**SOLIDIFICATION OF WASTE ACTIVATED SLUDGE FROM PETROLEUM REFINERY**

by

Fakrur Radzi bin Mohd Omar

Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Civil Engineering)

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# CERTIFICATION OF APPROVAL

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Civil Engineering Programme
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Approved:

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January 2008

## 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.

Fakrur Radzi bin Mohd Omar

# ABSTRACT

This Final Year Project is a study of Solidification/Stabilization of activated waste sludge from Petronas Penapisan Melaka Sdn. Bhd, PPMSB. Three cementitious materials were used to investigate solidifying and stabilizing the hazardous wastes containing heavy metals. The cementitious materials were Pulverized Fuel Ash (PFA), Ground Granulated Blast Slag (GGBS) and Lime. These materials will be the cement replacement of Ordinary Portland Cement (OPC). The project focused on the strength development and leaching rate of zinc and lead ion of the product. The strength was tested using Unconfined Compressive Stress (UCS) and leaching by Toxicity Characteristic Leaching Procedure (TCLP) and Atomic Adsorption Spectrometer (AAS). Usage of PFA and Lime gives significant value for strength development and leaching rate than GGBS. The concrete strength is up to 30 Mpa and percentage of immobilizing the zinc ion up to 94% and lead ion to 100%. Performance between PFA and Lime is about the same in terms of strength and leaching rate. Improvement shall be made in finding the most effective ratio of each binder. Combination of binders also shall be done to produce effective combination of S/S process for PPMSB sludge.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| S/S | Solidification/Stabilization |
| AAS | Atomic Absorption Spectrophotometer. |
| UCS | Unconfined Compressive Strength |
| PPMSB | Petronas Penapisan Melaka Sdn. Bhd |
| TCLP | Toxicity Characteristic Leaching Procedure. |
| XRD | X-Ray Diffraction |
| OPC | Ordinary Portland Cement |
| PFA | Pulverized Fuel Ash /Fly Ash |
| GGBS | Ground Granulated Blast Slag |
| Zn | Zinc |

# CHAPTER 1
# INTRODUCTION

## 1.1 Background of Study

Petronas Penapisan Melaka Sdn.Bhd, PPMSB is a petroleum refinery company wholly owned by Petronas. The refinery wastewater goes through aerobic biological treatment (activated sludge process) and consequently produces a huge amount of sludge daily. The sludge contains heavy metals (copper, lead, cadmium, arsenic, zinc) which have bad effect on human and the environment. The sludge is presently sent to Kualiti Alam for treatment and disposed in secured landfill. Solidification and stabilization (S/S) techniques are used to prevent or minimize the release of hazardous compounds from waste sludge into the environment by producing a solid mixture, improving handling characteristics, decreasing surface area for contaminant transport, reducing mobility of the contaminant transport and bonding the contaminate into a non-toxic form (Tuncan, 2000). They can be defined as mixing the sludge with solid additive materials like fly ash, cement, lime, cement kiln dust, sulfur or combination of them (Wright, 1991). It is recommended to use fly ash-cement mixtures for solidification of oil and gas sludge, because of their cohesive and adhesive characteristics (Morgan, 1984).

## 1.2 Problem Statement

Disposal of wastes containing heavy metals has become a major issue in protecting public health and the environment nowadays. With the increased petroleum production, the amount of the wastes/refinery sludge has also increased and the use of landfill area has also increase. Land filling hazardous wastes is widely practiced, but there are certain limitation such the heavy metals may leached to the environment.

Thus, a treatment shall be done before the wastes are disposed and the method used in this project is solidification and stabilization.

A major concern is the characterization and optimum parameters of the mixtures components and the mixing process itself, with an aim of utilizing the resultant environmental-friendly product as construction materials such as aggregates. For that, leaching factor becomes a major consideration as the metals may leach into the environment. Leaching can occur when the wastes is exposed to stagnant water, heavy rain or solvent. This will mobilize the heavy metals and spread into the soil and ground water table.

This study will be focused on Zinc ion immobilization and strength development in the PPMSB sludge using the solidification process. Kualiti Alam has set up the leaching limit of landfill for Zinc ion as 100mg/l. All hazardous wastes disposed to landfill shall satisfy the limit.

## 1.3 Objectives

Objectives of this project are to find the best binder that can immobilize the heavy metal (zinc ion) in the sludge efficiently using solidification method. The optimum mix ratio will also be determined. This project focuses on the formulation of Ordinary Portland Cement (OPC) with Pulverized Fuel Ash (PFA), Ground Granulated Blast Slag (GGBS) and Lime in solidifying the sludge. It shall satisfy both compressive strength and leaching requirements for landfill disposal.

## 1.4 Scope of Study

The scope of the study in this project includes sludge characterization and binder selection. The sludge will be solidified into concrete form and the strength development will be recorded. Then the sample will be tested for leaching behavior using Toxicity Characteristic Leaching Procedure (TCLP) and Atomic Adsorption Spectrometer (AAS) test for zinc ion.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Cement Based Stabilization

Cement-based stabilization is best suited for inorganic wastes, especially those containing heavy metals. As a result of the high pH of cement, the metals are retained in a form of insoluble hydroxide or carbonate salts within the hardened structure. Portland cement is the most widely used of all Stabilization/Solidification (S/S) binding reagents today. Portland cement is not only used alone, but also used in many other formulations combined with fly ash, lime, soluble silicates, clays and other materials. It is a type of hydraulic cement which upon addition of water produces a hardened paste. This paste will bind together aggregates and other substances to form concrete and stabilized waste. When cement and water are mixed together, a series of chemical reactions begins that result in stiffening, hardening, and evolution of heat and finally development of long term strength. The overall process is called hydration, since water-containing compounds are formed. In the presence of calcium hydroxide and alkalis in solution gives the plastic cement high pH, an important aspect of cement-based S/S.

For stabilization/solidification of petroleum refinery sludge, (Anderson, 1994) recommends to use cementitious material (cement, lime, fly ash, etc) as shown in Table 2.1. It involves the addition of cementitious materials, which limits the solubility or mobility of the waste constituents.

**Table 2.1: Potential Application of Stabilization/Solidification Processes**

| Stabilization/Solidification process | Kind of waste |
|---|---|
| Sorbents and surfactants | Oily wastes, industrial sludges, contaminated soils with inorganics and low levels of organics. |
| Emulsified asphalt | Petroleum-contaminated soils, waste from paint removal, metal plating wastes. |
| Bituminization | Low –level radioactive waste solutions, metal plating sludges. |
| Modified sulfur cement | Predried particulate wastes, contaminated soils, sludges, metals. |
| Cementitious materials | Contaminated soils, low-level radioactive wastes, sludges, oily wastes, tars, **petroleum refinery sludges**, metal containing wastes. |

The advantages of using cementitious material for S/S are:

i. Relatively low cost
ii. Good long term stability, physically and chemically
iii. Good impact and compressive strength
iv. Nontoxicity of the chemical ingredient
v. High waste loading possible
vi. High resistance to biodegration
vii. Low water solubility and leachability of some contaminants'
viii. Good mechanical and structural characteristic

Hence, in this project, the cementitious material will be used in S/S project.

## 2.2 Inorganic Cementitious Processes

### 2.2.1 Portland Cement

Cementitious stabilization is applicable to a wide range of industrial wastes and results in a very stable product. S/S techniques that utilize Portland cement, fly ash, cement kiln dust, quick lime and slag in various combinations have been used for a number of years all over the world. Setting and curing reaction vary among processes.

Most of the commercial cementitious S/S systems however solidify in highly similar systems.

Portland cement is the most widely used of all S/S binding reagents today. It is not only used alone, but also used in many formulation combined with fly ash, lime, soluble silicates, clays and other materials.

Portland cement is a type of hydraulic cement. It acts as a strong "glue" to bind together aggregates and other substances to form concrete, grouts, mortars and stabilized wastes. Table 2.2 shows the properties associated with five primary cement compounds.

**Table 2.2 : Properties of Major Cement Compound**

| Cement compounds | Properties |
|---|---|
| Tricalcium silicate | Hydrates and hardens rapidly<br>Responsible for initial set and early strength |
| Dicalcium silicate | Hydrates and hardens slowly<br>Contribute largely to strength increase at age beyond 1 week |
| Tricalcium aluminate | Liberates a large amount of heat during the first few days of hydration and hardening.<br>Contributes to early strength development. |
| Tetracalcium aluminoferrite | Reduce the clinkering temperature |
| Calcium sulfate | Known as gypsum, slows down the hydration rate.<br>Without gypsum, cement would set rapidly. |

### 2.2.2 Pulverized Fuel Ash (PFA) or Fly Ash

Fly Ash is a by-product of the combustion of pulverized coal in power plants. It is widely used to partially replace Portland cement in concrete to reduce materials cost and to improve some properties of the concrete. In this project, the PFA is obtained from Tenaga Nasional Berhad (TNB) Jana Manjung Power Plant at Manjung, Perak. The introduction of PFA will decrease the calcium/silicate, C/S ratio of calcium silicate hydrate, C-S-H and increase the retention of cationic contaminants in C-S-H. PFA react with lime much more slowly than the hydration of Portland cement. The presence of PFA decreases or eliminates the free lime content in hardened cement paste. The Pozzolonic reaction between PFA and Lime refine the pore structure of hardened paste and reduce the permeability of hardened paste.

Many of the laboratory research projects have used Portland fly ash to S/S hazardous, radioactive and mixed waste. It has also been used to solidify a heavy metal sludge containing cadmium, chromium, mercury and nickel. However some publications also report the use of PFA is not helpful during S/S of waste material. According to Akhter et al.(1990), concluded that PFA, used together with Lime, GGBS, or Portland cement, does not serve to improve performance when used as an additive.

### 2.2.3 Ground Granulated Blast Slag (GGBS)

Ground Granulated Blast Slag, (GGBS) is a by product from iron production. It has been widely used as a Portland cement replacement due to its low cost and beneficial effect on some properties of the corresponding concrete. GGBS may be used to replace cement up to 90% but generally replacement level of 40 to 50% is used. The benefits of using GGBS for S/S of wastes are:

i. It decreases the pH value of the initial pore solution to ~11, which increases the precipitation of some heavy metals.
ii. It lowers the oxidation-reduction potential, which reduces the solubility of most radionuclides and the corrosion of steel containers.
iii. It precipitates some metals as sulfides, which are even more insoluble than the corresponding hydroxides.
iv. It reduces the permeability of the waste form.

### 2.2.4 Lime

There are 2 types of lime, quick lime and hydrated lime. Quicklime is the product of calcinations of limestone consists of the oxides of calcium ad magnesium. Hydrated lime is a dry powder obtained by treating quicklime with sufficient water to satisfy its chemical affinity for water thereby converting the oxides to hydroxides. It has a slow setting time and lower early strength compared to Portland cement but the hydration of the lime-pozzolan cements are the same as those described for Portland cement. Lime has been successfully used for treatment and delisting of several hazardous wastes. Debroy and Dara (1994) evaluated the immobilization of zinc and lead present in waste sludge by encapsulation using lime-pozzolan admixtures. It was shown that encapsulation using lime can immobilize lead and zinc ions efficiently. Lime is often used to treat contaminated soils alone. It provides an alkali environment for precipitation of heavy metals. The strength development is gradual but continuous for long periods as the pozzolanic reactions are very slow. An increase in temperature accelerates the pozzolanic reaction between lime and soil and the strength development, significantly. According to Dermatas (1996), laboratory results have confirmed that heavy metals, such as Lead and Chromium were included and immobilized by the soil-lime pozzolanic reaction products.

Generally, successful solidification and stabilization (S/S) of metals may involve the following:

a) Control of excess acidity by neutralization
b) Destruction of metal complexes if necessary
c) Control oxidation state as needed
d) Conversion to insoluble species (stabilization)
e) Formation of a solid with solidification reagents

### 2.3 Application of Solidification/Stabilization (S/S)

In Malaysia, Kualiti Alam, is a company that is responsible for handling the hazardous waste. They also apply S/S to treat wastes. In the Solidification Plant, inorganic wastes, which do not fulfill the criteria to be disposed directly into the secure landfill, will be treated. Such wastes are typically metal hydroxide sludge containing heavy metals like lead, arsenic, nickel, zinc and chromium.

During the solidification process the heavy metals become insoluble and the wastes therefore can safely be disposed off in the secure landfill. Fly ash from the Incinerator Plant and sludge from the PCT Plant are also treated at their Solidification Plant.

At their Solidification Plant, waste is loaded into waste bunkers, where it is mixed with other similar waste. It is then loaded into the waste hopper before being transferred to the mixer by screw conveyors. In the mixer, waste is carefully mixed with consumables such as cement, lime and water. The system is able to handle waste that contains foreign materials such as stones, wood and scrap iron. A typical solidification recipe is as follows in Table 2.3( http ://www.kualitialam.com/treatment_solidification.htm )

Table 2.3 : Composition of Concrete Mix applied by Kualiti Alam S/S plant.

| Waste | Fly Ash | Cement | Lime | Sand | Water |
|---|---|---|---|---|---|
| 100 | 20 | 35 | 7 | 100 | 30 |

After treatment, the waste will appear as a concrete mixture. The mixture is disposed in the secure landfill for the final curing over a few days. The objective of the whole process is to fix all the heavy metals in the inorganic solid waste into a concrete/silica matrix for long-term disposal in the secure landfill. As a result, hazardous heavy metals will not leach out to the environment. Table 2.4 shows the type of hazardous wastes treated by Kualiti Alam using S/S methods and Figure 2.1 shows summary of S/S process made by Kualiti Alam.

Table 2.4 : Type of hazardous wastes undergoes S/S process in Kualiti Alam.

| | |
|---|---|
| N016 | Sludge from oil storage tank( low content of oil and grease) |
| N151 | Metal hydroxide sludge from wastewater treatment system |
| N203 | Residues from recovery of acid pickling liquor |
| N204 | Oxide or sulphate from wastewater treatment system |

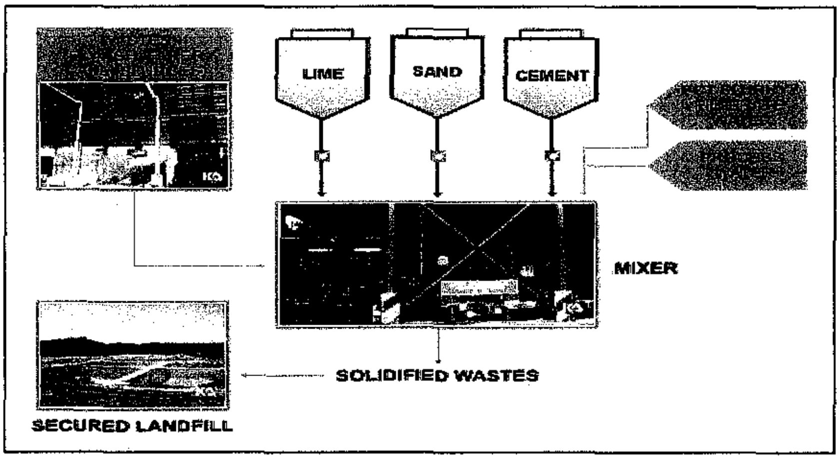


Figure 2.1 : Solidification/Stabilization process at Kualiti Alam

# CHAPTER 3
# METHODOLOGY

The overall methodology for this project is divided into four major parts, which are:

1) Preparation of the sludge waste prior to the characterization for heavy metal in the sludge.
2) Initial identification or characterization of petroleum refinery sludge and method of solidification.
3) Solidification of the sludge by using different matrixes of formulation solidification methods.
4) Testing the solidified sludge for strength and metal leaching.

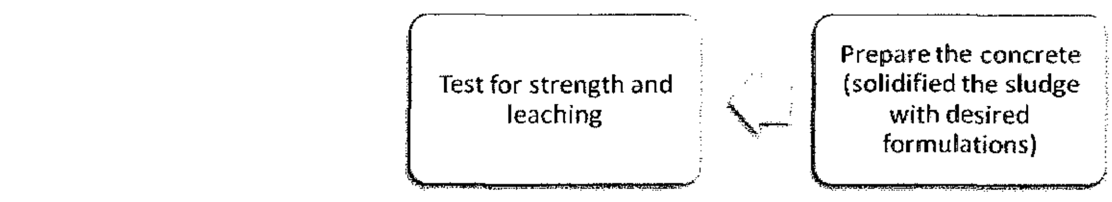


Figure 3.1: Methodology of the project

The brief description for each of the testing method such as XRD, TCLP, AAS and UCS are as discuss below:

## 3.1 Sludge Preparation

Zinc ion in the sludge will be determined by XRD. The sludge is dried in an oven at 105°C for two days. It is to deplete the organic content and also to reduce the moisture to an acceptable level. Then, it has been blended to gain smaller particle, greater surface area of the sludge. Lastly, TCLP and AAS test has been run to check the early metal concentration, zinc and lead in the sludge before S/S process.

## 3.2 Selection of Binder

Binders that will be used in this project are OPC, PFA, GGBS and Lime. The matrix formulations will be combinations between 2 binders and the sludge. Sludge will be acting as an additive to the concrete composition. Sludge content will be 15% from cement used in every mix ratio.

## 3.3 Solidification method

In this project, the concrete has been design as Grade 40 which will achieved at least 40Mpa at 28 days of curing. The design table is attached in Appendix. Three binders (PFA, GGBS, Lime) are used as cement additives and solidified with the sludge. Sludge ratio will be constant at 15% of cement content. It is to compare the efficiency of the formulation to gain highest strength and lowest leaching rate. The ratio for each sample shows in Table 3.1.

Table 3.1: Composition of Binder and Sludge

| Binder | Ratio |
|---|---|
| **OPC: PFA: Sludge** | 80:20:15<br>85:15:15<br>90:10:15 |
| **OPC: GGBS: Sludge** | 60:40:15<br>65:35:15<br>70:30:15 |
| **OPC: Lime : Sludge** | 80:20:15<br>85:15:15<br>90:10:15 |

## 3.4 Testing Procedure

### 3.4.1 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 $10^{0} < 2\Theta < 75^{0}$ in the step mode. The mean crystalline sizes of ZnO were determined from the line broading of the diffraction line for ZnO.

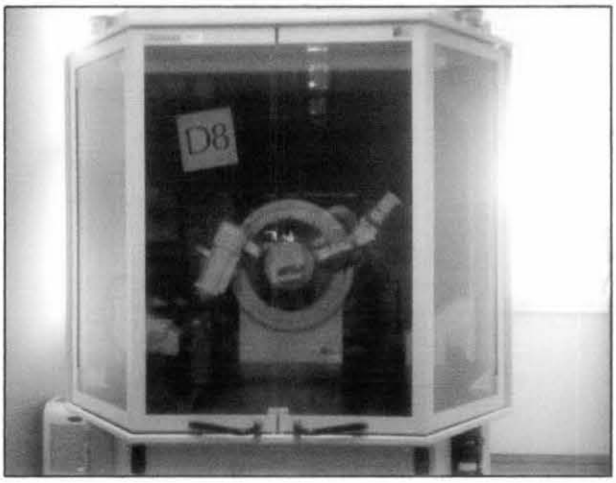


Figure 3.2 : XRD Machine

### 3.4.2 Toxicity Characteristic Leaching Procedure, (TCLP)

In TCLP test, samples was crushed into fine particle and extracted with a lechant (Acetic acid) at pH 3. The acetic acid is added only once at the start of the extraction. A liquid to solid ratio of 20: 1 was used for an extraction period of 18 hours. The leachate was then filtered prior to conducting the contamination analysis. The filtrate is acidified using concentrated Nitric and Hydrochloric acid and analyzes for zinc concentration using Atomic Adsorption Spectrophotometer (AAS).

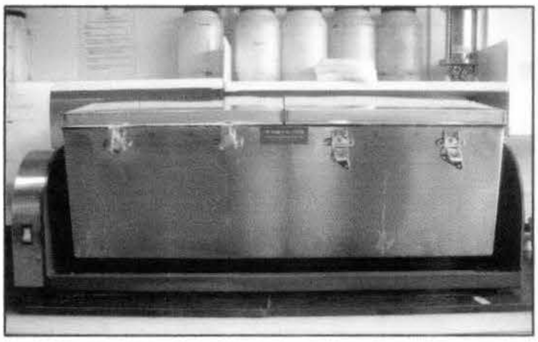

Figure 3.3: TCLP Machine

### 3.4.3 Atomic Absorption Spectrophotometer, (AAS)

AAS has been a standard tool employed by the analysts for the determination of the trace level of metals. In this technique, a fine spray of the analyst is passed into a suitable flame, frequently as acetylene oxide which converts the element to an atomic vapor is passed through radiation at the right wavelength to excite the ground state atom to the first excited electronic level. The amount of radiation absorbed can be measured and directly related to the atom concentration, a hollow cathode.

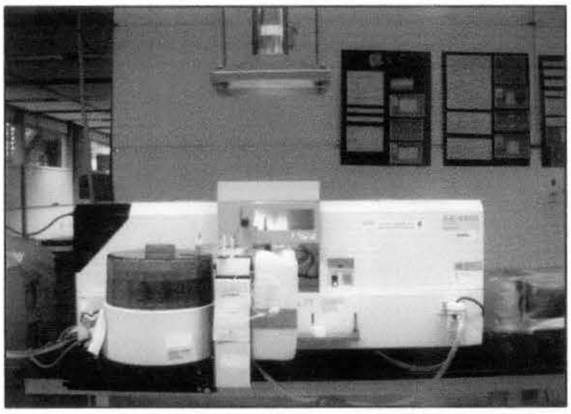

Figure 3.4: AAS Machine

### 3.4.4 Unconfined Compressive Strength (UCS)

Comparative performance of hardened concrete is investigated by measuring the development of compressive strength with curing age of 7, 28 and 56 days. Three samples will be tested for each test. Average value will be taken to ensure data precision. The compressive strength was taken as the maximum compressive load it could carry per unit area.

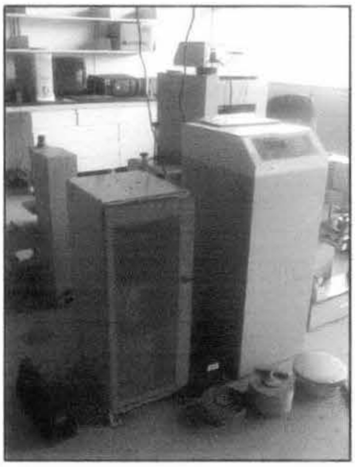

Figure 3.5: Compression Machine (ADR 1500)

## 3.5 Concrete Mixing Procedure

Mixing and sampling the fresh concrete is recommended by BS 1881 : Part 125 : 1986 . Fresh concrete will then poured into cube mould (100 x 100 x 100)mm. The purpose is to cure the concrete and perform several tests on the concrete. After pouring the fresh concrete in the mould, it will be vibrated in order to prevent from honey comb or void spaces of air in the concrete to exist. This is because honey comb could affect the strength or characteristics of the specimens.

After removal of mould on the second day, the concrete must be placed inside the curing tank until the day of testing. The purpose of curing is to avoid shrinkage cracking due to temperature fluctuation and also to gain the maximum strength of the concrete. For new concrete this usually involves casting specimens from fresh concrete and testing them for various properties as the concrete matures. The 'concrete cube test' is the most familiar test and is used as the standard method of measuring compressive strength for quality control purposes.

# CHAPTER 4
# RESULTS AND DISCUSSION

## 4.1 X-Ray Diffraction, XRD

XRD allows a particular mineral to be identified. Figure 4.1 shows the graph that tells the presence of Zinc in the sludge. The overlap between black and red peak shows the present of the Zinc ion. But XRD test did not tell the quantity ion present in the sludge. AAS shall give the amount of heavy metal present.

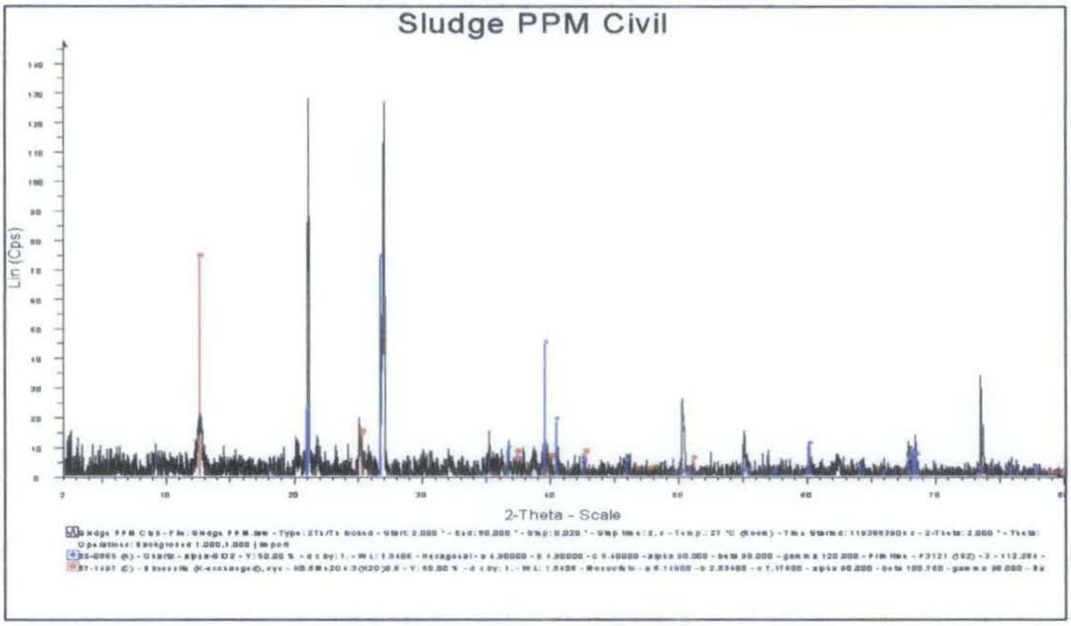


Figure 4.1: XRD results

## 4.2 Unconfined Compressive Strength, UCS

Table 4.1 shows the strength of solidified concrete at 7, 28 and 56 days and percentage of concrete strength at final day, 56 days. Figure 4.1 shows graphs of concrete strength development at 7, 28 and 56 days.

Table 4.1 Strength of Solidified Concrete

| Set of Concrete | Ratio OPC:(PFA/GGBS/Lime):Sludge | Design Concrete 40 (Mpa) | Strength of concrete after S/S (Mpa) | | | % of concrete strength |
|---|---|---|---|---|---|---|
| | | | 7 days | 28 days | 56 days | |
| A | 90:10:15 | 40 | 16.6 | 25.1 | 30.0 | 63.0 |
| B | 85:15:15 | | 17.1 | 26.4 | 30.1 | 66.0 |
| C | 80:20:15 | | 7.9 | 17.2 | 29.15 | 39.0 |
| D | 50:50:15 | | 10.3 | 15.1 | 22.5 | 37.7 |
| E | 55:45:15 | | 10.1 | 13.2 | 21.7 | 33.0 |
| F | 60:40:15 | | 8.6 | 11.4 | 22.0 | 28.5 |
| G | 90:10:15 | | 10.2 | 19.2 | 25.6 | 48.0 |
| H | 85:15:15 | | 13.2 | 24.1 | 28.2 | 60.0 |
| I | 80:20:15 | | 18.3 | 22.0 | 29.3 | 55.0 |
| J | 100:0:0 | | 30 | 60.8 | 70.2 | 152.0 |

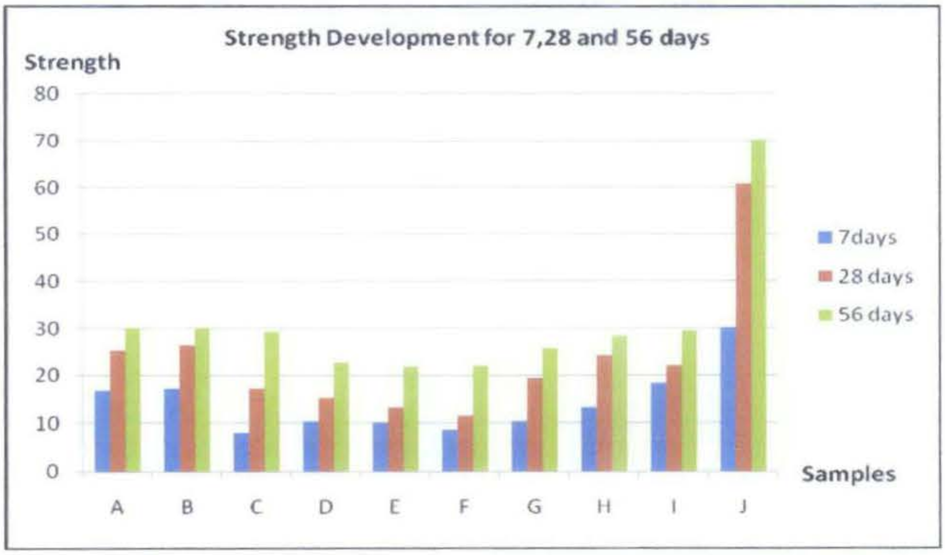


Figure 4.2 : Strength Development for 7, 28 and 56 Days

For concrete strength test, the design concrete mix is for Grade 40 concrete (40MPa) as target strength to achieve at 28 days. The strength developed by a concrete increases for many month under favorable conditions, but in the majority of specifications the strength is specified at an age of 28 days.

The ratio that gives highest percentage of strength development is 85:15, OPC:PFA which is 66%. Table 4.1 clearly shows that formulation using OPC:PFA gives higher strength than OPC:GGBS. At $28^{th}$ and $56^{th}$ day, OPC:PFA has exceeded OPC:GGBS about 10 N/mm$^2$. It can be concluded that formulation of OPC:PFA produces higher strength than OPC:GGBS.

Formulation on OPC:Lime gives slightly lower strength than OPC:PFA. The optimum mix for OPC:Lime is 80:20 which gives 60% of strength development at 28 days. The optimum mix for OPC:PFA is 85:15 and is 6% higher than OPC:Lime. Thus, it shows that the best formulation of OPC among PFA, GGBS and Lime that produces highest strength development is OPC:PFA. However it still failed to achieved the design mix which is 40MPa at 28 days.

For control sample which contains 100% OPC for cement content shows very impressive results as the strength is up to 152% or 60.8 MPa for 28 days of curing. It is expected to be higher than the design strength because when designing the mix, the best practice is not to set at the minimum strength. It also may caused by inconsistent ratio of cement water ratio in the concrete during casting process. Low water content will produces higher strength of concrete.

## 4.3 Toxicity Characteristic Leaching Procedure, TCLP

Equation used to calculate leaching rate.

*Type equation here.*

$$I = \frac{a_n V}{A_0 S \tau_n}$$

*Where:*

$a_n$ = *amount of heavy metal leach at n day*

*V/S = Volume of the concrete / Area of the surface of concrete.*

$A_0$ = *Amount of heavy metal before s/s*

$t_n$ = *Curing period*

Table 4.2 Leaching Amount of Zinc Metal after S/S

| **Set of Concrete** | **Ratio OPC: (PFA/ GGBS/ Lime): Sudge** | **Limit for Zinc (mg/l)** | **Concentration of leaching before S/S (mg/l)** | **Concentration of leaching after S/S (mg/l)** | | **% of zinc immobilize** | **Rate of leaching (cm/day)** |
|---|---|---|---|---|---|---|---|
| | | | | **28 days** | **56 days** | | |
| **A** | **90:10:15** | | | ND | 6.90 | 93.3 | 0.002 |
| **B** | **85:15:15** | | | ND | 7.37 | 92.8 | 0.013 |
| **C** | **80:20:15** | | | ND | 7.10 | 93.1 | 0.012 |
| **D** | **50:50:15** | | | ND | 6.52 | 93.7 | 0.011 |
| **E** | **55:45:15** | **100** | **103** | 4.37 | 7.37 | 92.8 | 0.013 |
| **F** | **60:40:15** | | | 3.23 | 5.81 | 94.4 | 0.010 |
| **G** | **90:10:15** | | | ND | 6.50 | 93.7 | 0.011 |
| **H** | **85:15:15** | | | ND | 4.68 | 95.5 | 0.001 |
| **I** | **80:20** | | | ND | 5.84 | 94.3 | 0.010 |

*ND = Not Detectable

The Zinc concentration in the sludge is 103mg/l and has exceeded the limit to dispose to landfill which is 100mg/l. this result is done by TCLP and AAS experiment. From Table 4.2, almost all reading is not detectable at 28$^{th}$ day of curing. It indicates that the zinc ion has been completely immobilized by S/S method. However at the 56$^{th}$ day, zinc ion started leach out from the concrete. Yet, leaching rate is very small and can be neglected.

## 4.4 Error in experiment

Through out the experiment there are some errors occur which affect the result of the experiment. The errors will be discussed below:

### *4.4.1 Concrete mixtures composition.*

Proportionate composition must be prepared. There is no exact composition, thus trial and error is required to obtain the best composition. Water to cement ratio is also important factor that will affect the S/S process. Error during weighing and preparing the exact amount of material can affect the result.

# CHAPTER 5
# CONCLUSIONS AND RECOMMENDATIONS

The XRD test shows presence of zinc ion in the PPMSB sludge and AAS indicate that zinc ions are slightly exceeded the Kualiti Alam limit, 100mg/l by 105mg/l for disposal to secured landfill. All of the binders show outstanding results as they are effectively immobilize the heavy metal more than 90%. The percentage is taken at the longest day testing which is 56 days of curing.

Matrix formulation of OPC: PFA and OPC: Lime is far better than OPC: GGBS in compressive strength as it gives up to $8N/mm^2$ difference in final strength. As expected, the introduction of GGBS in the concrete is to precipitate and preventing heavy metals from leaching, not for strength. GGBS also give effect on concrete properties such as gaining high workability and increased the concrete setting time.

15% of sludge as cement additives has significant affect on the strength development as the highest strength achieved is 66% of design mix and not even half of the control strength. It is mainly because the sludge is largely organic matter, and it will deteriorate with time. Organic compounds retard the cement setting process by forming a protective layer around the cement grain, thus hindering the formation of calcium hydroxide

PFA and Lime gives almost the same results on the strength and leaching rate. PFA formulation slightly exceeds the Lime formulation by about $1N/mm^2$ in strength but Lime has shown better performance by encapsulating zinc ion. Thus, it shows that both PFA and Lime gives comparable performance in S/S process for waste containing heavy metals. However, this project has successfully been done and fulfills the objectives to find the best formulation between OPC, GGBS and Lime that gives desirable strength and lowest leaching rate.

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# APPENDICES

## APPENDIX 1

## CONCRETE MIX DESIGN FOR GRADE 40

| Stage | Item | | Values |
|---|---|---|---|
| 1 | 1.1 | characteristic strength | compressive 40 N/mm at 28 days |
| | | | Proportion defective 5% |
| | 1.2 | standard deviation | |
| | 1.3 | margin | k=1.64, 1.64x8 = 13N/mm$^3$ |
| | 1.4 | Target mean strength | 40+13 = 53N/mm$^3$ |
| | 1.5 | Cement Type | OPC |
| | 1.6 | Aggregate type: coarse | uncrushed |
| | | aggregate type : fine | uncrushed |
| | 1.7 | Free water/cement ratio | 0.47 |
| | 1.8 | Maximum free-water/cement ratio | 0.55 |
| | | | |
| 2 | 2.1 | cement content | 160/0.47 = 340kg/m$^3$ |
| | 2.2 | maximum cement content | 0 |
| | 2.3 | minimum cement content | 290kg/m$^3$ |
| | | | |
| 3 | 3.1 | relative density of aggregate(SSD) | 2.6 |
| | 3.2 | Concrete density | 2400kg/m$^3$ |
| | 3.3 | Total aggregate content | 2400-340-160=1900kg/m$^3$ |
| | | | |
| 4 | 4.1 | grading of fine aggregate | zone 3 |
| | 4.2 | Proportion of fine aggregate | 25 to 30, say 27 % |
| | 4.3 | fine aggregate content | 1900x0.27 = 515 kg/m$^3$ |
| | 4.4 | coarse aggregate content | 1900- 515 = 1385 kg/m$^3$ |

Quantities

| per m$^3$ (to nearest 5kg) | | per trial mix of 0.009m$^3$ |
|---|---|---|
| Cement | 340 | 3.06 |
| Water (kg or l) | 160 | 1.44 |
| Fine aggregate | 515 | 4.635 |
| Coarse aggregate (kg) | 1395 | 12.465 |

*Percentage of PFA, GGBS and Lime is taken from total amount of Cement used

**APPENDIX 2**

**LIMIT OF HEAVY METAL DISPOSED TO LANDFILL**

**2) LANDFILL CRITERIA**

Free from bad smell/odour
No presence of fumes/gas
No presence of free liquid/water

| **Parameter** | **Limit** | **Parameter** | **Limit** | **Parameter** | **Limit** |
|---|---|---|---|---|---|
| Total Solids | >20% | f. Copper | 100 mg/L | Chloride | 2% |
| pH Slurry | 5.5 - 12 | g. Lead | 5 mg/L | Oil and | 1000 mg/kg |
| | | h. Mercury | 0.2 mg/L | Grease | <10% |
| Leachable Metals | 5 mg/L | i. Nickel | 100 mg/L | TOC | 0.5 mg/kg |
| | 100 mg/L | j. Selenium | 1 mg/L | Cyanide | |
| a. Arsenic | 400 mg/L | k. Silver | 5 mg/L | | |
| b. Barium | 1 mg/L | l. Tin | 100 mg/L | | |
| c. Boron | 5 mg/L | m. Zinc | 100 mg/L | | |
| d. Cadmium | | | | | |
| e. Chromium | | | | | |

## APPENDIX 3

Calculation for preparing standard solution of Zn :

$M_1V_1 = M_2V_2$

Where, $M_1$ = initial concentration of the solution

$M_2$ = desired concentration of the solution

$V_1$ = required volume of a acid at concentration $M_1$

$V_2$ = Required volume of a acid at concentration $M_2$

Standard solution of 0.5ppm:

$M_1(500ml) = (0.5)(1000)$

$M_1 = 1ml$

Standard solution of 1.5ppm:

$M_1(500ml) = (1.5)(1000)$

$M_1 = 3ml$

Standard solution of 4 ppm:

$M_1(500ml) = (4)(1000)$

$M_1 = 8.0ml$

## APPENDIX 4

## RESULTS AND DATA

Data Sample Leaching calculation.

| Ratio | leaching | leaching corrected | % immobilize | leaching rate. |
|---|---|---|---|---|
| A | 0.39 | 6.90 | 93.3 | 0.002 |
| B | 0.36 | 7.37 | 92.8 | 0.013 |
| C | 0.35 | 7.1 | 93.1 | 0.012 |
| D | 0.32 | 6.52 | 93.7 | 0.011 |
| E | 0.36 | 7.37 | 92.8 | 0.013 |
| F | 0.28 | 5.81 | 94.4 | 0.010 |
| G | 0.39 | 6.5 | 93.7 | 0.011 |
| H | 0.23 | 4.68 | 95.5 | 0.001 |
| I | 0.29 | 5.84 | 94.3 | 0.010 |

1. Leaching taken from AAS data.

Leaching corrected

50g sample mixed with 1000ml lechant

Volume sample = mass/density

= 0.1g/1020kg/m3

=98 m3

For concrete, density = total mass/volume

=2658m3

2. % immobilize = $\frac{\text{initial- final (Zn)}}{\text{initial}}$

$= \frac{103- 6.9\ (Zn)}{103}$

= 93.3%

3. Leaching rate =

$$l = \frac{a_n \ V}{A_0 \ S t_n}$$

$a_n$ = *amount of heavy metal leach at n day*
*V/S = Volume of the concrete / Area of the surface of concrete. (Vol= 1000cm3, area=10cm2)*
$A_0$ = *Amount of heavy metal before s/s(38.352mg/l)*
$t_n$ = *Curing period(28 days)*

$$= \frac{6.9*1000}{103*100*28}$$

50 gm of sludge waste is diluted in 1000ml acidic fluid

50 gm sludge → 1000 ml acidic fluid

50 gm sludge is converted into volume:

[50 gm/1020 kg/m3] x[ 1 kg/1000gm] x[$10^6$ ml/1$m^3$] = 49 ml

*Density of Sludge is = 1020 kg/$m^3$

So, 49 ml of sludge waste is diluted in 1000 ml acidic fluid

49 ml sludge → 1000 ml acidic fluid

49 x Factor = 1000

So ,Factor = 1000/49

= 20.41

Concentration get from AAS is 5.05 ppm

So, exact concentration should be multiply with factor which is 20.41

- Concentration of Zinc ion in fresh sludge = 5.05 ppm x 20.41

  = 103.1 **ppm**

## Appendix 5 : Milestone for the First Semester of 2-Semester Final Year Project Jan 2008

| No. | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Project work continue | ■ | ■ | ■ | ■ | | | | | | | | | | | |
| | Lab work (concreting work) | | | | | | | | | | | | | | | |
| | Lab work (testing) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| 2 | Submission Progress Report 1 | | | | ● | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| 3 | Project Work Continue (Lab Testing) | | | | ■ | ■ | ■ | ■ | Mid-semester break | | | | | | | |
| | | | | | | | | | | | | | | | | |
| 4 | Submission Progress Report 2 | | | | | | | | | ● | | | | | | |
| | | | | | | | | | | | | | | | | |
| 5 | Project Work Continue (Lab Testing) | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | |
| 6 | Poster Exhibition | | | | | | | | | | | ● | | | | |
| | | | | | | | | | | | | | | | | |
| 7 | Submit 1st Draft of Interim to Supervisor | | | | | | | | | | | ● | | | | |
| | | | | | | | | | | | | | | | | |
| 8 | Submission of Final Dissertation Final Draft | | | | | | | | | | | | | ● | | |
| | | | | | | | | | | | | | | | | |
| 9 | Oral Presentation | | | | | | | | | | | | | | | ● |
| | | | | | | | | | | | | | | | | |
| 10 | Submission of Project Dissertation | | | | | | | | | | | | | | | ● |

● Suggested milestone

■ Process