Carbon Fixation by Phase Change In Waste Immobilization

by

Siti Nurfatihah binti Mohd Mohiden
15573

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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Approved by,

_____
(Dr Asna binti Mohd Zain)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

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

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SITI NURFATIHAH BINTI MOHD MOHIDEN

ABSTRACT

The purpose of carrying out this project is to find the best S/S admixture and cement as a binder by testing its compressive strength and also to study the carbon emission from the treated sludge waste by running the carbon footprint analysis. This is because, the improper disposal of refinery sludge waste which contain heavy metals and other toxic material can be harmful to the environment. The scopes of this project are waste and cement matrix characterization, the laws, regulation and standards in the stabilization/solidification technology, hydraulic of cement hydration and also the study for effect of adding various admixtures into cement matrix in term of strength and leach ability. Based on the past research, the result expected is that the cement matrix with 0.45 W/C ratio, 0.60 C/Sd ratio and 15% of binder content will produced the highest Unconfined Compressive Strength (UCS) reading. Other than that, the previous research paper also stated that the function of adding admixtures as good binder in cement matrix is undeniable according to the result. As a conclusion, by proving that the heavy metal contents and toxic material can be effectively entrapped and also by proving that the carbon dioxide emission can be prevented by using the stabilisation and solidification (S/S) technology, the industry will have more reason to employ this S/S technology as their routine method to treat the sludge waste. It has been found that the best mixture for sludge fixation is 5 % metakaolin with 0.45 W/C ratio and 0.60 C/Sd ratio with 34.21 MPa strength value.

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CHAPTER 1

INTRODUCTION

1.1 Background Study

The oily sludge waste from the refinery waste can be treated in various ways including biodegrading, oxidation, incineration and also stabilization/solidification. Treating this abundant waste is crucial as improper disposal of this hazardous waste could lead to serious environmental pollution. The production capacity, the properties of crude oil (e.g. density and viscosity), processing scheme of the refineries and oil storage method will determine the amount of the sludge produced [1]. Hence, the refinery with higher production capacity will produce more petroleum sludge and the estimation showed that for every 500 tons of crude oil being processed, 1 tons of petroleum sludge is produced. In Malaysia alone, 3 refinery companies consist of PETRONAS, SHELL and PETRON have the processing capacity of 440,000, 125,000 and 88,000 barrels per day (bpd) respectively [2-4]. The figure sum up that refining capacity in Malaysia is 653,000 bpd or 32,519,400 tonnes per year and it is estimated that 65,039 tonnes of petroleum sludge is produced in Malaysia in a year.

The oily sludge waste is encompasses of series of petroleum hydrocarbons (PHCs), water, heavy metals and solid particles [1]. As the large fraction of the oily sludge waste is comprises from hydrocarbon, burning this oily sludge waste will cause a massive Carbon Dioxide (CO_2) emission to the environment. CO_2 emission into the environment can contribute in imbalance of greenhouse effect as the green plants are not able to convert the abundant of CO2 into usable Oxygen (O_2). The imbalance in greenhouse effect also leads to global warming. Stabilization/solidification methods on the other hands, is proven as the safe method

to treat the sludge waste and had received the recognition from USEPA as accepted technology [5]. Solidification and stabilization is a process of encapsulate a waste (i.e. Oily sludge waste) into solid form and at the same time immobilized the hazardous components in the waste [5]. In order to immobilize the hazardous components, the waste must be mixed with binder that acted as the solidifying agent and let it chemically reacted [5].By using the stabilization/solidification methods, the hazardous components such as mercury, zinc, CO_2 and PHCs itself will be trapped and immobilized.

However, the reliability of this technology is affected by one of the important factor which is the presence of admixture in the cement based matrix [6]. The presence of this addition reagent is meant to improve the handling and physical characteristics of the sludge waste, to decrease the toxicity of the sludge waste components, and to limit the solubility of any contaminant. Other than that, the presence of admixture also affected the in and out transfer of hazardous sludge component by decreasing the surface area of the waste. Other than the presence of admixture factor, the reagent/admixture type, reagent addition ratio (mix ratio), curing time, and temperature also another important factors that affected the stabilization/solidification process of sludge waste [7]. However, many past researchers could adjust the final strength and durability values by changing reagent mix ratios and the optimum mix ratios was produced in previous literature. Different type of admixtures will produced different strength, durability and leaching behaviour as they alter the waste component in various ways.

1.2 Problem Statement

Petroleum sludge waste is produced around 60 million tons per year and more than 1 billion tons of petroleum sludge waste has been accumulated, worldwide [1] and Malaysia alone produce 65,039 tonnes of sludge per year [2-4]. Improper sludge disposal such as improper land disposal, might lead to some serious situation as the present of the toxic substances in the oily sludge pose a major threat to the environment. According to Environmental Quality Act (EQA) 1974, oily sludges are

coded as SW 311 for waste oil/ oily sludge and SW 314 for oil or sludge from oil refinery plant maintenance operation.

The soil morphological change occurs when the oily sludge is dumped on the environment, for example the land disposal method can cause the physical and chemical properties of the soil are disturbed [8]. The oily sludge component can be permanently trapped in soil pores, adsorbed onto the surface of soil mineral element, or form a permanent cover on soil surface, due to high viscosity of oily sludge [9]. Therefore, as an alternative, a stabilization/solidification (S/S) technology is introduced to overcome these devastating effects by land disposal.

By using S/S technology, the movement of hazardous component in petroleum sludge waste can be further investigate and on the other hand, will be able to replace the existing sludge treatment method like incineration that involve combustion of the hydrocarbon waste which later on emitted carbon dioxide, carbon monoxide from incomplete combustion and other hazardous gasses. By applying S/S method, carbon dioxide emission and other hazardous gasses can be prevented. From the past research, S/S with admixture as a binder along with the cement is proved to have higher strength and lower leach ability compare to the S/S with cement binder. In order to make the S/S technology is used in the real field, the best binder admixtures must be investigated among these six admixtures which are; Metakaolin, bentonite, zeolite, fly ash, Rice Husk Ash (RHA), and activated carbon. Test must be carried out to see if this method is applicable or will it diminish the identity of the cement as a building block material.

1.3 Objective

The objectives or aims of this project are:

i. To obtain the best S/S admixture and cement as a binder by testing its compressive strength.
ii. To study the effect of adding various admixtures into cement matrix in term of strength.
iii. To investigate the characteristic of Sludge Waste

iv. To immobilize the Sludge Waste through S/S method

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1.4 Scope of Study

Throughout the research, the author will be exposed to the following:

i. Waste characterization by testing total solid, specific gravity, and moisture content of the waste.
ii. Cement matrix characterization to fulfil the requirement to be used in construction by testing its unconfined compressive strength (UCS) and pH value.
iii. Studies on the laws, regulation and standards required for a cement mixture.
iv. The basics of hydraulics cement system and the effect of admixtures on cement formation for solidification and stabilization.
v. The effect of adding various admixtures into cement matrix in term of strength.

CHAPTER 2

LITERATURE REVIEW

To achieve main goal of this project which is to obtain the best S/S admixture and cement as a binder, a lots of information and literature must be retrieved. In this part, the author will further describe on the project background in details.

2.1 Stabilization and Solidification Technology

Stabilization and solidification (S/S) is a technology where additives such as binder and sorbent is added into hazardous waste sludge to immobilize the harmful component from the waste. The binder is a reagent that is accountable to enhance the strength of the mixture as well as improving stabilization while a sorbent is a reagent that are capable to retain contaminants in the stabilized matrix. One of the mechanism involve in this S/S technology is macro encapsulation, where hazardous wastes are physically captured inside a bigger soil matrix. On the other hands, microencapsulation mechanism is also involved in the microscopic level to detain the waste along with the crystalline structure of the solidified matrix. Absorption and adsorption mechanism also take place in the S/S technology to trap the waste more tightly. A study is essential especially when a particular waste is stabilized by means of a specific binding matrix, to review the possibility of using the mixture matrix as building material and at the same time provide the alternative use on the waste instead of disposing it [10]. By reducing the surface area exposed to leaching or by covering the wastes with low-permeability materials, contaminant migration can be restricted [11]. This technology can be described as eliminating and impeding the mobility of contaminants rather than destructing it [11].

2.2 Hydrocarbon Waste

An oily sludge from PETRONAS Penapisan Terengganu (PPT) Sdn Bhd will be used in this project. The oily sludge is one of the wastes that fall into hydrocarbon waste category. The term 'Oil Sludge' refers to a type of waste produced due to storage of crude oil or products that contain the mixture of oil, water and solids. Normally, the simple waste oil contains less water than sludge which is very viscous and also contains a high percentage of solids. On the other hands, a distinctive physical form of petroleum sludge waste is the stable water-in-oil (W/O) emulsion [12].Oily sludge sources in the upstream operation comprise of slop oil at oil wells, sediments in the crude oil tank bottom and also residues of drilling mud [13]. In the downstream operation, sources of oily sludge including; (a) slop oil emulsion solids; (b) heat exchange bundle cleaning sludge; (c) residues from oil/water separator, such as the American Petroleum Institute (API) separator, parallel plate interceptor, and corrugated plate interceptor (CPI); (d) sediments at the bottom of rail, truck, or storage tanks; (e) sludge from flocculation–flotation unit (FFU), dissolved air flotation (DAF), or induced air flotation (IAF) units, and (f) excess activated sludge from on-site wastewater biological treatment [1].

Generally, an oily sludge components are divided into four main fractions, including aliphatics, aromatics, nitrogen sulphur oxygen (NSO) containing compounds, and asphaltenes [14]. 75% of the PHCs in oily sludge is made up from aliphatics and aromatic hydrocarbon [15], and the most common compound found are alkanes, cycloalkanes, benzene, toulene, xylenes, naphthalene, phenols, and various polycyclic aromatic hydrocarbon (PAHs) like anthracene and chrysene [16]. Presently, various forms of waste streams produced from various refineries are yet to be systematically grouped or characterized for additional understanding. The nonspecific wastes (F-list) are encompasses from seven different groups, according to regulation 40 CFR 261.31 and petroleum refinery wastewater treatment sludge is one of them. As implied by EPA as F037 and F038, this group can be further divided into two groups, depending on the separation stage of the sludge that can be primary or secondary.

2.3 Admixtures

Most of the recent research focused on the stabilization and solidification with ordinary Portland cement (OPC) mixed with pulverized fly ash because it is proven for its effectiveness but still under further research because of the limited supply of fly ashes and high cost of cement in Asian country [17]. Fly ash is the by-product of the combustion of coal used for electricity generation. Therefore, fly ashes are produced in large quantities, estimates amounting up to 780 million tons annually [18]. They consist of finely divided ashes produced by burning pulverized coal in power stations [19].

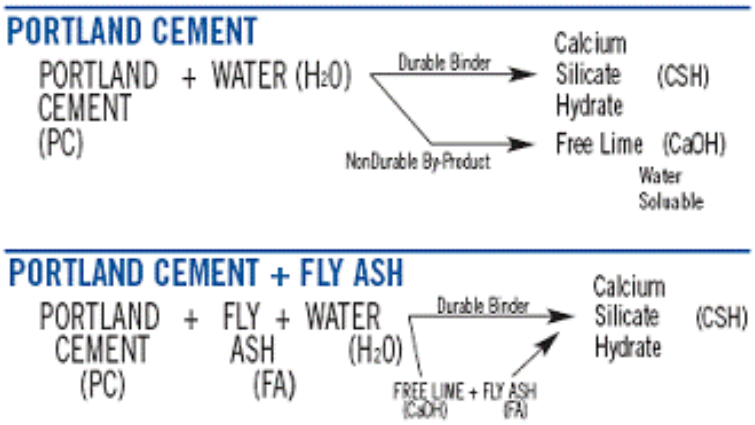

Figure 2.1: The differences in reaction with and without the addition of fly ash in cementing process [20]

However, other type admixtures are also under recent research such as bentonite, zeolite, Rice Husk Ash (RHA), activated carbon and also Metakaolin. Bentonite is a type of clay that is commonly produced from modification of volcanic ash, consisting mostly of smectite minerals, usually montmorillonite that acts as an active protective layer of geosynthetic clay liners and this bentonite deposits are normally acquired by quarrying [21].

Zeolites are the solids with a relatively open, three-dimensional crystal structure built from the elements aluminium, oxygen, and silicon, with alkaline-Earth metals (such as sodium, potassium, and magnesium) plus water molecules trapped in the gaps between them and they very stable to resist the kinds of environmental

conditions that challenge many other materials [22]. On the other hands, RHA is a by-product from rice milling industry, acts as a very good insulator and also a good super-pozzolans that will be very useful in concrete mixing [23]. Other than that, activated carbon is known for its adsorption capability within a broad range of organic materials [24]. Metakaolin is also another type of pozzolans that react with calcium hydroxide. All of these admixtures will be used in this project.

2.4 Hydration of Cementing Process

One of the stabilization and solidification method exists is the cementing stabilization process. It is a process of stiffening and hardening of one or more cement material, where metals are retained in a form of insoluble hydroxide or carbonate salts due to the alkaline property of the cement material. Ordinary Portland cements or shortly called as OPC is commonly used because of its cheap price and versatility in the construction. The cementing stabilization process take place in the presence of the cementing hydration where the powdered cement changed to thin cement slurry when water is added. A series of hydration process of OPC is quite complex compared to traditional cement where the hydration process can be broken down into several distinct periods. The first stage is where the more reactive aluminate and ferrite phases react as shown in part (a) of Figure 2. The second phase took place in the first few minutes of hydration as the aluminium and iron phases react with gypsum to form a shapeless gel and short rods of ettringite at the surface of the cement grains as shown in part (b).

In part (c), it can be seen that about 30% of cement reacts to form calcium hydroxide and C–S–H in the duration of 3 to 24 hours after hydration started. After that, acceleratory period commenced after 18 hours of hydration where Calcium Aluminate (C3A) continues to react with gypsum to form longer ettringite rods. As shown in part (e), the deceleration period of hydration takes place after 1 to 3 days where monosulfate is produced from the reaction of C3A with ettringite. The gap between the hydrating shell and anhydrous C3S is narrowed down to less than 1 μm as the Inner C–S–H" continues to grow near the C3S surface. Finally, the gap

between the “hydrating shell” and the grain is completely filled with C–S–H after two weeks of hydration and the “outer C–S–H” becomes more fibrous as shown in part (f). it can be concluded that the rate of hydration is likely to depend on the diffusion rate of water or ions to the anhydrous surface [25].

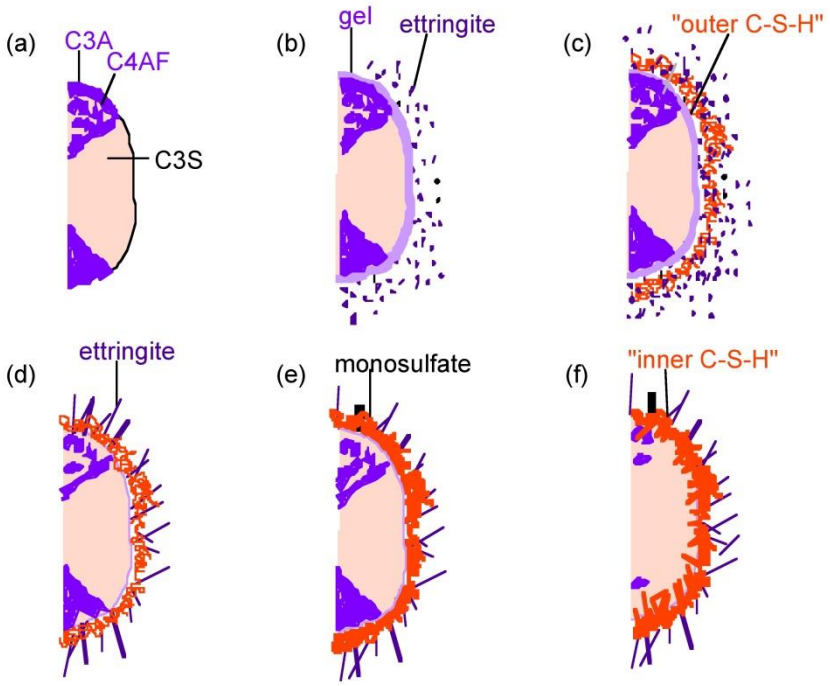

Figure 2.2: The distinct stages of OPC hydration [25]

2.5 Unconfined Compressive Strength (UCS)

The author has done a few extended researches and improving report writing to produce a quality report. Other than that, the author also grabs the chances to collect data from previous research paper that circulate around the same topic. In one of the report, the finding showed that the highest compressive strength with admixture zeolite is 31 MPa with 10% zeolite composition and 40% sludge content in mixture [6]. In other research paper, it is found out that the cement mixture with ratio cement to sludge (C/Sd) of 60, W/C of 0.45 and 15% of activated carbon produced the highest Unconfined Compressive Strength (UCS) which is 43.75 MPa after 28 days compared to the cement matrix with lower percentage of activated carbon. Furthermore, the other research paper that study about cement matrix with Metakaolin as binder also produced a finding that the cement matrix of 0.45 W/C

ratio, 0.60 C/Sd ratio and 15% of metakaolin yielded the highest UCS 79.58 MPa after 28 days of curing. Besides that, the other research paper that investigated the cement matrix with fly ash as a binder concluded that the cement matrix with 0.45 W/C ratio, 0.60 C/Sd ratio and 15% of fly ash produced the highest UCS reading which is 39.75 MPa after 28 days of curing [26].

From this previous finding, it can be expected that the cement matrix with 0.45 W/C ratio, 0.60 C/Sd ratio and 15% of binder content will produced the highest UCS reading. For the leach ability results, all the research paper concluded that by adding the binder in the cement matrix, the leach ability of the cement matrix is decreased which means that this stabilization/solidification method could entrap the heavy metal and toxic component from the sludge [6, 26]. As for the porosity and permeability results, one research paper deduced that the increment in porosity and permeability value of cement matrix reduces the credibility of zeolite as a binder [6]. However, the other research paper mentioned that the increasing fly ash percentage as binder generated the desired lower accessible porosity which the approved the theory of adding the fly ash in the cement mixture can assist the stabilization/solidification of heavy metal waste and toxic materials [26].

CHAPTER 3

METHODOLOGY

3.1 Material and Apparatus

To carry out this final year project, a series of experiment must be carried out by the author. In order to achieve this goal, the material and apparatus should be listed out to plan the experiment well.

3.1.1 Material

1) Ordinary Portland Cement (OPC)
2) Oily sludge sample from PETRONAS Penapisan Terengganu
3) Kaolin
4) Zeolite

3.1.2 Apparatus

1) Volumetric flask
2) Crucible
3) Oven
4) Filter funnel
5) Filter paper
6) Desicccator
7) Weighing scale
8) Furnace

3.2 Experimental Methodology

The S/S technology requires description of the waste as well as the binder to comprehend the physiochemical of the cement matrix. The existence of admixture in this mixture should be monitored in order to recognize its general properties and applications to validate its purpose in the cement based matrix. The unconfined compressive test (UCS will be carried out on the cement based matrix as evaluation criteria for the S/S technology once the waste, binder and admixture characterization are specified.

3.2.1 Cement Mixing Ratio Planned For Testing

Based on the mixtures of the mixing ratio from Table 1, the planned test for the 'Cement Mix Matrix' can be seen. The project will be carried out at the same water to cement (W/C) ratio for all series of experiment. This is because the sludge itself already high content of water, adding more water will cause the cement become too watery and will have a low compressive strength.

The various admixture compositions of 5%, 10% and 15% will be for Cement to Sludge (C/Sd) ratio 60. By completing each test the author will be able to observe the best cement mix matrix ratio and the best binder/admixtures in immobilizing the toxic material from the sludge. Other than that, the effectiveness of the cement in immobilizing hydrocarbon waste in metakaolin and zeolite cement can be observed by carry out a series of test.

Table 3.1: Cement to Sludge (C/Sd) ratio and Cement to Binder (C/B) Ratio that will be used in the project.

	Cement, Water, Sludge (Hydrocarbon Waste) and Cement to Sludge Ratio (C/Sd)	
Binders C/B (Percentage %)	Metakaolin	Zeolite
5	60	
10		
25		

3.2.2 Cement Mixing Procedure

The procedure is as follows:

1) Obtain properties needed for mix calculation (sludge density, solid content & water content).
2) Calculate the ratio needed for the mixing based on mix calculation template prepared as shown in the Appendix I.
3) Apply thin layer of oil (engine oil) onto the mould. This is to avoid the dried cement block sticking on the mould and to make it easier to be removed from the frame.
4) Mix the cement, sludge, water and binder accordingly to type of sample being prepared.
5) Carry out slump test using k-slump tester & pH test by using pH paper for the cement mixture sample.
6) Place the mix evenly into the mould (layer by layer). Let the mixing (mould) dry in ambient conditions for approximately 24hours.
7) Open the moulds after 24 hours and weigh mass and measure its dimensions for each block for day one for weight and dimension analysis.

8) Place the blocks in a curing cabinet until desired testing period (day 1, 3, 7, 14 and 28) of the blocks compressive strength.
9) Clean the mould by rinsing it with water first. Then soak the mould in 2.5% decontamination solution and 5% nitric acid, HNO3 solution and leave over night when soaking in each solution. By doing so the dried cement on the mould will deteriorate making cleaning process easier.

3.2.3 Waste, binder and admixture characterization

As for this project, a series of procedure to find out the physical and chemical characteristic of the waste, binder and admixture are proposed. This step is crucial for the author to understand the mechanism in the mixture matrix later on.

3.2.3.1 Specific Gravity

Specific gravity of a material means 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 mixing calculation purpose (Cement to sludge ratio). To estimate the extent of waste volume expansion due to treatment, the specific gravity measurement of before and after must be known. 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 3.2: Temperature Correction Factor, F

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

3.2.3.2 Moisture Content

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

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 ◦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.

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

3.2.3.3 Total Solid

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 ◦C to 105 ◦C and once done, cool the container by placing it in desiccators 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 ◦C to 105 ◦C. After 1 hour, place the container with sludge into the desiccators 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.

$$\% \, Total \; solids = \frac{(A-B)\times 100}{C-B} \quad (4)$$

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

3.2.4 S/S Evaluation

3.2.4.1 Unconfined Compressive Strength (UCS) Test

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

3.2.4.2 X-Ray Diffraction (XRD)

XRD is used to identify chemical composition and crystallographic structure of a sample. A monochromatic X-ray is projected into a sample which is crystalline material at a certain angle. Diffraction ill occur when the distance traveled by the rays reflected from the planes differs by a complete number of wavelengths. The sample of sludge was scanned using nickel filtered radiation in the range of I 0° <28 < 75° in the step mode.

The mean crystalline sizes of ZnO were determined from the line broading of the diffraction line for ZnO.

3.3 Gantt chart and Key Milestone

A Gant chart is constructed to represent this project and a few key milestones have been identified throughout the course of this project and these milestones signify a few critical progresses that provided a great impact on the project.
List of Key Milestone for:

FYP I

1) Preliminary research work and literature review
2) XRD analysis on previous sample
3) Detailed literature review

FYP II

1) Characterization of hydrocarbon waste
2) Experimentation continuation and analysis
3) Results and discussion summarization

		FYP I															FYP II												
No	Details	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Sem Break	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1.	Preliminary Research Work and Literature Review																													
2.	Proposal defend																													
3.	Detailed Literature Review																													
4.	Characterization of hydrocarbon waste																													
5.	Experimentation Continuation and Analysis i. Cement Based Matrix Test ii. Compressive Strength Test																													
6.	Results and Discussion Summarization																													

Legend: Key Milestone
Project Activities

Figure 3.1: Gant chart for project

CHAPTER 4

RESULT AND DISCUSSION

This chapter discusses the results gathered from cement block samples prepared and tested for its unconfined compressive strength (UCS). As explained earlier unconfined compressive strength test is used to determine whether the cement mixture is suitable to be used for construction material. As like all construction material the most important factor is of course its strength.

4.1 Mixing Calculation

The first result obtained from this research is calculation carried out to find the mixing calculation of the cement mixture. The density of the materials used was obtained from device called a pycnometer. In addition moisture content analysis was carried out on the sludge samples to calculate the amount of water present in the sludge. 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. The test to determine the total amount of solid and moisture content in hydrocarbon waste (sludge) used was carried at once and the results obtained are as below.

Table 4.1: Material and their density reading

Material	Density (Kg/m^3)
Sludge	1000
Cement	3140
Zeolite	2634.1
Metakaolin	2589.23
Activated Carbon	2100
Bentonite	2650
Fly ash	2290

Table 4.2: Result of Total Solid (TS) and Moisture Content (MC) of sludge

Trial No.	1	2	3
A	99.38	60.48	60.73
B	282.65	135.89	149.47
C	107.39	64.63	65.04
Total Solid (TS)	0.043706	0.0550325	0.0485689
Moisture Content (MC)	0.956294	0.9449675	0.9514311
Average TS	0.0492		
Average MC	0.9508		

A: mass of dish

B: mass of wet sample & dish

C: mass of dried residue & dish

Based on test carried out the total amount of solid observed to be in hydrocarbon sludge is approximately 5% of its total weight and a moisture content of approximately 95%.

Once all information is gathered for the total solid content and moisture content, 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. Steps of calculation are included in the appendices section of the report (Appendix II).

Overall, the mass of each component is tabulated as below:

Table 4.3: Real mass for mixture component for for C/Sd = 60 and C/W = 0.45 and A/C = 0.05

Component	Mass
Cement	2.836
Raw Sludge	1.013
Admixture	0.149
Water	0.313

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 admixtures to cement ratio. Once the mixing calculation is completed, the next thing to look into is the mixing procedure for the mixture.

Table 4.4: Proposed Set of Ratios for Cement + Water + Waste Sludge + Admixtures

Admixtures	Composition of Admixture (%)	Cement to Sludge Ratio (C/S d)	Water to Cement Ratio (W/C)
metakaolin	5	60	0.45
	10		
	15		
Zeolites	5	60	0.45
	10		
	15		

4.2 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 zeolite. 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. The moulds are then left to harden at room temperature (22^{o}C to 25^{o}C) with 65-75 % relative humidity for 24 hours. Cover the mould with Perspex cover to prevent

further excessive loss of water from evaporation. After 24 hours, the molded cubes removed from its caste and must be kept in the curing chamber for further dry curing.

4.3 Unconfined Compressive Strength (UCS) Test for Controlled Sample

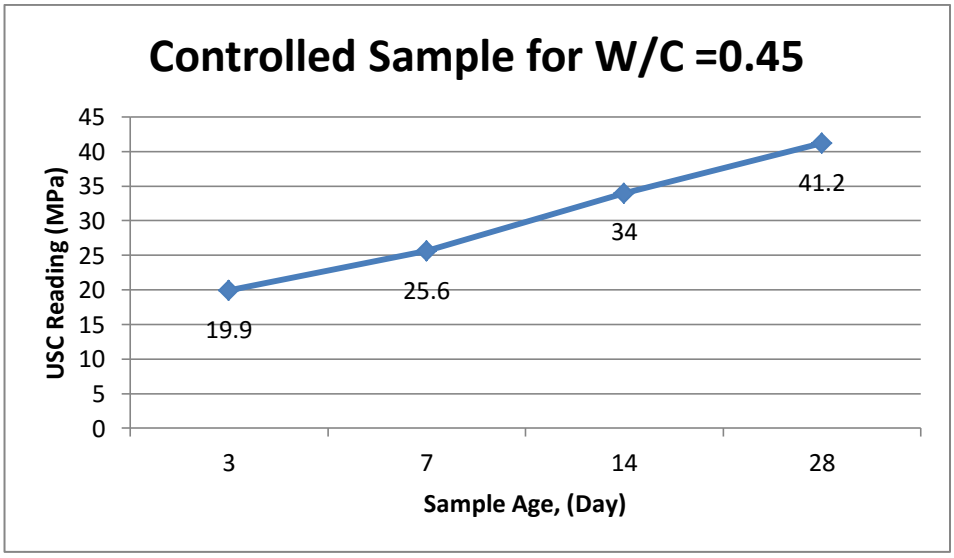

Figure 4.1: Compressive Strength of Water: Cement Ratio = 0.45

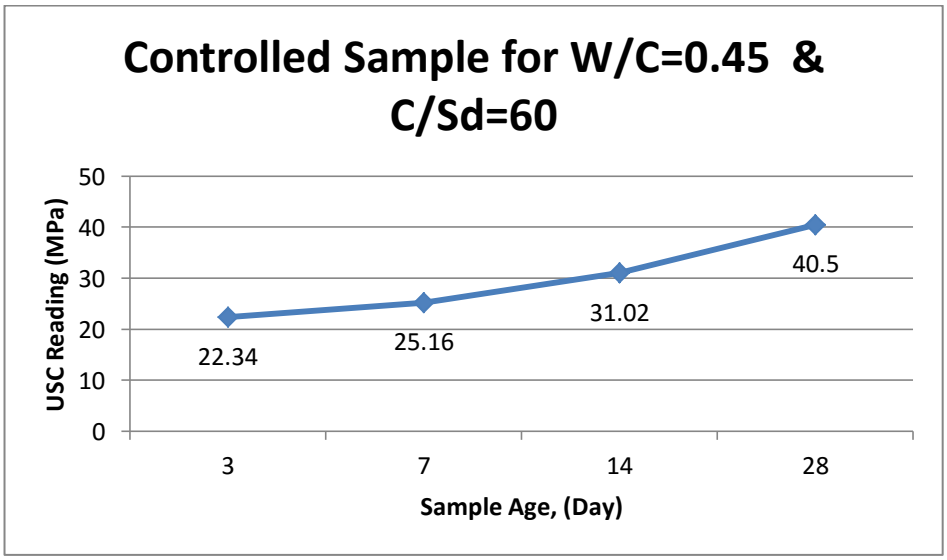

Figure 4.2: Compressive Strength of Cement: Sludge Ratio= 60 at W/C Ratio of 0.45

Minimum stress that the load needed to withstand is approximately 17.2-20.7 MPa on day 28 [27]. This is the standard compressive strength that the cement

mixture needs for construction use. Based on Figure 5 after day 7 are all the samples are cement mixture are acceptable by the S/S standard for cement. Due to the standard set by the standards, which states all values must be compared for its compressive strength on day 28 [27]. Therefore the main comparison for the cement mixture compressive strength should be based on day 28.

4.4 Unconfined Compressive Strength (UCS) Test for Cement Mixture

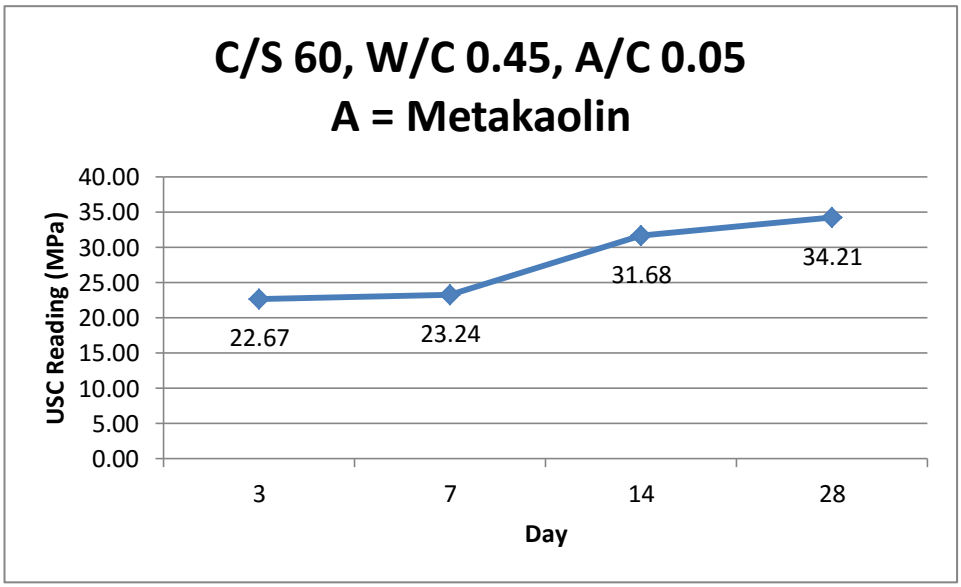

Figure 4.3: Compressive Strength of C/Sd= 60 at W/C =0.45 with 5% Metakaolin

For mixture sample of C/S 60, W/C 0.45 and B/C 0.05, the compressive strength increase respectively to the sample age.

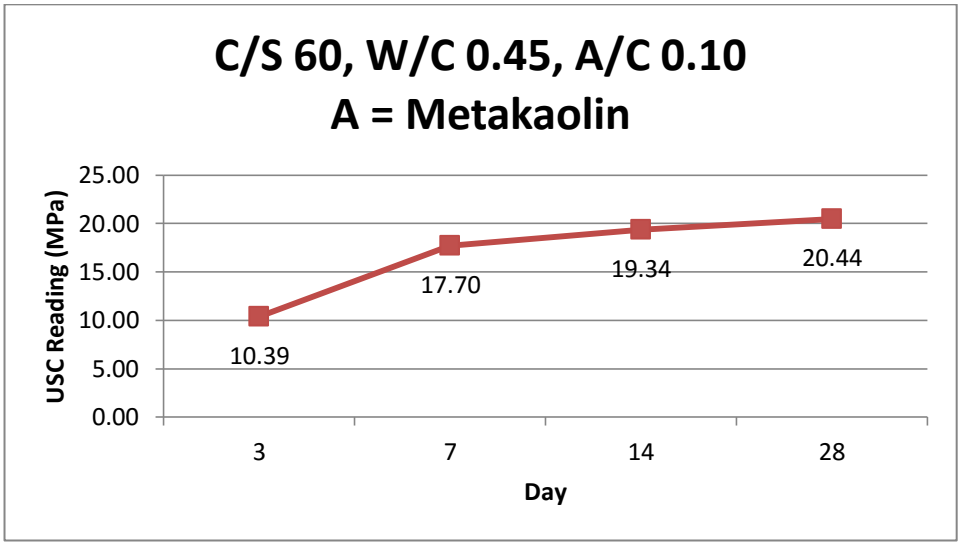

Figure 4.4: Compressive Strength of C/Sd= 60 at W/C =0.45 with 10% Metakaolin

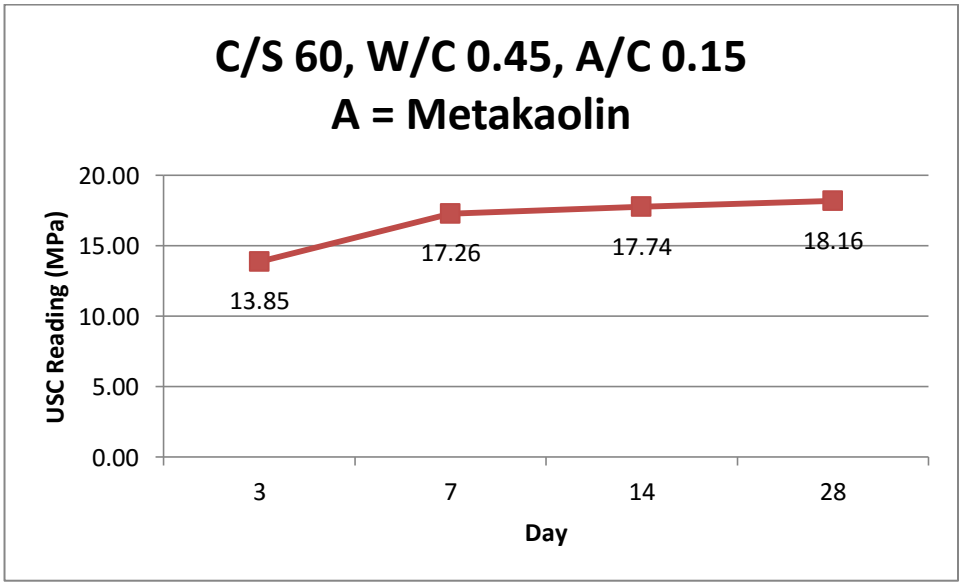

Figure 4.5: Compressive Strength of C/Sd= 60 at W/C =0.45 with 15% Metakaolin

As for all sample with Metakaolin as admixtures, all of them have an increase in compressive strength with respect to the sample aging day.

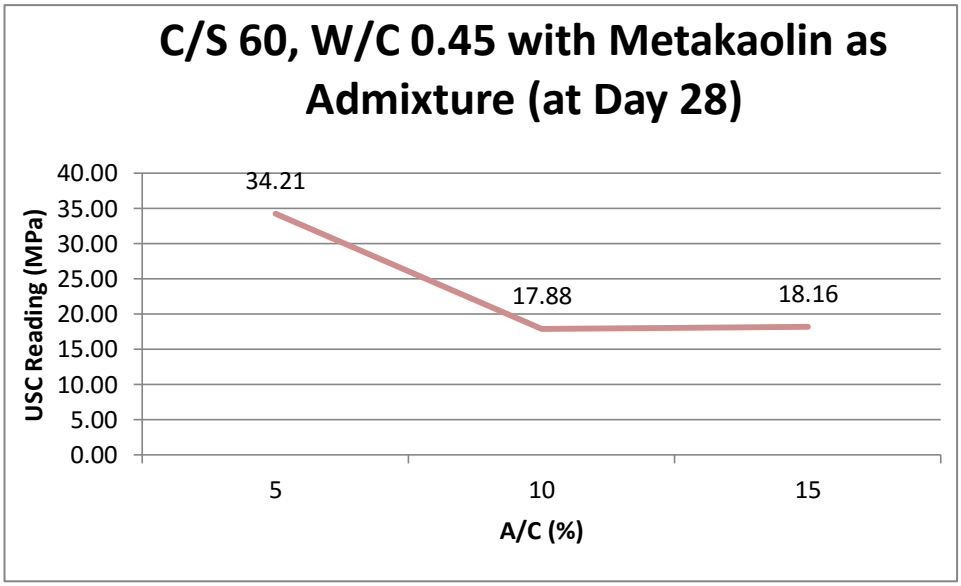

Figure 4.6: Compressive Strength of C/Sd= 60 at W/C =0.45 with various percentage of Metakaolin

However, from Figure 4.6, it can be observed that the mixture with 5% of metakaolin have the highest compressive strength of 34.21 MPa at day 28. As stated in the literature, the mixture with 15% Metakaolin has the highest strength but in other way around if compared with this result.

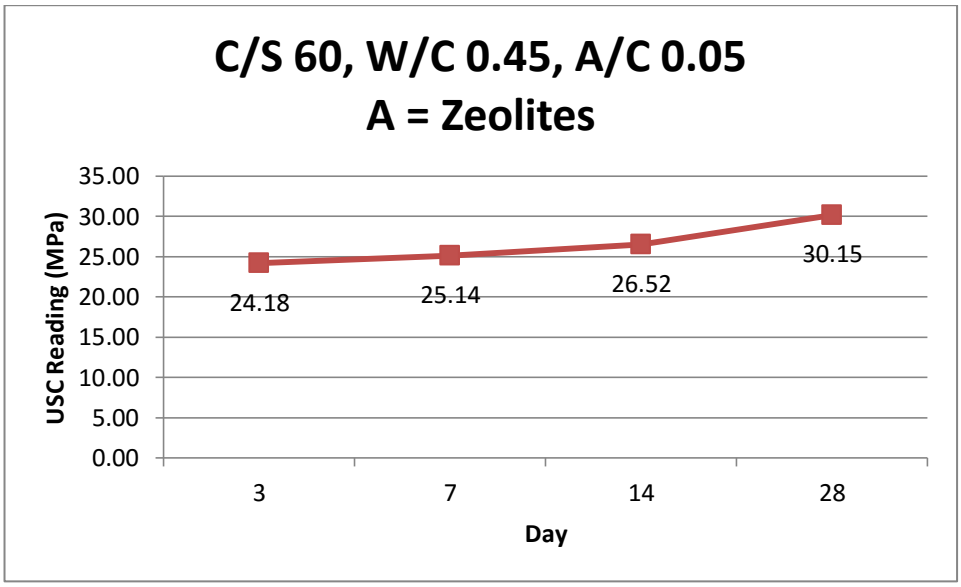

Figure 4.7: Compressive Strength of C/Sd= 60 at W/C =0.45 with 5% Zeolites

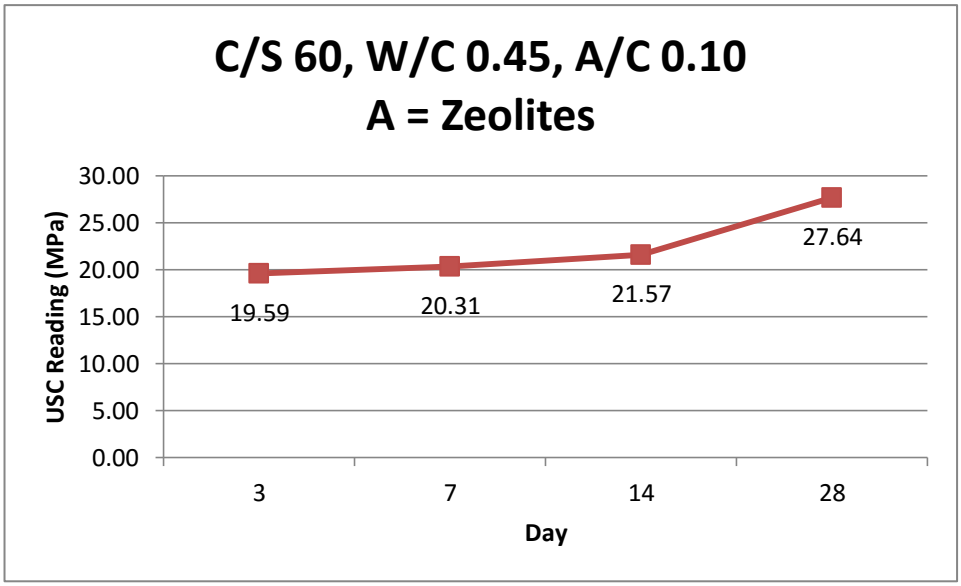

Figure 4.8: Compressive Strength of C/Sd= 60 at W/C =0.45 with 10% Zeolites

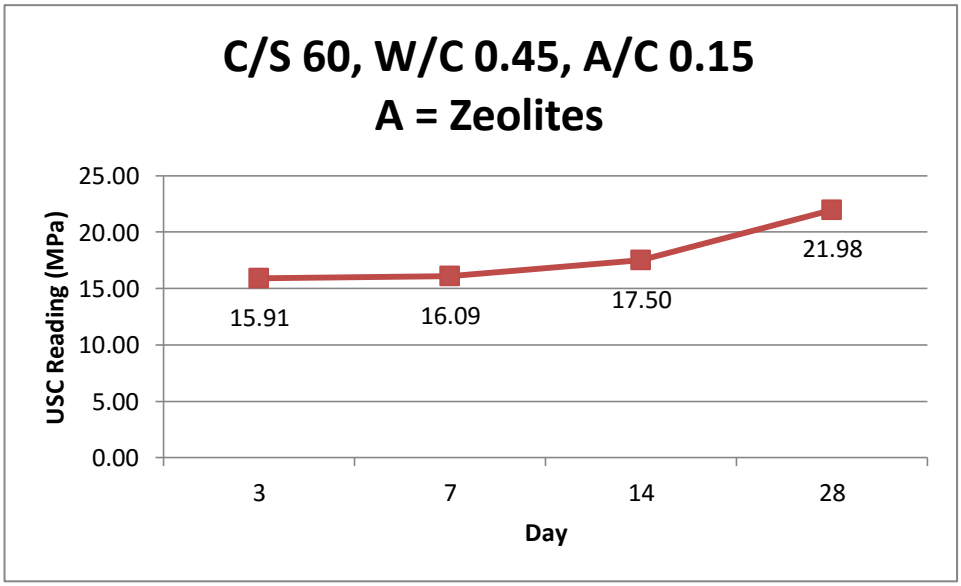

Figure 4.9: Compressive Strength of C/Sd= 60 at W/C =0.45 with 15% Zeolites

Similarly to mixture with metakaolin as admixtures, the mixtures with zeolites as admixtures also have an increase in compressive strength with respect to sample aging day. This observation represented that the sample harden over time during its curing period.

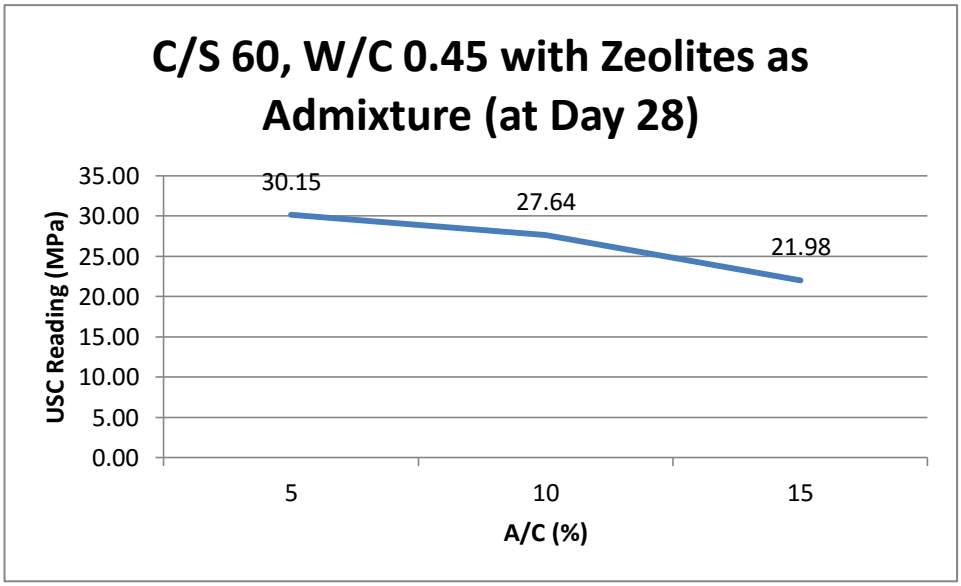

Figure 4.10: Compressive Strength of C/Sd= 60 at W/C =0.45 with various percentage of Zeolites

Based on Figure 4.10, the mixture with 5% Zeolites have the highest compressive strength compared to other mixtures.

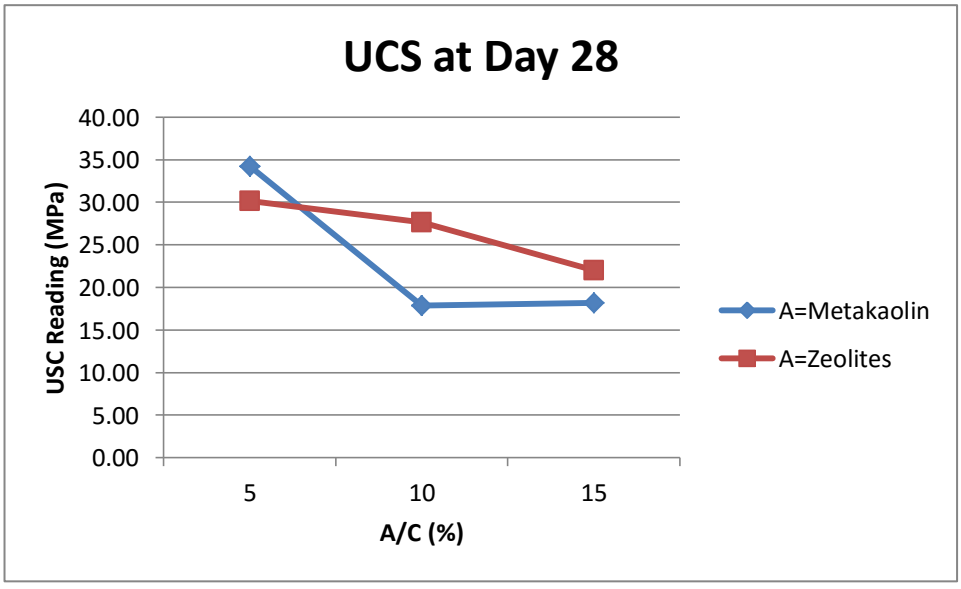

Figure 4.11: Compressive Strength for Metakaolin versus Zeolites as admixtures at Day 14

As illustrated in Figure 4.11, it is best to say that mixture of W/C 0.45, C/Sd 60 with 5% of Metakaolin is the best mixture because it has the highest compressive strength among all.

Table 4.5: Minimum Specified Compressive Strength [28]

TYPE OR LOCATION OF CONCRETE CONSTRUCTION	MINIMUM SPECIFIED COMPRESSIVE STRENGTH (f'_c at 28 days, psi)
Basement walls[c] and foundations not exposed to the weather	2,500[a]
Basement slabs and interior slabs on grade, except garage floor slabs	2,500[a]
Basement walls[c], foundation walls, exterior walls and other vertical concrete surfaces exposed to the weather	3,000[b]
Driveways, curbs, walks, patios, porches, carport slabs, steps and other flatwork exposed to the weather, and garage floor slabs	3,500[b]

For SI: 1 pound per square inch = 0.00689 MPa.
a. Concrete in these locations that can be subjected to freezing and thawing during construction shall be of air-entrained concrete in accordance with Table 1904.2.1.
b. Concrete shall be air entrained in accordance with Table 1904.2.1.
c. Structural plain concrete basement walls are exempt from the requirements for special exposure conditions of Section 1904.2.2 (see Section 1909.1.1).

Based on the Table 4.5, the acceptable range of compressive strength for building in New York is 17.24 MPa to 24.13 MPa and above. Thus, it can be said that all of the mixtures is acceptable in term of compressive strength to be used as building material.

4.5 XRD Result

The XRD analysis was carried out for two mixtures which has the highest Unconfined Compressed Strength (UCS) which is the mixture of;

1) W/C=0.45, C/Sd=60 with 5% metakaolin or simply called as Metakaolin 5%
2) W/C=0.45, C/Sd=60 with 5% zeolites or simply called as Zeolites 5%

For Sample (1), which is the metakaolin 5 % sample, the peak counts from the XRD result diagram showed that numerous of newly formed mineral exist in the matured cement matrix such as Calcite, Portlandite, Ettringite, Quintinite, Muscovite and also kaolinite.

As for Sample (2), the result from the XRD analysis showed that the Calcite, Portlandite, Quintinite, Quartz, Muscovite and Zeolite mineral are formed in the cement matrix.

The Disgram for both sample can be seen in Appendix IV. This result showed that, from original powder phase of cement and metakaolin with an addition of sludge and water, the new mineral phase if formed. The forming of this new mineral or crystal are responsible for encapsulating and fixed the carbon content in the mixture instead of releasing it to the environment.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

As a conclusion, to achieve the goal to find best S/S admixture, the experimental procedure should be carried out first. As the outcome, it is found that mixture of W/C 0.45, C/Sd 60 with 5% of Metakaolin is the best mixture. With the present of the RDX test result, it can be deduced that the carbon and other hazardous substances in the sludge has been encapsulates and fixed by Solidification and stabilisation process. Other than that, by proving that the carbon dioxide emission can be prevented by using the stabilisation and solidification (S/S) technology, the industry will have more reason to employ this S/S technology as their routine method to treat the sludge waste.

5.1 Future Work

The result obtained in this project can be related to the size factor of the admixtures during the cement mixing. So, it will be sufficient if the size of admixtures such as kaolin and zeolites can be measured first as it will affect the porosity of the cement and hence also affected their strength. However, more improvement of project work can be done in the future such as by using new type of admixtures and by running more useful test on the sample mixture such as porosity test, leaching test and so on.

5.2 Recommendation

As a recommendation, the author suggested that if the S/S technology is found to be effective, an extensive research on how to make it applicable to the real industry should be done. This extensive research should be done in a big scale to

monitor the real effectiveness when the technology is used on high quantity of waste sludge. Other than that, energy contained by the sludge waste should be used properly after the calorific value of sludge waste has been identified. It will prove how much we are losing energy in the form of sludge by sending them through non-environmental friendly process such as incineration process. Furthermore carrying out a larger sample size for testing will give a clearer data collection of the S/S technology. Other than that all tests must be carried out based on standards already available to us. Accurate and precise measuring equipment's will give better results. It is also important to calibrate all instrumentation as this will also affect data. To sum up, 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.

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APPENDICES

APPENDIX I: SAMPLE MIX DESIGN CALCULATION

Sludge moisture content = 95.09 %

Specific gravity = 1.000

Type of sludge: Petroleum Refinery Sludge

No. of sample: a) UCS Sample – 6 moulds

b) TCLP Sample – 1 mould (2 x 500 ml)

Total initial volume: a) UCS Sample

$$6 \text{ moulds} \times 3 \text{ cubes} \times (1.25 \times 10^{-4}) \text{ m}^3$$

$$= 2.25 \times 10^{-3} \text{ m}^3$$

b) TCLP Sample

$$1 \text{ moulds} \times 1 \text{ L}$$

$$= 1 \times 10^{-3} \text{ m}$$

$$\text{Total volume, } V_T = (2.25 \times 10^{-3} + 1 \times 10^{-3}) \text{ m}^3$$

$$= 0.00325 \text{ m}^3$$

Calculation for Cement to Sludge Ratio (C/S d) = 60

Assume;

Cement Dry Mass = 60 kg

Sludge Dry Mass = 1 kg

Raw Sludge Mass = 1 kg / Total Solid

= 1 kg / 0.049102

= 20.3658 kg

In the presence of cement replacement material such as zeolite or other admixtures, the mass of cement reduced according to the percentage of admixture added.

For example:

Percentage of Admixture Zeolite: 15 %

Mass of Zeolite based on cement mass = 60 kg x 0.15

= 9 kg

Remaining Amount of Cement in Mixture = 60 kg – 9 kg

= 51 kg

Based on the mass calculated for cement, zeolite 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 Zeolite = 9 kg / 2634.10 kg/m^3

= 0.003417 m^3

Volume of Raw Sludge = 20.3658 kg / 1000 kg/m^3

= 0.02037 m^3

Volume of water needed = 0.45 × 51 kg / 1000 kg/m^3

= 0.02295 m^3

Total Volume of Mixture = 0.01083 m^3 + 0.00228 m^3 + 0.02037 m^3 + 0.0153

=0.06297 m^3

Ratio of Calculated Volume/ Ratio of Required Volume

= 0.06297 m^3 / 0.00325 m^3

= 19.39

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

Mass of Cement Required = 51 kg / 19.39= 2.630 kg

Mass of Zeolite Required = 9 kg / 19.39= 0.464 kg

Mass of Raw Sludge Required = 20.3658 kg / 19.39= 1.050kg

Mass of water needed = 0.45 × 51 /19.39 = 1.1836 kg

Amount of water in sludge = 1.050 kg x Moisture Content

= 1.050 kg x 0.950898

= 0.9984 kg of water in sludge

Amount of water added = 1.1836 kg - 0.9984 kg

= 0.185 kg

APPENDIX II: MIXING CALCULATION

Table 1: Mixing calculation for Metakaolin as a binder

Ratio	Ratio	Ratio	Kg	Kg	m3	Kg	kg	m3	kg	m3	kg	m3	m3	Ratio
C/Sd	W/C	A/C	S Raw	S dry	S Volume	C	C used	C volume	B used	B volume	W needed	W volume	Total	Needed
60	0.45	0.05	20.36	1	0.0203	60	57	0.0181	3	0.0011	25.65	0.025	0.065	20.10
60	0.45	0.10	20.36	1	0.0203	60	54	0.0171	6	0.0023	24.3	0.024	0.064	19.74
60	0.45	0.15	20.36	1	0.0203	60	51	0.0162	9	0.0034	22.95	0.022	0.063	19.39

Ratio	Ratio	Ratio	kg	kg	kg	kg	kg	kg
C/Sd	W/C	A/B	S real	C real	B real	W real	W in sludge	W Additional
60	0.45	0.05	1.013	2.836	0.149	1.276	0.963	0.313
60	0.45	0.10	1.031	2.734	0.304	1.231	0.981	0.250
60	0.45	0.15	1.050	2.630	0.464	1.183	0.998	0.185

Table 2: Mixing calculation for Zeolite as a binder

Ratio	Ratio	Ratio	Kg	Kg	m3	Kg	kg	m3	kg	m3	kg	m3	m3	Ratio
C/Sd	W/C	A/C	S Raw	S dry	S Volume	C	C used	C volume	B used	B volume	W needed	W volume	Total	Needed
60	0.45	0.05	20.37	1	0.0204	60	57	0.0182	3	0.0011	25.65	0.0257	0.0653	20.09
60	0.45	0.10	20.37	1	0.0204	60	54	0.0172	6	0.0023	24.30	0.0243	0.0641	19.74
60	0.45	0.15	20.37	1	0.0204	60	51	0.0162	9	0.0034	22.95	0.0230	0.0630	19.38

Ratio	Ratio	Ratio	kg	kg	kg	kg	kg	kg
C/Sd	W/C	A/B	S real	C real	B real	W real	Water	W Additional
60	0.45	0.05	1.013	2.837	0.149	1.276	0.964	0.313
60	0.45	0.10	1.032	2.736	0.304	1.231	0.981	0.250
60	0.45	0.15	1.051	2.632	0.464	1.184	0.999	0.185

APPENDIX III: UNCONFINED COMPRESSIVE STRENGTH (UCS) TEST RESULT

Table 1: UCS reading at different ratio for metakaolin

Ratio	Ratio	Ratio	UCS reading (Mpa)															
			Day 3				Day 7				Day 14				Day 28			
C/Sd	W/C	B/C	1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
60	0.45	0.05	23.63	24.29	20.10	22.67	22.43	22.74	24.54	23.24	28.64	32.85	33.55	31.68	29.68	33.76	39.20	34.21
60	0.45	0.1	10.47	10.30	10.40	10.39	18.98	17.81	16.31	17.70	19.41	18.99	19.62	19.34	18.23	22.76	20.33	20.44
60	0.45	0.15	12.95	14.69	13.90	13.85	19.11	15.41	17.26	17.26	18.40	15.63	19.19	17.74	14.36	26.44	13.68	18.16

Table 2: UCS reading at different ratio for zeolite

Ratio	Ratio	Ratio	UCS reading (Mpa)															
			Day 3				Day 7				Day 14				Day 28			
C/Sd	W/C	B/C	1	2	3	Average	1	2	3	Average	1	2	3	Average	1	2	3	Average
60	0.45	0.05	25.15	27.56	19.83	24.18	27.02	22.81	25.60	25.14	26.75	27.21	25.60	26.52	30.96	27.80	31.68	30.15
60	0.45	0.1	17.94	21.39	19.43	19.59	14.58	21.96	24.40	20.31	20.68	22.53	21.51	21.57	24.24	32.41	26.28	27.64
60	0.45	0.15	17.20	12.11	18.42	15.91	15.91	16.88	15.49	16.09	16.30	17.58	18.62	17.50	20.46	22.45	23.03	21.98

APPENDIX IV: XRD ANALYSIS RESULT

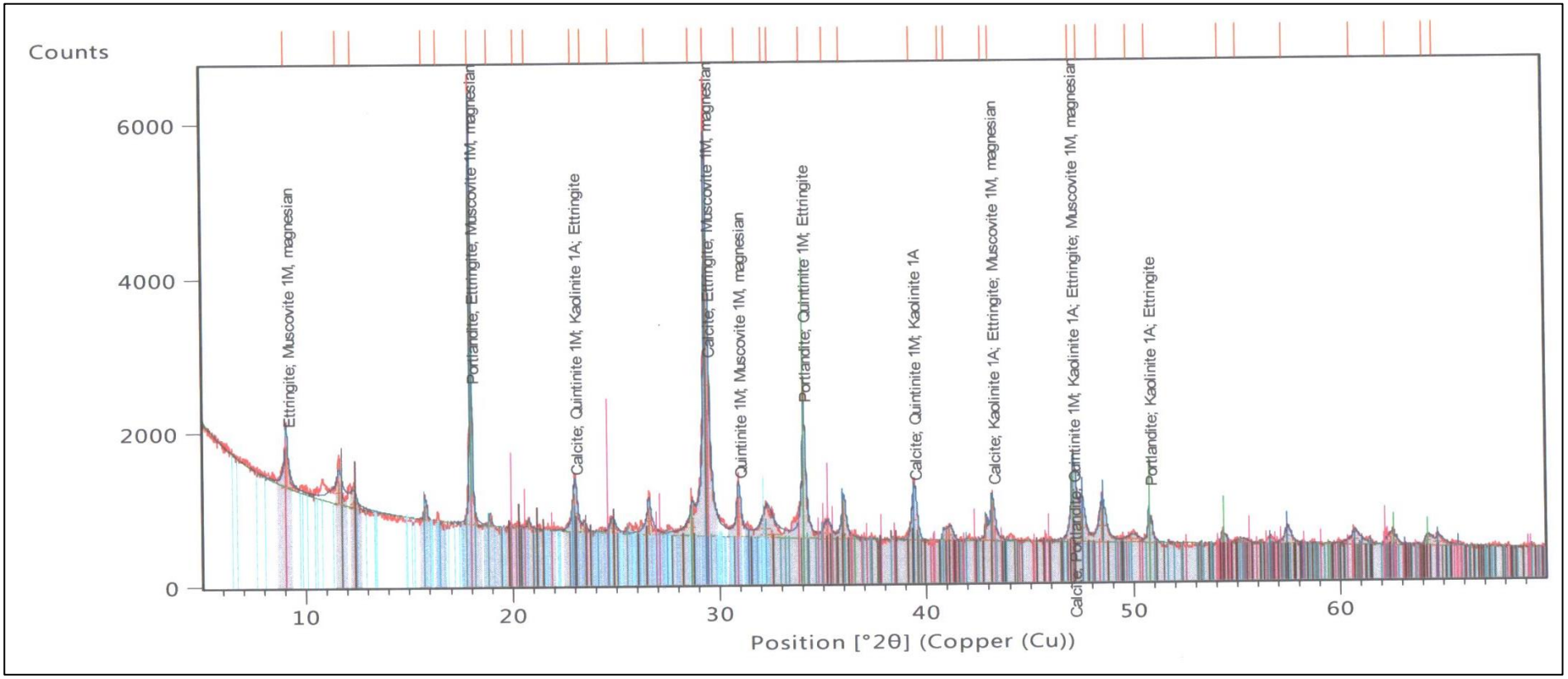

Figure 1: XRD pattern for Metakaolin 5%

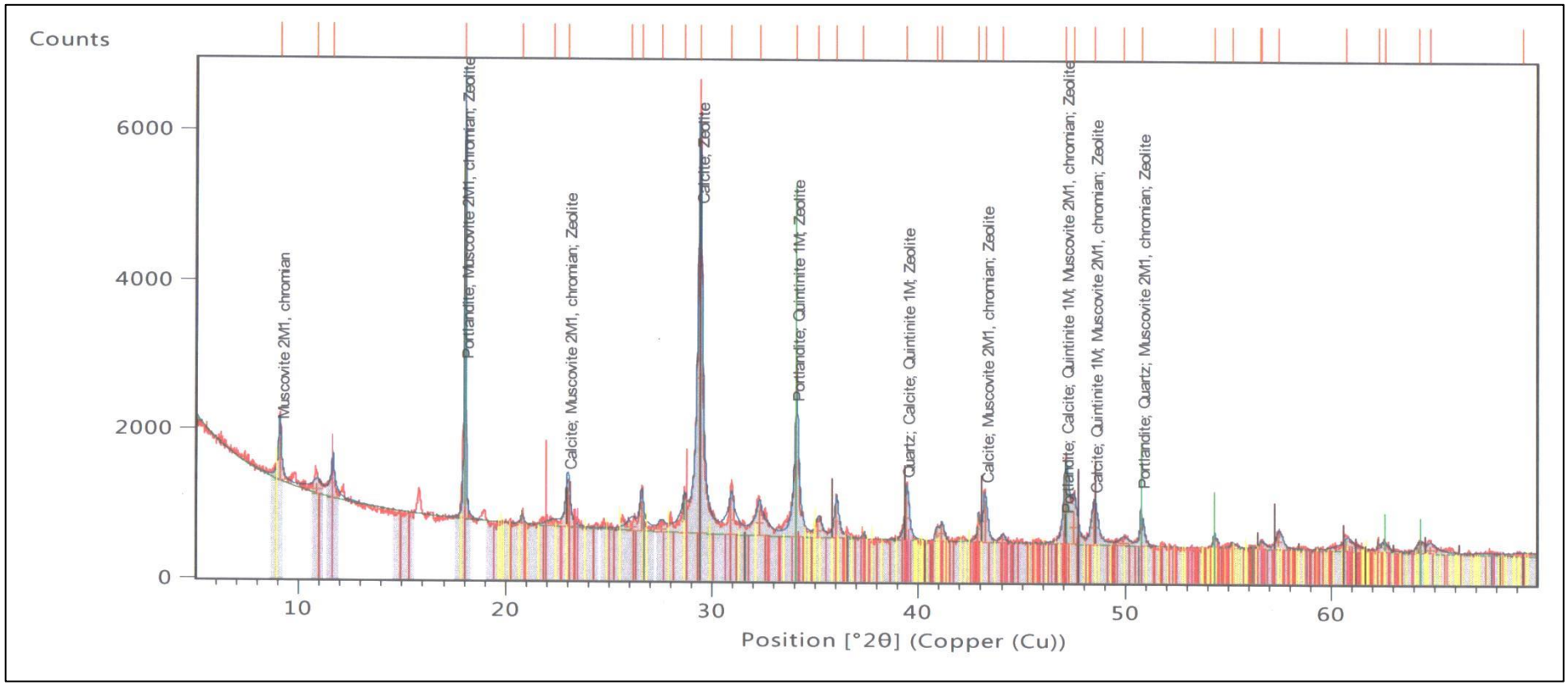

Figure 2: XRD pattern for Zeolites 5%