal to **Dr. Asna binti Mohd Zain**, without her guidance and endless support, this project would have never met the end. 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.

A special gratitude to Ms Azriha Anuar for her assistance on the Atomic Absorption Spectrometry, Mr Shahrul, for the Compression Test Machine, as well as Mr Saharuddin for the chemicals and equipments provided throughout the project.

I am here now due to my parents and I believe this report should be dedicated to them, signifying the end of the remarkable journey in my education life. I thank them for being there with me, supportive and encouraging through my ups and downs and lastly in completing my degree.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

1.1 Background

Petroleum refinery sludge wastes are very well related to a high amount of environmental risk. This is mainly due to the fact that the wastes discharged from petroleum refineries are hazardous to the surroundings due to its toxicity behaviour. Overwhelming technologies and discovery of advanced engineering aspects have contributed to intensify the complexity of the wastes generated in the industry (Wei & Huang, 2001). This means that current technologies are contributing to the increase in toxicity of the wastes disposed from industrial activities. Traditional methods of disposing wastes into the ocean or land without treatment have long been minimized and the concept of pollution control has evolved the environment's sustainability and quality.

The industrial sectors have always been looking out for ways to minimize or eliminate hazardous wastes such as the harmful greenhouse gases, sulfurs, cyanide, methane and lead chemicals, metal ashes and sludge wastes. Mohd Dinie and Mashitah Mat Don (2013) shared that 28.34% of the waste generated in central and southern Malaysia comes from industries and constructions. Currently, the industrial waste management in Kualiti Alam, Malaysia undergoes a small scale waste stabilization process but focuses mainly on implementing the final disposal of wastes through landfilling as the financial costs for it is relatively low. However, landfilling causes a big problem for the environment as the wastes may contaminate the ground from the leaching of heavy metals and other hazardous chemical substances.

Immobilization of wastes is gaining its recognition as one of the essential technologies to recycle waste, mainly hazardous industrial wastes. This stabilization and solidification (S/S) process works as such that the wastes are trapped within solid cement which consists of high integrator strength and minimizing the escape of wastes as leachate. This study focuses on utilizing Ordinary Portland Cement (OPC) Type I which is used for general constructions of pavements and beams (Hewlett, 1998). To further study this, the wastes and cement will also be combined with activated carbon, an excellent adsorbent due to its tiny pores structure which gives a high surface area (Bansal & Goyal, 2005). This then creates a high surface reactivity for adsorption of heavy metals in the wastes onto its surface. The cement then solidifies the retained compounds in the activated carbon and prevents it from escaping.

1.2 Problem Statement

Cement based stabilization technique is best suited for hazardous industrial waste management and disposal due to the high pH of cement which assists in retaining the hazardous chemical compounds and heavy metals within the cement solid matrix. However, a major setback with OPC is it has a very porous solid matrix which can increase the loss of certain hazardous materials through leaching. Therefore, it is understood that the OPC itself is not sufficient enough to retain the waste within the cement matrix.

Furthermore, the addition of wastes can interrupt the setting of silicates and aluminates that forms in the OPC when hydration reactions occur for the bonding of the cement. In addition, the oil and grease content present in the petroleum sludge waste hinders the bonding of silicates and aluminates. Hence, this lowers the compressive strength of the solidified waste in cement. Therefore, there is higher possibility for the cement to crack and release these hazardous materials once it is under the landfill due to high pressure or force exerted on the solidified waste.

A further study is to be done by incorporating selective additives such as activated carbon during the mixing of cement as it is believed to be able to improve the overall waste treatment and minimize wastes leaching due to its excellent adsorbent properties. Hence, it is predicted that this technique could create a more environmental-friendly waste treatment and move towards a more sustainable approach of re-using wastes into useful materials without neglecting the safety of the environment.

1.3 Objective

- **Determine the best ratio for cement-sludge-activated carbon for S/S of petroleum sludge waste.**
  Estimate ratio for mixing cement-sludge-activated carbon batching. Determine best ratio of cement to water, cement to sludge and activated carbon according to American Society for Testing and Materials (ASTM) standard and Environmental Protection Agency, United States of America (US EPA) standard.

- **To produce low presence of heavy metal compounds in the leachate.**
  Leaching tests are to be done on the solidified waste according to US EPA. Achieve presence of heavy metals in leachate equal to or lower than limit set by US EPA.

- **To produce solidified waste with minimal void pores to promote low permeability.**
  Permeable porosity tests are to be done on the solidified waste according to ASTM standard. Calculation of permeable pore voids is done to determine the porosity level of the solidified wastes. Further prove of this objective is done via visual aids.

1.4 Scope of Study

This study focuses on publishing data that relates to the ways in which the incorporation of hazardous wastes such as petroleum refinery sludge waste bearing heavy metals affect the properties of cement and other binders which are essential for the S/S process. Emphasis of this study is given on the mixing proportion effect, pore structure and environmental factors affecting S/S process. Activated carbon is the focus of a stabilizer for this study. Since it is an excellent adsorbent, the study focuses on how effective the addition of activated carbon in the cement binder can be in order to ensure the hazardous chemical compounds from the wastes retain within the cement and do not leach out.

The physical stability and strength of the solidified waste is studied using unconfined compressive strength (UCS) test using 2 inches cube specimens. This test measures the shear strength of a material without lateral confinement using a compression machine. It can also indicate the optimum water to cement ratios and curing times for the batching process. The minimum requirement for compressive strength according to ASTM C109 is 13.7MPa after 24 hours of curing, whereas under the provision of US EPA, the compressive strength that needs to be achieved for stabilized materials is 0.35MPa as of 28 days after the curing process.

Leachability of waste is studied using toxicity characteristic leaching procedure (TCLP). Leaching test measures the potential release of contaminants from the stabilized waste. The waste is exposed to an acidic solution for a certain period and the amount of metals in the extract is measured comparatively to the baseline leaching data of the untreated waste and further confirming with an established standard referring to US EPA. This study analyses the difference of the amount of heavy metals present in the leachate with and without the activated carbon additive during the S/S process.

Table 1-1: Parameters for experiments

Physical Properties		
Compressive Strength		≥0.35MPa
Chemical Properties		
Metal Concentration in TCLP leachate		mg/L
	Cr	50
	Cu	250
	Pb	50
	Ni	250
	Zn	250

(Source: US EPA & Method 1311 - TCLP)

Specific criteria shown in Table 1-1 will be used to achieve the targeted objectives for this study. The UCS result achieve should exceed the minimum pressure of 0.35 MPa. The presence of heavy metals stated above should be lesser than the above mentioned limits as set by US EPA following the guide to disposal of chemically stabilized and solidified wastes. These concentrations are confirmed by conducting the TCLP tests and identifying the substance presence using the Atomic Absorption

Spectrophotometer (AAS).

Micro-characterization is a special method developed for material science testing, applicable for specialized and detailed characterization of materials for the S/S treatment. Field-Emission Scanning Electron Microscope (FESEM) is used to study the shape, size and arrangement of the topographic features making the solid. It specifically examines the surface of solid materials and observes three-dimensional structures of a sample. Additionally, the Energy-Dispersive X-ray (EDX) incorporated in the FESEM does multi-element analyses that can be useful in determining the physiochemical form of the contaminants in the samples.

CHAPTER 2: LITERATURE REVIEW

Oil consumption rates have seen to be increasing and conventional crude oil reserves are declining tremendously in the recent years. Therefore, as alternative, heavier carbonaceous liquids are being recovered and transformed into fuels and chemicals (Headley et al, n.d.). These new crude oil sources are becoming more competitive as there are improvements in oil recovery techniques and technologies. Since heavier carbonaceous liquids are used, the wastes generated from it contain heavier hazardous chemical compounds too. Hence, these wastes can cause more negative environmental issues as compared to the conventional crude oil.

2.1 Petroleum Refinery Sludge

According to a study done by Headley et al (n.d.), the contents of the sludge are mainly 44% solids, 33% oil and 23% water. Based on saturates, aromatics, resins, asphaltenes (SARA) analysis done in Headley's study, the oil contains 36% saturates, 31% aromatics, 18% resins and 6% asphaltenes. It is understood that saturates and aromatics contain biodegradable substances. Therefore, it is proven that 67% of the oil content in the sludge consists of biodegradable components. Hence, it is fairly safe to say that sludge can be re-used to incorporate with cement as an environmental-friendly construction material.

Table 2-1: Metal content in sludge

Element	Measured Concentration (μg/g)	Expected Concentration (μg/g)
Chromium	6.9	13.5
Copper	77.9	44.5
Nickel	926	428
Zinc	629	278

(Source: Headley et al, n.d.)

Headley's study further analyses on the metal content of the sludge. Table 2-1 shows the concentrations of each metal expected and measured which were present in the sludge. As mentioned by Headley et al (n.d.), all metals except for chromium are present in solid phase because the measured concentration is more than the expected concentration. Therefore, is it predicted that these metals can be removed from the sludge through filtration.

Further study by Headley et al (n.d.) on the allowable limits for metals and other polycyclic aromatic hydrocarbons (PAH) were compared to concentration limits set by the Canadian Council of Ministers of the Environment (CCME). It is concluded that the concentration of the metals present in the sludge are below the allowable limit. The concentrations of the PAH present however are higher than the allowable limit. Headley et al (n.d.) suggested that a dilution factor for 16 should be calculated in order to reduce the concentration of PAH below the allowable limit if the sludge is to be incorporated in soil.

2.2 Immobilized Waste

According to a journal written by van der Wegen (1997), immobilization of wastes is a treatment that allows minimal leaching of pollutants by changing its physical and chemical properties. Immobilization is done so that the treated wastes can be re-used as building and construction materials. This assists in reducing the capacity of landfilling and the use of raw materials in construction. Immobilization also reduces the leachability of the wastes, which then allows it to be safely landfilled for soil protection. Both these method require low cost for removal of wastes.

Silva et al (2007) stated that the solidification and stabilization treatment can be used to treat various hazardous wastes containing metals, organics and soluble salts. Malviya and Chaudhary (2006) further commented that this technique is particularly used to treat wastes containing heavy metals. Strength and leach resistance are the two essential parameters to test the effectiveness of this treatment (Malviya & Chaudhary, 2006). This shows that stabilization and solidification is a vital process in the immobilization of wastes. It affects the quality and safety if the sludge were to be re-used as part of construction materials.

2.3 Activated Carbon

Rho, Arafat, Kountz, Buchanan, Pinto & Bishop (2001) shared that the efficiency of the immobilized wastes, mainly organic wastes, can be improvised by adding activated carbon, organophilic clay, natural minerals and inorganic compounds. This is because the most common organic compound in the waste, phenol, prevents the hydration of the cement used to solidify the wastes (Rho et al, 2001). In order to know how effective will the addition of activated carbon affect the strength, leachability and permeability of the waste, the adsorption and kinetics study of the activated carbon should be analysed.

Due to activated carbon being costly, therefore, the study on the use of reactivated carbon was done (Rho et al, 2001). Without the use of reactivated carbon, the leaching of phenol was at 87%. After using the reactivated carbon, the leaching was only at 11%. Rho et al (2001) also cited that there is minimal difference between the adsorption efficiency of activated carbon and reactivated carbon. Nevskaia, Santianes, Munoz & Guerrero-Ruiz (1999) also furthered the investigation that in order to improve waste treatment, the kinetic study of the activated carbon can determine when its adsorption efficiency will diminish.

2.4 Cement Binder

Cement is a common use for binding materials together in a confined matrix. The type of cement used for this study is Ordinary Portland Cement Type 1. Based on a book edited by Hewlett (2004), an article written by Peter J. Jackson illustrated a table of types of cement. It showed that Portland cement is a pulverization of hydraulic calcium silicates and calcium sulfates. Portland cement is known to have good strength capacity even under water. Spence and Shi (2004) mentioned that OPC is preferred due to its low cost, long term stability and produces appropriate compressive strength.

Table 2-2: Chemical Composition of OPC

Compound	Compound Concentration in OPC (%)
CaO	64.96
SiO_2	22.41
Al_2O_3	4.55
MgO	3.25
Fe_2O_3	3.15

Source: C.Y.Yin et al, 2006

According to Malviya and Chaudhary (2006) the amount of cement used to solidify the waste is from 5% to 20%. It is understood that although the quantity of the cement is low, the compressive strength of the solidified waste depends on the quality of the pore structure of the solidified waste. Further research also allowed understanding that the strength of the solidified waste decrease as water amount increases. Detailed research has proven that the optimum water/binder ratio is 0.4-0.5 and the water/solid ratio is 0.4-0.6.

2.5 Leaching

According to a book written by Geankoplis (2003), leaching can be defined as the diffusing of solutes into a solvent. Metals are very often being removed as soluble salts through the leaching process. 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. Based on Karamalidis and Voudrias (2007), oil sludges could not be stabilized and the leaching of methylene chloride was as high as 186% in excess. This study was done without the presence of activated carbon.

2.6 Permeability

According to Allen et al (1993), 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. Krus, Hansen, Kunzel (1996) mentioned that according to previous studies, it was determined that cement paste materials exhibit strange behavior in absorption of water as compared to bricks and limestones. Water which is a strongly polar liquid, can slip in between the mineral layers of the material, widen up the distances between them and create new pore spaces (Krus et al, 1996). This shows that determining porosity of a material through water saturation is more accurate as water can slip in microstructures which are not accessible by smaller Helium atoms. According to Zain and Mahmud (2010), water to cement ratio and porosity are important factors that determine the strength of the solidified waste.

CHAPTER 3: METHODOLOGY

3.1 Waste Characterization & Sample Preparation

Sludge sample is collected from the refinery plant and kept safely in the cold room at temperature ranging from 15 – 25℃. Analysis is conducted on the sludge to identify physical and chemical observations. The physical and chemical tests were done based on standard methods for the analysis of water and wastewater (APHA).

3.1.1 Specific gravity

Specific gravity of a material is the ratio of the dry solid portion mass to the amount of equivalent volume of water. The measurement of specific gravity is for the purpose of the mixing calculation for the cement to sludge ratio. The apparatus required is just a marked flask or container to hold a known volume of sludge. The procedure is as follows:

1. Record the sample temperature, T.
2. Weigh empty container and record weight, W.
3. Fill empty container to mark with sample, weigh and record weight, S. Measure all masses to the nearest 10 mg.
4. Fill empty container with distilled water up to equivalent volume of sample, weigh and record weight, R. Measure all masses to the nearest 10mg.

$$specific\ gravity = \frac{weight\ of\ sample}{weight\ of\ equal\ volume\ of\ water\ at\ 4℃} = \frac{S - W}{R - W} \times F \qquad (3.1)$$

The equation above is used to calculate the specific gravity of the petroleum waste. F is referred to the correction factor for the temperature of the petroleum sludge at which it was measured. The correction factor can be referred to the Table 3-1 below.

Table 3-1: Temperature correction factor, F

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 demonstrates the amount of free water present in a moist sample. Under the S/S technology, it is essential to conduct this procedure to determine the material handling properties. Hence, the amount of additional water required for the S/S binder can be calculated. The procedure is as follows:

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℃ 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.

$$Moisture\ Content, \% = \frac{C - D}{C - E} \times 100 \quad (3.2)$$

The equation above is used to calculate the moisture content of the petroleum sludge. The total solid content of the petroleum sludge is the remaining percentage of the content deducted from the moisture content as calculated using the equation above.

3.1.3 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), cadmium (Cd), nickel (Ni), and iron (Fe).

Table 3-2: Cement, Sludge and binder ratios

Component	C/Sd	W/C	C/B
Ratio 1	60	0.45	0
Ratio 2	60	0.45	0.05
Ratio 3	60	0.45	0.10
Ratio 4	60	0.45	0.15

For the simplicity of this study, the sample range of each combination of water, sludge and cement are arranged as shown in Table 3-2 below. Cement to sludge (C/Sd) and water to cement (W/C) ratios were taken from previous study as these ratios showed the highest UCS results. Each combination of ratio is prepared and solidified with variations of the cement to binder (C/B); in this case, the binder is the activated carbon. Upon completion of the solidification process, UCS test is done on all the samples on days 1, 7, 14, 21 and 28 and the average compressive strength is measured. The sample with the highest UCS strength will be chosen as the best combination of ratio for further study of leaching and permeability tests.

3.2 Test Methods

3.2.1 Unconfined compressive strength (UCS)

The wastes, cement and water mixture are placed in a 50x50x50mm mold for casting the solidified blocks according to standard test method ASTM C109-91. 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 UCS test is performed using a compression machine which will determine the strength in terms of pressure. 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. Figure 3-1 shows the sequence of steps to conduct the UCS test on the solidified wastes samples.

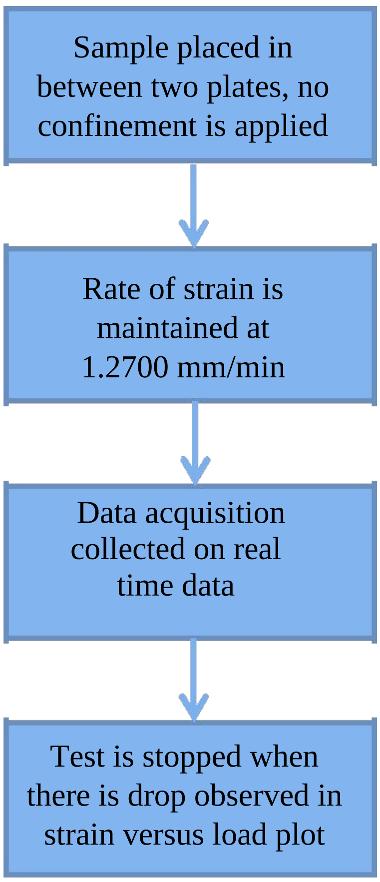


Figure 3-1: UCS test flowchart

3.2.2 Toxicity characteristic leaching procedure (TCLP)

TCLP is mainly conducted to determine the mobility of the organic and inorganic compounds present in liquid, solid or multiple phases. Its result can determine whether the presence and amount of contaminants in the leachate meets the US EPA guidelines. The solidified sludge is crushed and prepared to conduct TCLP test to determine the amount of certain organic or metal presence in the leachate. This test is done according to the US EPA standard method 1311 as shown sequentially in Figure 3.2.

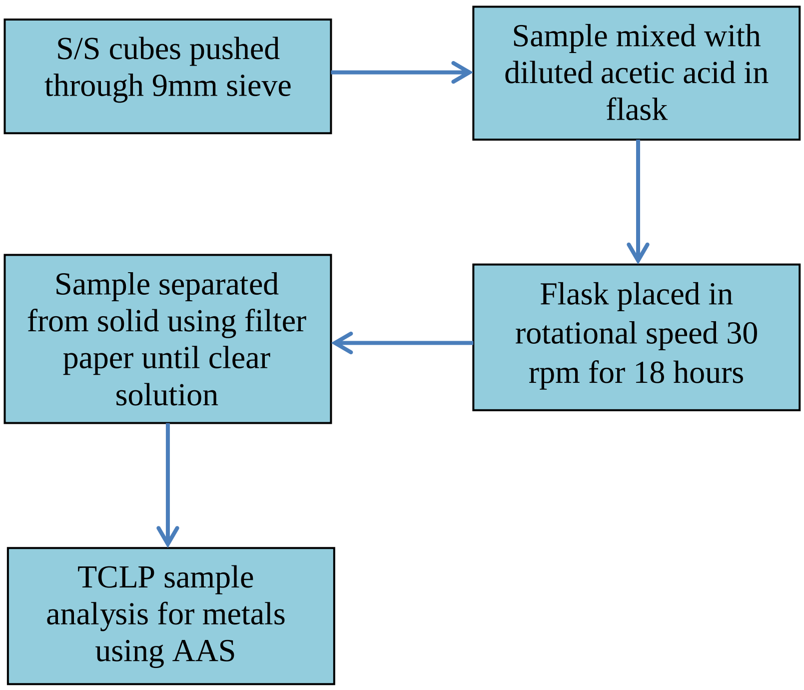


Figure 3-2: TCLP test flowchart

3.2.3 Permeable porosity

Porosity of the solidified wastes is measured according to the ASTM C642. The main objective of this test is to measure the void in hardened concrete. This studies the percentage of absorption of the solidified wastes as compared to the untreated control concrete. Figure 3-3 illustrates the procedure of this test.

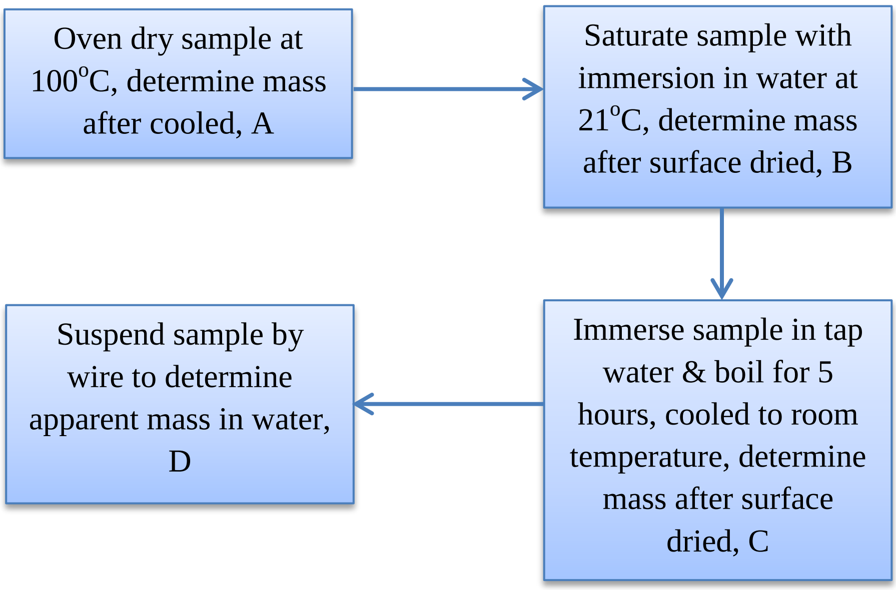


Figure 3-3: Permeable porosity test flowchart

Absorption after immersion, % = [(B – A)/A] x 100 (3.3)

Absorption after immersion & boiling, % = [(C – A)/A] x 100 (3.4)

Dry bulk density, g1 = [A/(C – D)] ρ (3.5)

Where, ρ – Density of water

Bulk density after immersion = [B/(C – D)] ρ (3.6)

Bulk density after immersion & boiling = [C/(C – D)] ρ (3.7)

Apparent density, g2 = [A/(A – D)] ρ (3.8)

Volume of specimen (include solid, permeable & impermeable voids) = 125cm^3

Volume of permeable void space, % = (g2-g1) / g2 x 100 (3.9)

3.2.3 Field emission scanning electron microscopy (FESEM)

A field-emission cathode in the electron gun of a scanning electron microscope (SEM) provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1 ½ nm. That is 3 to 6 times better than conventional SEM. A smaller area of contamination spots can be examined at electron accelerating voltages compatible with the Energy Dispersive X-ray (EDX) Spectroscopy. Figure 3-4 illustrates the sample preparation for FESEM.

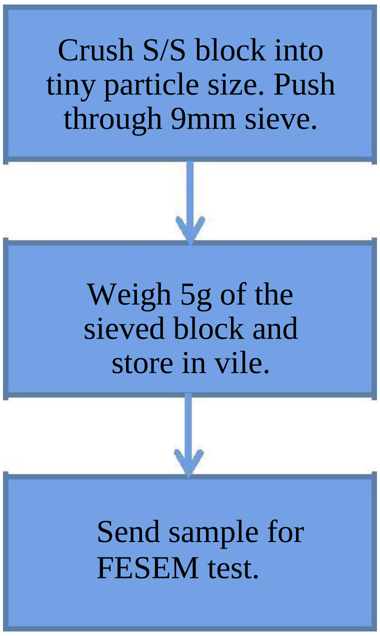


Figure 3-4: FESEM test flowchart

3.3 Key Milestones

Several milestones are set as shown in Figure 3-4 below to ensure the smooth flowing of the experiment conducted for the project. Each milestone is set with a dateline according to the month in both the first and second semester of the final year project.

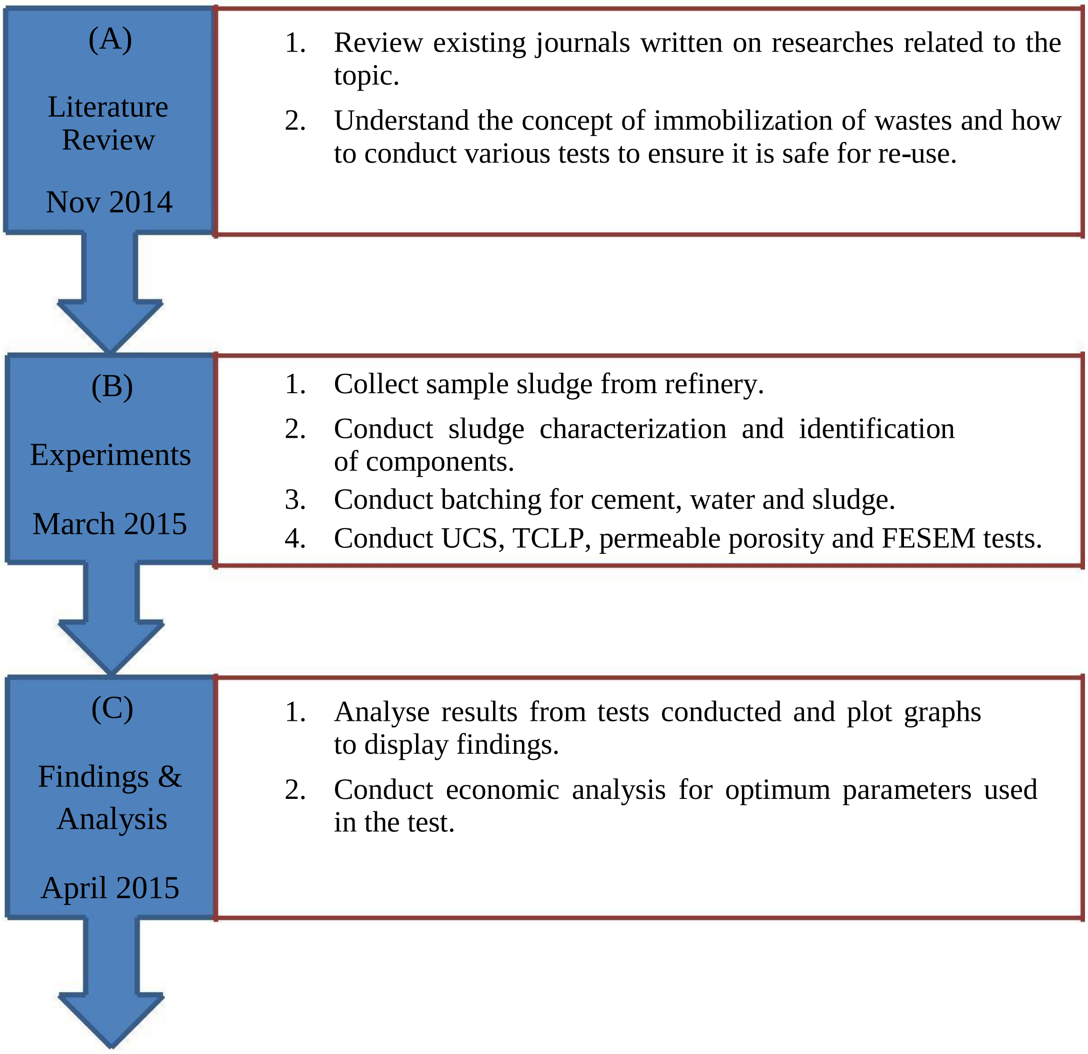


Figure 3-5: Key Milestones

3.4 Gantt Chart

Gantt chart is done to illustrate the start and finish dates of the entire project. For this study, a Gantt chart is prepared as shown in table 4 to illustrate the key milestones set in detail. A visual timeline is set to keep track of the specific tasks that needed to be done. A good anticipation of relating tasks can be accomplished for a better chance of completing the tasks as per scheduled on time. Table 3-4 tabulates the details which are required to be achieved every week.

Table 3-3: Gantt chart

Details	**Week**													
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Literature Review	■	■												
Request for sludge sample	■	■	■											
Conduct batching procedure				■	■	■	■							
Conduct UCS test						■	■	■	■					
Conduct TCLP test								■	■	■	■			
Conduct Porosity & FESEM test								■	■	■	■			
Analysis of findings and report writing									■	■	■	■		

As of week 13, all tests have been conducted. The progress of this study was moving along and according to this Gantt chart as shown in table 3-3. Upon the completion of the UCS test after day 28, the TCLP and porosity tests were done slightly delayed in week 12. The schedule for FESEM test is tentatively at the end of March (week 10), however, due to tight schedule of testing, it was conducted in week 11.

CHAPTER 4: RESULTS AND DISCUSSION

The results illustrated below will be of the waste characterization as mentioned in the methodology. Thereafter, detailed results of the UCS, leaching and permeability tests will be tabulated or illustrated.

4.1. Waste Characterization

Specific gravity of the sludge was determined as follows in Table 4-1:

Table 4-1: Specific gravity

Specific Gravity	Sample 1	Sample 2	Sample 3
Temperature, **T** (℃)	25	25	25
Mass of Empty Container, **W** (g)	238.20	240.30	239.14
Mass of Empty Container + Sludge, **S** (g)	300.88	301.83	301.22
Mass of Empty Container + Distilled Water @ 4℃, **R** (g)	414.25	410.32	413.89
Mass of Sludge (g)	200.04	200.99	200.38
Mass of distilled water (g)	176.05	172.12	175.69
Specific Gravity	1.14	1.15	1.14
Average Specific Gravity	**1.14**		

Moisture content of the sludge was determined as shown in Table 4-2 below:

Table 4-2: Moisture Content

Specific Gravity	Sample 1	Sample 2	Sample 3
Mass of Empty Container, **E** (g)	100.84	101.81	101.01
Mass of Empty Container + Sludge, **C** (wet) (g)	300.88	301.65	300.41
Mass of Sludge (wet) (g)	200.04	199.84	199.40
Mass of Empty Container + Sludge, **D** (dry) (g)	151.28	151.34	151.43
Mass of Sludge, B (dry) (g)	50.44	49.53	50.42
Moisture Content (%)	74.78	75.21	74.34
Average Moisture Content (%)	**74.78**		

Total solid of the sludge can be calculated as shown below:

$$Total\ solid, \% = 100\% - Moisture\ content, \%$$
$$Total\ solid, \% = 100\% - 74.78\%$$
$$\boldsymbol{Total\ solid}, \% = \mathbf{25.22}\%$$

Table 4-3: Characteristic and condition for materials

Material	Parameter	Value
Petroleum Sludge	pH	7.06
	Density, kg/m^3	1136.288
	Moisture Content, %	74.784
	Total Solid, %	25.216
Cement	Density, kg/m^3	3140.000
Activated Carbon	Density, kg/m^3	1821.568
Water	Density, kg/m^3	1000.000
Mixture	Volume of mold, m^3	= 15 cubes x (0.05 x 0.05 x 0.05) = 0.001875
	Humidity, %	90 – 98
	Curing Temperature, ℃	25 – 30

Table 4-3 tabulates the characteristic of sludge, cement, activated carbon and condition required to cure the mixing ratios. Firstly, the sludge is added into the electric mixer for homogeneous mixing for approximately 2-3 minutes. During mixing, cement was added slowly followed by the addition of the activated carbon. The mixture was continuously mixed for 5 minutes. Water was slowly added to the electric mixer to further homogenize the mixture. Once the homogenous slurries can be observed, it was quickly added into the 50 x 50 x 50 caste mould. The moulds were then cured at room temperature with 92% relative humidity for 24 hours. After 24 hours, the moulded cubes were removed from its caste and kept in the curing chamber for further dry curing.

4.2 Unconfined Compressive Strength (UCS)

The objective of this test was to observe the development of cement strength with maintaining the C/Sd ratio of 60 and W/C ratio of 0.45, while manipulating the C/B ratio between 0 to 15%. The C/Sd ratio is kept at 60 because in previous study, the strength of the cement matrix kept increasing with the increase of the binder only at this ratio. The W/C ratio is kept at 0.45 to prevent dehydration of the samples as previous study showed that 0.35 ratios or lower caused the sample to be very dry, thus making the mixing process difficult. The optimized ratio can be determined from the strength growth curve to further study the characteristics of the stabilized and solidified cement matrix. The unconfined compressive strength was measured accordingly based on the different day interval which are day 1, 7, 14, 21 and 28. Since the tests were done on a weekly basis, graphs will be shown for tests conducted for all ratios in each week as a comparative measure.

Table 4-4: Average UCS for each ratio

Ratio	**(C/Sd)**	**(W/C)**	**(C/B)**	**Average Unconfined Compressive Strength (MPa)**				
				Days				
				1	**7**	**14**	**21**	**28**
1	60	0.45	0	3.87	22.40	29.24	35.32	35.87
2	60	0.45	0.05	4.95	28.24	31.84	33.06	35.64
3	60	0.45	0.10	6.73	29.42	32.23	34.14	40.94
4	60	0.45	0.15	4.15	28.15	35.50	38.43	43.75

Table 4-4 tabulates the average UCS for each ratio. According to the table, ratio 4 shows the highest UCS test. This could be because as more activated carbon is added to the mixture; the cement matrix becomes more rigid, thus, increasing the strength of the cement matrix. Therefore, mainly ratio 4 was taken into account for further study of leaching, permeability and morphological study.

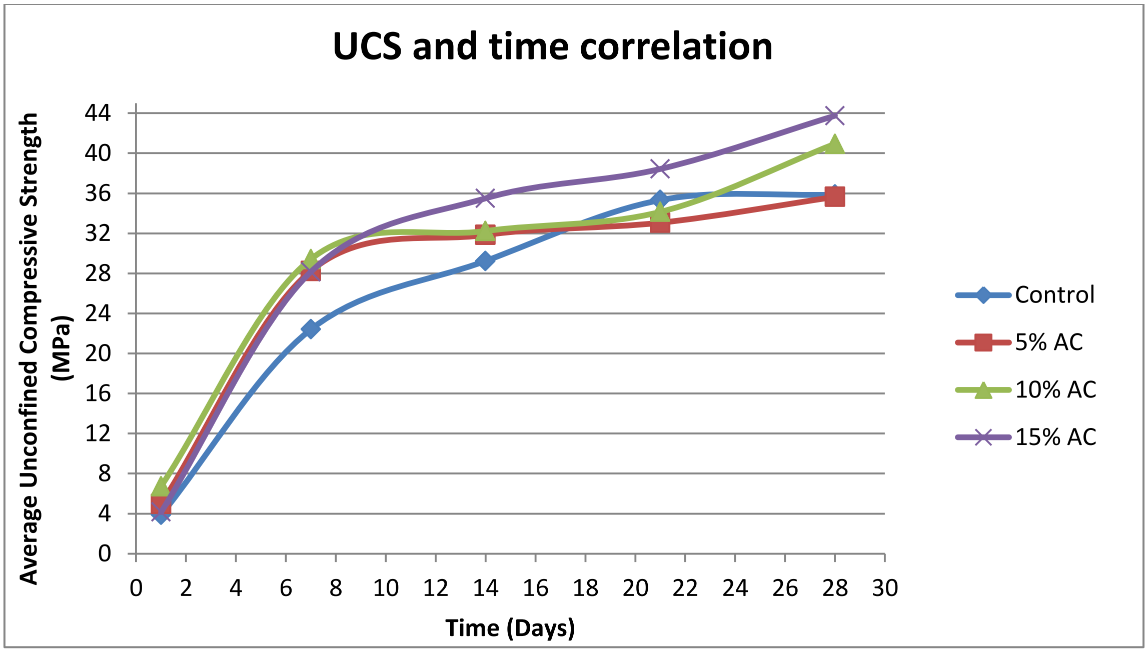


Figure 4-1: Average UCS for all ratios

Figure 4-1 above shows a graph of average UCS for all four ratios depicted from days 1, 7, 14, 21, and 28. As seen in the graph, the ratio with the highest UCS as of day 28 is ratio 4, which consists of C/Sd ratio of 60, W/C ratio of 0.45 and 15% AC. It developed a low unconfined strength at low amount of activated carbon and producing the highest strength in the presence of high amount of activated carbon in the mixture. Based on the chart, it can be deduced that the highest C/Sd ratio, 60 with high amount of activated carbon of 15% produced the strongest cement matrix of 43.75 MPa. As depicted in the scope of study, the US EPA considers a stabilized material is satisfactory if the UCS results is 0.35 MPa or greater. In this case, it has exceeded the target very much above the required minimum limit. However, according to ASTM standard, it does not meet the requirement of 13.7MPa at 24 hours. This could probably be due to the humidity variations in the surrounding which was lower as the sample was left to cure outside the humidity chamber as instructed by ASTM C109-91 procedure. This minimum requirement of USEPA of 0.35 MPa anyhow has been proven to provide a stable foundation including for construction equipment, impermeable caps and cover materials. Therefore, it can be deduced that this ratio of mixture is safe and best suited for S/S process.

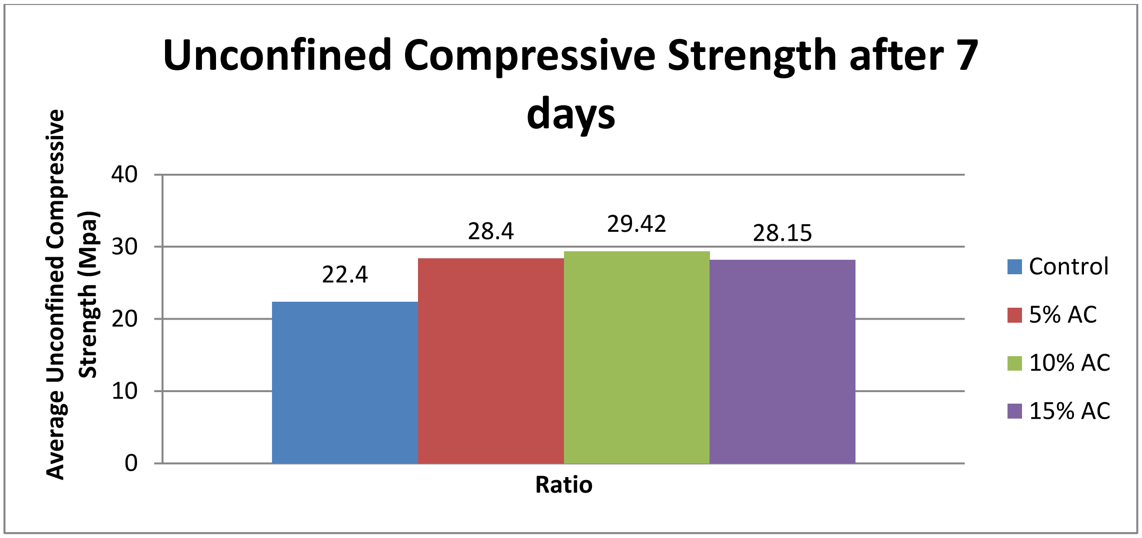


Figure 4-2: Average UCS for all ratios at day 7

Figure 4-2 above shows a graph of average UCS for all four ratios depicted from day 7. The UCS results for all three ratios with activated carbon additions exceed that of the control ratio. The strength for ratio with 15% activated carbon is minutely lower than the other two ratios but this is not a serious issue to be concerned as the sample strengths were taken as an average is deviations are bound to occur. Nevertheless, the result does show that the addition of activated carbon does increase the strength of the cement.

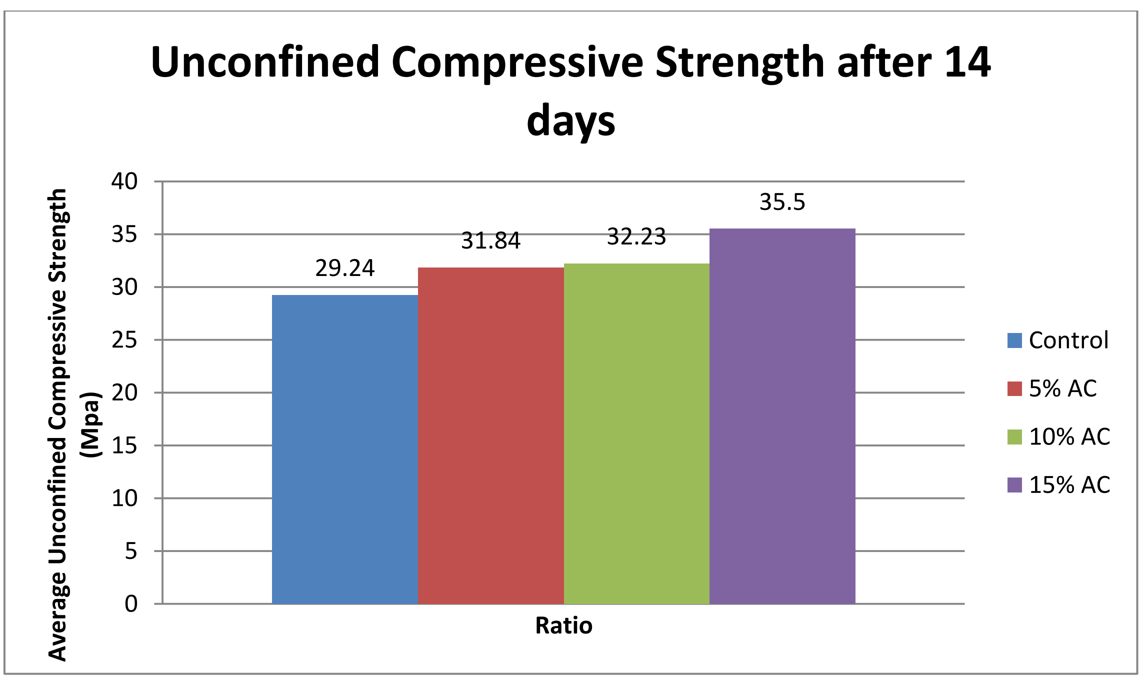


Figure 4-3: Average UCS for all ratios at day 14

Figures 4-3 above shows a graph of average UCS for all four ratios depicted from day 14. As seen in the graph, the UCS results for all three ratios with AC additions also exceed that of the control ratio which is without the addition of AC, just as the results obtained from day 7. However, for ratios with 5% and 10% addition of activated carbon showed that the rate of increase in the strength has become slower.

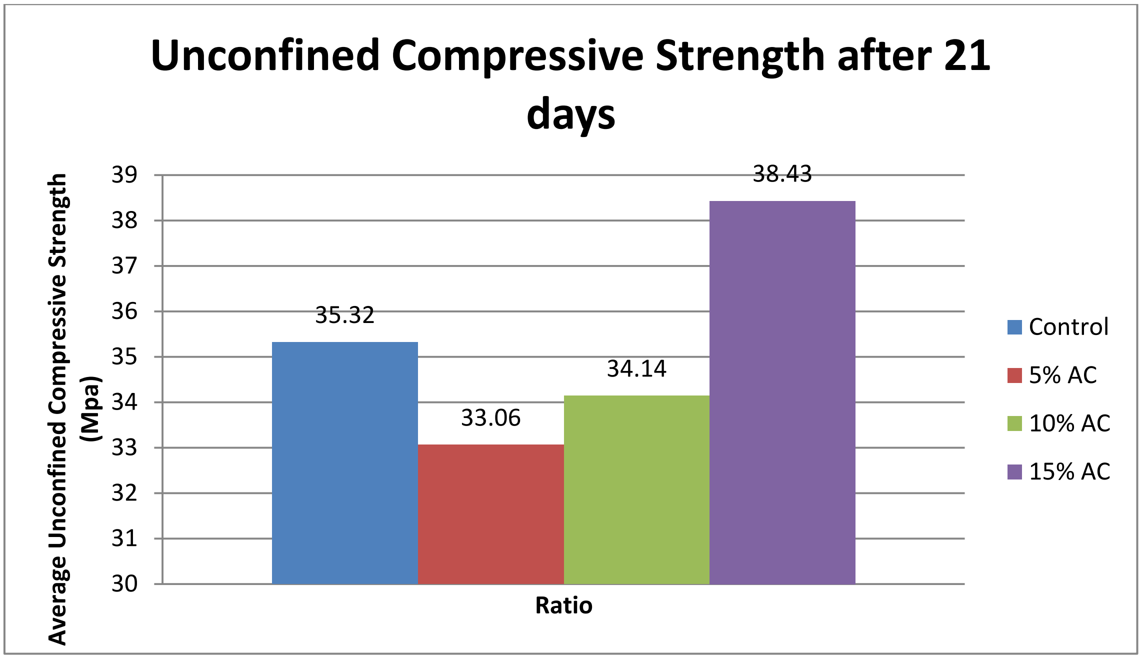


Figure 4-4: Average UCS for all ratios at day 21

Figure 4-4 above shows a graph of average UCS for all four ratios depicted from day 21. As seen in the graph, the UCS results for ratio with 5% and 10% activated carbon are lower than the ratio without activated carbon. This could be due to the higher presence of sludge by weight in these two ratios as compared to the ratio with 15% addition of activated carbon. The presence of sludge can deteriorate the setting of silicates in the cement, resulting in lower strength. However, the UCS result for ratio with 15% activated carbon kept increasing compared to the ratio without the presence of activated carbon.

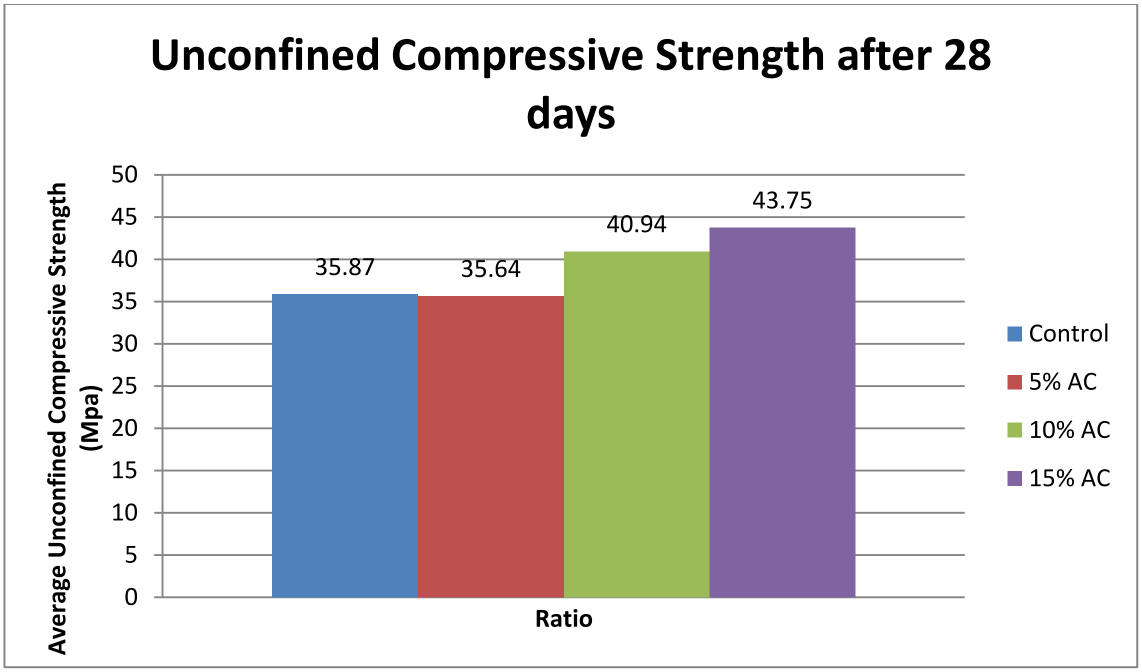


Figure 4-5: Average UCS for all ratios at day 28

Figure 4-5 above shows a graph of average UCS for all four ratios depicted from day 28. As seen in the graph, the UCS results for ratio with 5% activated carbon almost the same as the ratio without activated carbon. However, the UCS result for ratio with 10% and 15% activated carbon are higher compared to the ratio without the presence of activated carbon. As of day 28, the highest average UCS measured is 43.75MPa which is for the ratio containing C/Sd ratio of 60, W/C ratio of 0.45 and 15% AC. Therefore, it can be deduced that ratio 4 shows a very promising combination of ratios for the S/S process of petroleum sludge using activated carbon as an addictive.

4.3 Leaching Test (TCLP)

Leaching tests are done to evaluate the performance of treated wastes for landfill disposal and thus providing a basis for designing leachate treatment systems. For effective S/S process, the binder must react with free water in the waste and form a solid matrix. It must bind with the metals to reduce their chemical nature and leachability. TCLP method 1311 procedure was followed as a standard outlined by US EPA. Refer to Appendix V for the flowchart of the whole process. The extraction fluid used in this set of experiment would be 5.7 ml of 96% acetic acid diluted in 1L of distilled water with pH within 2.88 ± 0.05. The samples were crushed to a particle size smaller than 9.5mm. The extraction liquid is added at a liquid to solid ratio of 20:1. The flasks were covered with paraffin film, wrapped with aluminium foil and mechanically shaken for 18 hours at 300 rpm at room temperature (25 - 33℃). After that the leachate was filtered acidified with 1ml nitric acid and tested using AAS. The possible metals to be detected are zinc (Zn), lead (Pb), chromium (Cr), copper (Cu) and nickel (Ni). Prior to determining the concentration of the metals in the leachate using AAS, standard calibration curve were prepared by preparing standard solutions beforehand.

Table 4-5: Metal content from TCLP result

Component	Concentration (ppm)							
	Cr	Cu	Pb	Ni	Zn	Cd	Fe	Mn
Standard B	1.00	1.00	0.50	1.00	1.00	0.02	5.00	1.00
Raw Sludge	0.60	5.45	5.40	3.09	5.12	1.08	8.23	3.20
0% AC	0.04	0.00	0.00	0.04	0.03	0.09	0.36	0.06
15% AC	0.07	0.00	0.02	0.03	0.04	0.01	0.12	0.01

Under Environmental Quality Act (EQA) 1974 with amendment in 2009, 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 as attached in Appendix IV. The raw sludge showed a significantly high content of copper, lead and zinc. As shown in table 4-5, all metal contents in raw sludge exceed the regulatory limit in Standard B outlined by EQA 1974. However, after being stabilized and solidified using cement and activated carbon, almost all metals showed untraceable amount of metals from the petroleum waste. Based on the reading obtained in table 4-5, it can be deduced that the leaching out of dissolved metal in the waste are significantly low and below the regulated presence of metals in industrial wastewater effluent of EQA 1974.

4.4 Permeability Test

Permeability can be used as an indication of the decrease in mobility of treated waste and the rate of transfer of contaminants from solid mass to the extraction fluid. In this study, permeability is studied relatively through the porosity test since permeability governs the rate of flow of a fluid into a porous solid. Hence, the volume of permeable void space is identified first to understand the porosity parameter.

Table 4.6: Porosity calculation

Parameter	0% AC	15% AC
A, g	246.34	314.21
B, g	275.32	329.38
C, g	287.65	366.53
D, g	103.81	207.49
Absorption after immersion, %	11.76	4.83
Absorption after immersion & boiling, %	16.77	16.65
Dry bulk density (g1), Mg/m^3	1.34	1.98
Bulk density after immersion, Mg/m^3	1.50	2.07
Bulk density after immersion & boiling, Mg/m^3	1.56	2.30
Apparent density (g2), Mg/m^3	1.73	2.94
Volume of permeable void space, %	22.54	32.65

The waste in the solidified/stabilized samples was generally adsorbed or encapsulated in the product matrix. The addition of activated carbon enhanced the metals adsorbing and was beneficial for immobilization. On the other hand, the adding of activated carbon had a strong effect on the porosity of the S/S process samples, increasing the volume of permeable void space by 31%, which might lead to easily leaching out of the metals because the most rapid diffusion of the metals in hydration cement matrices was through the pore network.

4.5 Surface Morphology (FESEM)

FESEM was done to identify the binder reaction phases and correlate results of the physical and chemical tests with the performance of the S/S process using activated carbon as the added binder. FESEM microscopically visualized the physical entrapment of metals and demonstrates the formation of altered or new crystal structure in some phases which appear to be chemically bonding some organics or metals.

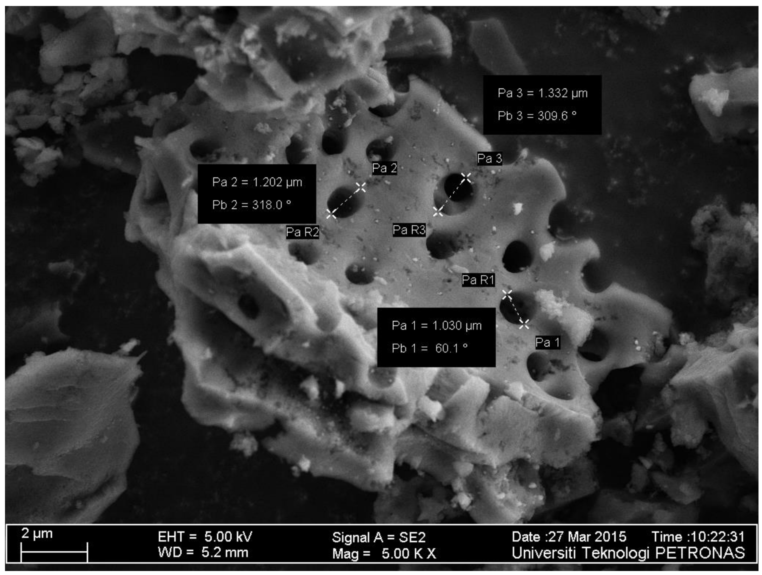


Figure 4-6(a): Image of activated carbon with pore size

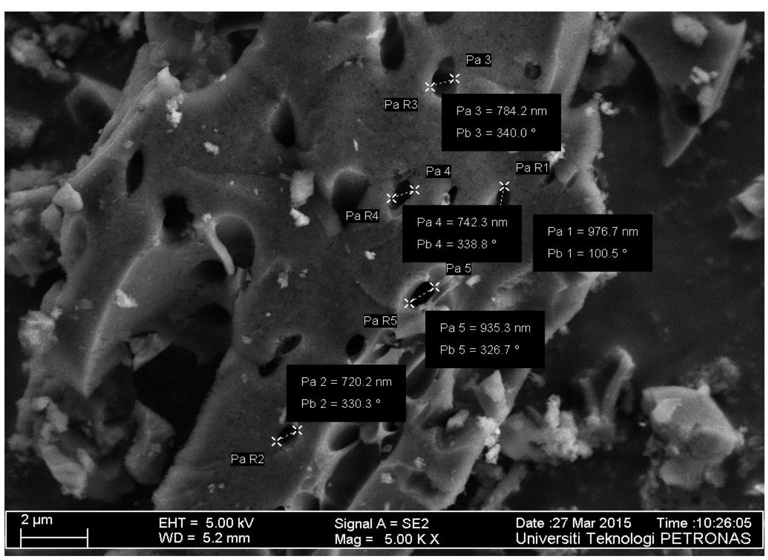


Figure 4-6(b): Image of activated carbon with pore size

Figures 4-6.1 and 4-6.2 above illustrates the microscopic view of the surface of the activated carbon used for this study with visible pores. The range of the pore size for the activated carbon as scanned and illustrated in the figures above is between 720.2nm and 1.332μm. Therefore, the estimated size of the pore based on the figures above is calculated to be at an average of 0.965 μm.

Table 4-7: Image of ratio 1 and ratio 4 samples

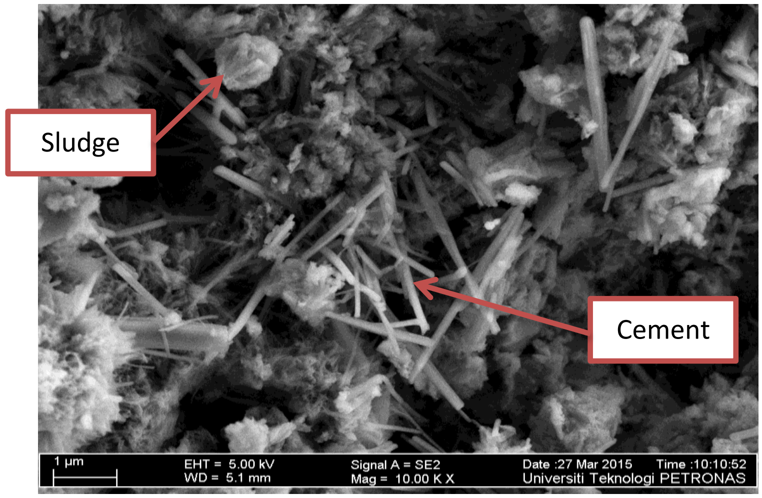
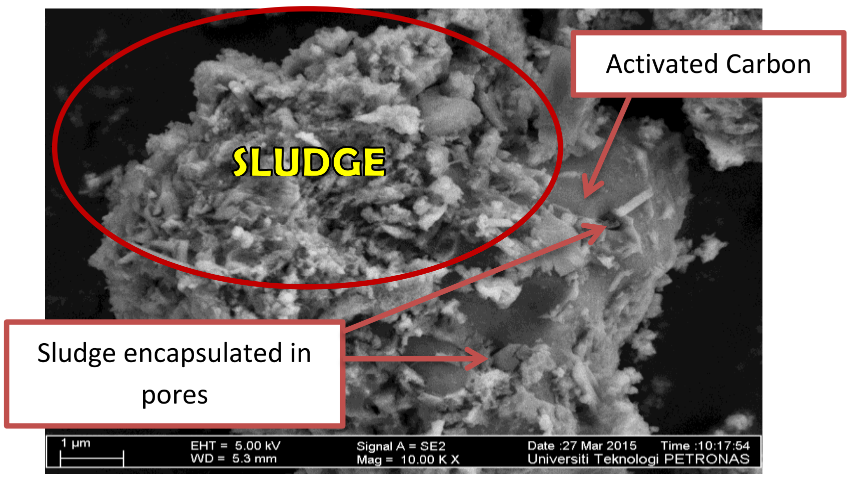
Ratio	Picture
0% AC	
15% AC	

Table 4-5 shows the images of the surface structure for ratio 1 and ratio 4. As seen, the cement surface structure formed for ratio 1 are of thin and long crystal-like structure which are very visible with the absence of activated carbon. With the addition of 15%

activated carbon, it can be clearly seen in the image that the pores of the activated carbon have encapsulated the sludge. A large and compact amount of sludge is able to be bounded onto the surface of the activated carbon due to the mixture of cement which provides the chemical binding and solidification aspect of the S/S process.

Table 4-8: Elements analysed on surface of sample using EDX

Element	Weight Percent, %	
	0% AC	15% AC
C	30.59	32.39
O	39.87	39.94
Mg	0.58	0.90
Al	2.76	1.47
Si	5.41	4.77
S	0.72	0.92
Ca	19.04	18.65
Fe	1.02	0.96

Table 4-8 tabulates the results of the elements that were successfully traced using the EDX to identify components present in the samples. With the addition of 15% activated carbon, the weight percent of aluminium reduced from 2.76% to 1.47%, whereas for iron, the weight percent reduced from 1.02% to 0.96%. This further verifies that the addition of activated carbon can reduce the traceability of metal elements on the surface of the cement mixture matrix and confirms the entrapment of these metals inside the pores of the activated carbon as can be seen in the picture depicted in Table 4-7.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

From this study, it can be concluded that increase in the petroleum sludge waste ratio and activated carbon ratio increases the strength of the stabilized and solidified cement cubes. The C/Sd ratio of 60, and W/C ratio of 0.45 with highest C/B ratio of 15% gives out the maximum strength of 43.75 MPa, highest strength compared to other C/B ratio applied. Porosity increased as much as 31% when the C/B increased to 15%. Metals content test proved the immobilization of selected metals with all metals below allowable limit after confined with cement together with activated carbon. No patterns or trend 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 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. Further study can be done to determine if the micro-encapsulation is an effective technique without bonding. Furthermore, study to determine the amount of organic compounds that can be included in inorganic waste streams without requiring pre-treatment before S/S process. Further study should also be done as to incorporate these S/S technologies in construction materials.

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APPENDICES

Appendix I: Calculation of C/Sd Ratio = 60 and W/C ratio = 0.45

Assume,

Cement Dry Mass	= 60 kg
Sludge Dry Mass	= 1 kg
Raw Sludge Mass	= 1 kg / Total Solid
	= 1 kg / 0.2521
	= 3.9667 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 Activated Carbon: 15%

Mass of Activated Carbon based on Cement mass	= 60kg x 0.15
	= 9 kg
Remaining amount of cement in mixture	= 60 kg – 9 kg
	= 51 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	= 51 kg / 3140 kg/m^3 = 0.01624 m^3
Volume of Activated Carbon	= 9 kg / 1821.568 kg/m^3 = 0.00494 m^3
Volume of Raw Sludge	= 3.9667 kg / 1136.288 kg/m^3 = 0.00349 m^3
Total Volume of Mixture	= 0.01624 m^3 + 0.00494 m^3 + 0.00349 m^3
	= 0.02467 m^3

Ratio of Calculated Volume/ Ratio of Required Volume

= 0.02467 m^3 / 0.001875 m^3

= 13.157

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 = 51 kg / 13.157 = 3.8763 kg

Mass of Activated Carbon Required = 9 kg / 13.157 = 0.6840 kg

Mass of Raw Sludge Required = 3.9667 kg / 13.157 = 0.3015 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 3.8763 kg = 1.7443 kg

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

Amount of water in sludge = 0.3015 kg x Moisture Content

= 0.3015 kg x 0.747837

= 0.2255 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.

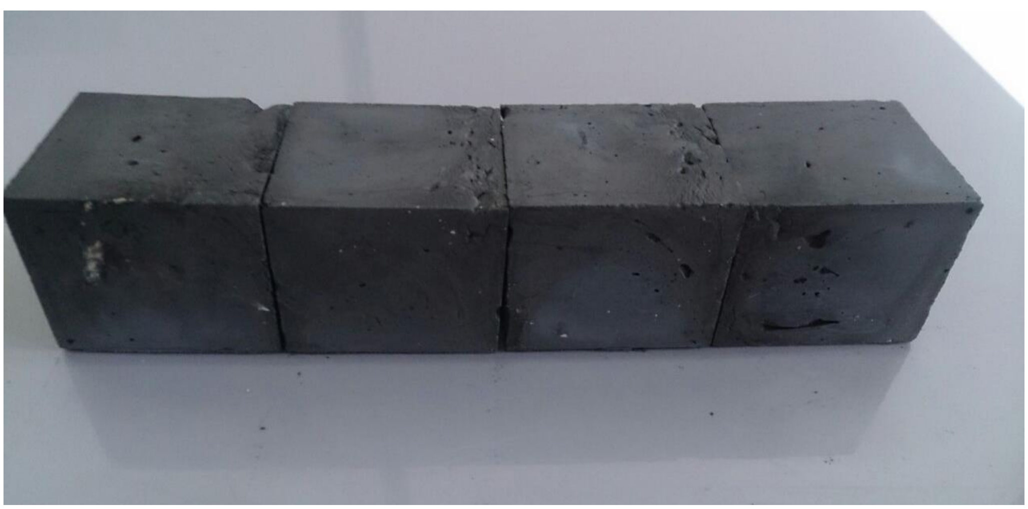
Amount of water need to be added = 1.7443 kg – 0.2255 kg = 1.5188 kg

Appendix II: Mixing Calculation for C/Sd = 60, W/C = 0.45

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	0.0016	0.0233	12.4212	4.5889	0.3193	0.2415	1.8263
60	0.45	0.1	3.9657	1	0.0035	60	54	0.0172	6	0.0033	0.0240	12.7901	4.2220	0.3101	0.4691	1.6680
60	0.45	0.15	3.9657	1	0.0035	60	51	0.0162	9	0.0049	0.0247	13.1589	3.8757	0.3014	0.6839	1.5187

Note: Appendix II is excel sheet done based on sample calculation shown in Appendix I

Appendix III: Images of cement mixing and curing



Appendix IV: Environmental Quality (Sewage & Effluents) Regulation, 1979

THIRD SCHEDULE

ENVIRONMENTAL QUALITY ACT, 1974

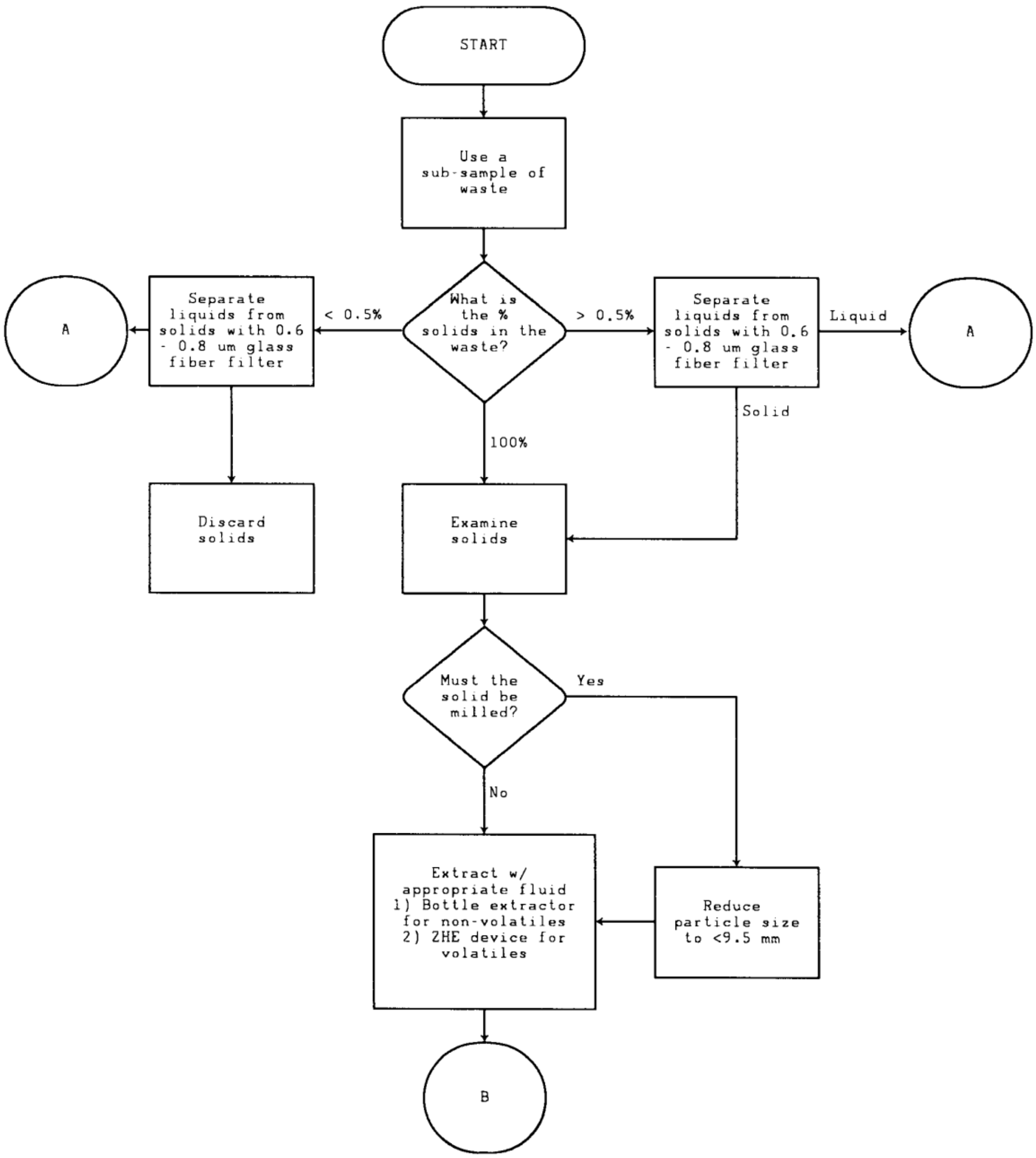
ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS) REGULATIONS, 1979

(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

Appendix V: Toxicity Characteristic Leaching Procedure



Appendix V: Toxicity Characteristic Leaching Procedure (con't)