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Treatment of Petroleum Sludge By Using Solidification/Stabilization (S/S) Method : Effect of Hydration Days to Heavy Metals Leaching and Strength

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Abstract. Petroleum sludge is one of the major solid wastes generated in the petroleum industry. Generally, there are numbers of heavy metals in petroleum sludge and one treatment that is gaining prominence to treat a variety of mixed organic and inorganic waste is solidification/stabilization (S/S) method. The treatment protects human health and the environment by immobilizing contaminants within the treated material and prevents migration of the contaminants. In this study, solidification/stabilization (S/S) method has been used to treat the petroleum sludge. The comparison of hydration days, namely, 7th and 28th days in these cement-based waste materials were studied by using Synthetic Precipitate Leaching Procedure (SPLP). The results were compared to the United States Environmental Protection Agency (USEPA) standards. The results for leaching test concluded that less percentageOPC gave maximum concentration of heavy metals leaching due to deficient in Calcium Oxide (CaO), which is can caused weak solidification in the mixture. Physical and mechanical properties conducted such as compressive strength and density test. From the results, it shows addition up to of 30percentage PS give results which comply with minimum landfill dispose limit. The results shows correlation between strength and density are strong regression coefficient of 82.7%. In conclusion, S/S method can be alternative disposal method for PS in the same time complies with standard for minimum landfill disposal limit. The results for leaching test concluded the less OPC percentage gave maximum concentration of heavy metals leaching.

1. Introduction

According to Department of Environment (DOE), Malaysia, petroleum sludge is classified as a scheduled waste and it has to be land filled at a secure landfill to meet the guidelines as proposed by DOE of Malaysia [1]. Scheduled wastes shall be stored in containers which are compatible with the scheduled wastes to be stored, durable and which are able to prevent spillage or leakage of the scheduled wastes into the environment.

Heavy metal contaminations in waste are causing a serious threat to the environment and human health [2]. One of the technologies that is gaining prominence to treat a variety of mixed organic and inorganic waste is solidification/stabilization (S/S) method [3]. The entrapment of waste that express hazardous characteristics within a cementations matrix (solidification) and the binding of contaminants (organic or inorganic) of a hazardous stream into a stable, insoluble form (stabilization) are the mechanisms that best describe the principle behind solidification and stabilization (S/S) treatment. This method works with the help of cement as a binder. This binder has been used to treat plating wastes that contain metals such as cadmium, chromium, copper, lead, nickel and zinc [5]. Cement is frequently selected as the binder where it able to (a) chemically bind free liquids, (b) reduce the permeability of the waste form, (c) encapsulate waste particles surrounding them with an impermeable coating, (d) chemically fix hazardous constituents by reducing their solubility, and (e) facilitate the reduction of the toxicity of some contaminants [6].

If cement is cured for only three days, it will reach about 60percentage of the strength of continuously cured cement; if it is cured for seven days, it will reach 80percentage of the strength of continuously cured cement. If curing stops for some time and then resumes again, the strength gain will also stop and reactivate [4]. If a concrete is not well cured, particularly at the early age, it will not gain the required properties at desired level due to a lower degree of hydration, and would suffer from irreparable loss [4]. Improper curing would entail insufficient moisture and this has been found to produce cracks, compromise strength, and reduce long-term durability [5].

The main aim of this study was to determine the comparability of heavy metals leaching in varying percentage of Petroleum Sludge (PS) and Ordinary Portland Cement (OPC) at different curing day namely, 7^{th} and 28^{th} day. In addition, this study also measures the compressive strength and density for each sample.

2 Raw Materials and Methodology

This section is elaborate on preparation of raw materials used and methodology to execute the testing.
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2.1 Preparation For Raw Material

Ordinary Portland Cement (OPC) Type I was used as binder in this study. OPC was received from Kok Xin Hardware, Parit Raja. The OPC was kept in an airtight container and stored in the humidity-controlled room to isolate from the atmospheric humidity. Petroleum sludge (PS) samples were collected from PETRONAS Refinery at Melaka. The petroleum sludge was dried in the oven for 48 hours at a temperature of 110˚C.

2.2 Method for XRF

The determination heavy metals concentrations in raw materials were carried out using XRF in Analytic Laboratory UTHM. The calibration of the instrument for each metal was performed according to its wavelength and standard solutions.
The sludge was zapped by the X-ray beam because other X-rays to be generated. Some of these X-rays escape from the sludge and collected by a suitably-positioned X-ray detector. Many of these collected X-rays have energies which are characteristic of the atomic number of the atom in which they were generated. By measuring the energies of the X-rays, it can tell what elements they came from. If these energies measured under carefully-controlled conditions and count the X-rays from each element over a period of time, the proportions of each element in the sludge can be calculated.

2.3 Design Mixture

The design mixtures for this study are presented in Table 1. The sludge was added together with OPC then allowed it to homogenize for approximately 5 minutes in order to eliminate any lumps that may have formed. Secondly, water was added gradually at water-to-mixture (W/M) ratio of 0.5 or 0.60. After mixing, the mixture was cast into 50 mm x 50 mm x 50 mm cube molds in 3 layers; with each layer will be compacted by manual compactor to yield good packing of the mixture. All the samples were triplicates for 2 hydration durations which are 7th and 28th days in a cabinet at a controlled condition (Temperature= 25±2˚C, Humidity> 90%).

Table 1 : Design mixture used in this study

Sample	PS	OPC
PS 1	0%	100%
PS 2	10%	90%
PS 3	20%	80%
PS 4	30%	70%
PS 5	40%	60%

*by % weightage (250g)

2.4 Method of leaching Tests
Crushed block leaching test, namely Synthetic Precipitate Leaching Procedure (SPLP) as described in SW-846 (USEPA, 1992) Method 1311 was conducted on the block samples subsequent to 7 and 28 days of air drying. The cube samples of 250 g weight were crushed and sieved to less than 9.5 mm. 50g of solidified samples was weighed and placed in a bottle prior to the addition of leaching solution to provide a ratio of 1:20 mass ratio of leachant to solidified sample. According to the SPLP procedures described in SW-846 Method 1312, [7] if the sample is a waste or wastewater, the extraction fluid employed is the pH 4.2 solution. Therefore, for this study, an extraction fluid with pH 4.2 solution was used. The mix of 60percentage of sulfuric acid and 40percentage of nitric acid was diluted in distilled water until the pH was 4.2.

Then, the samples were prepared in a screw-capped polyethylene bottles, which were filled with crushed samples of 20 g and leaching fluid of 400 ml at the solid/liquid ratio of 1:20. The bottles were agitated at 30 RPM for 18 hours in an end-over-end manner. The leachate collected, then was filtered by using 7 µm glass fiber filters, and was preserved with nitric acid to a pH less than 2. Finally, the sample was analyzed using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) to determine the concentration of dissolved metals.

2.5 Measurement of Compressive Strength Test
The compression test using an axial load is applied using either strain-control or stress-control condition [6]. The compression device is a hydraulically-actuated loading piston, electronically controlled, with the capability of infinite rates of strain and stress loads. A load cell of maximum 5kN capacity is fastened to the piston to measure load on 7th and 28th day curing sample. Test data are displayed on control panel board readouts. The results are obtained were compared with BS standard to determine the minimum requirement for further applications of treated sludge S/S matrices as a secondary raw material.

2.6 Measurement of density test
Bulk density is measured by calculating the volume of the s/s matrices and weight. The test involves the measurement of height and width of each sample. Finally, the weight of the matrices is divided by its total volume. [7].

3 Results and Discussion

This section is divided into two subsections, namely, heavy metals concentration in raw materials and comprehensive strength and density in raw materials.

3.1 Heavy metals concentration in raw materials
The concentrations of heavy metals in the raw materials are shown in Table 2. The results indicated that only Copper (Cu) shows the concentration of both materials below USEPA standard. Whereas, Zinc (Zn) concentration in OPC was below USEPA standard, not for PS. In contrast, Barium (Ba) shows below concentration than the standard in PS, not for OPC. While others heavy metals such as Lead (Pb) and Arsenic (As) were higher than the standard for both materials. Based on these metals

concentrations, remediation methods such as S/S method is required to reduce the toxicity of these hazardous metals from the environment. Research by Abdul Awal & Warid, (1999) shows the similarity of OPC concentration meanwhile Bayoumi, (2009) shows slight differences in PS concentration due to different resources of material.

Table 2: heavy metal chemical composition of raw materials Not synchronize with the table color coding

Heavy metals	Formula	Concentration OPC	PS	Standard USEPA
Copper	**Cu**	**8±**	**18.0±**	**100**
Lead	**Pb**	**15±**	**25.1±**	**5**
Zinc	**Zn**	**81±**	**189±**	**500**
Arsenic	**As**	**19±**	**39.7±**	**5**
Barium	**Ba**	**211±**	**50.4±**	**100**

* [yellow] Above USEPA standard [green] Below USEPA standard

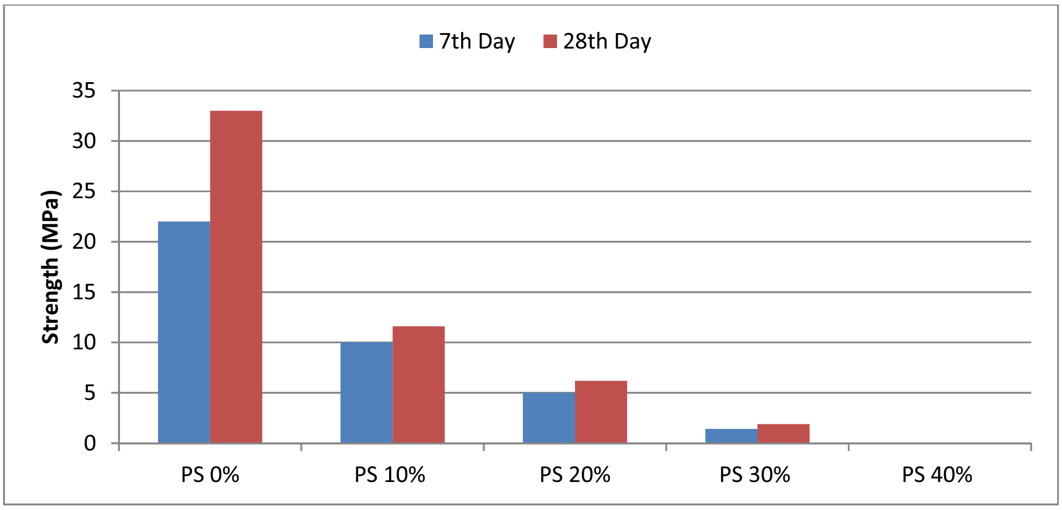

Figure 1 : Compressive strength at 7th and 28th day curing for PS + OPC

3.2 Comprehensive strength and density in raw materials

The suitable optimum design mixes were determined by conducting two mixture materials tests. Figure 1 shows the results of strength for PS mixed with OPC at 7th and 28th day of curing. The results for compressive strength test shows the more percentage PS added, the strength also decreasing. From the figure, the increasing of PS in mixture from 0percentage to 40percentage reduced the mixture strength from 22, 10, 5, 1.41 and 0 in MPa respectively for the 7th day of curing. For the 28th day of curing It show the same pattern on the 7th day of curing where test results showed an increment from 22 to 33, 10 to 11,5 to 6.2, 1.41 to 1.89, and 0 in MPa respectively. The result pattern shows at 7th day of curing are predicted same at 28th day curing as the mature phase for S/S matrices are 28th day curing .

Addition up to 30 percentage PS complied with minimum limit requirement for landfill disposal, which more than 0.35MPa [8]. However, the addition of 40 percentage PS, the compressive strength cannot be measured or tested. Thus, for determination of optimum design mixture 30 percentage PS was selected. This reduction due to the physical characteristic which determined by density of design mixture itself, which are not showing any contributing to strength development.

Generally, there is a linear relationship between strength and density of the sample. A study by [9], demonstrated that the strength of materials, such as concrete and soil is influenced by other properties such as binder content, density, water content, curing period and method of compression. As an example, [10] found that 7 days compressive strength of lightweight concrete and ordinary concrete increases linearly with the density of the samples. Therefore, in this study, the relationship between strength and density will be discussed.

In addition, the density of all samples increased when the curing times increased. Similar findings were reported by [11] as well as [12] who studied the effect of curing time on the behavior of cement admixed with clay. They argued that densities increased with the curing time and cement content due to the amount of cementing product. Consequently, the amount per unit volume increases.

From the Figure 2, it can be described that the density of S/S sample decreased with the additional of PS. For example, density of sample PS 0 percentage at 28 days is 2455 Kg/m^3. This value decreased to 2340, 2233, 2123 and 2009 in Kg/m^3 respectively, when the sample was incorporated with increasing percentage of PS. For this reason, the result clearly explained that the low density of the PS design mixture itself has affected the density of S/S sample. However, for this purpose, the low density of S/S sample provides a significant advantage which is easier to handle and generally low cost of transportation.

Figure 2 presents a compressive strength against density at 28 days. The influence of strength of the density values is shown by using regression coefficient. Distribution of data shows a linear relationship between the compressive strength and density as follows.

$$\sigma = 2419.5 + 1.184\,\rho \qquad (4.1)$$

*With σ is a compressive strength (MPa) and α is density (Kg/m^3) of sample.

Statistical analysis showed that there is a significant relationship between the two variables as a linear equation (4.1) described that one unit density of 2419.5 decreases the strength is 1.184 approximately. In addition, the value indicates that the strength decrease with the density. Apart from that, the strong regression coefficient of 82.7% shows the variability in compressive strength. Thus, the variability in compressive strength contributes by the physical characteristics of the mixture which is the density.

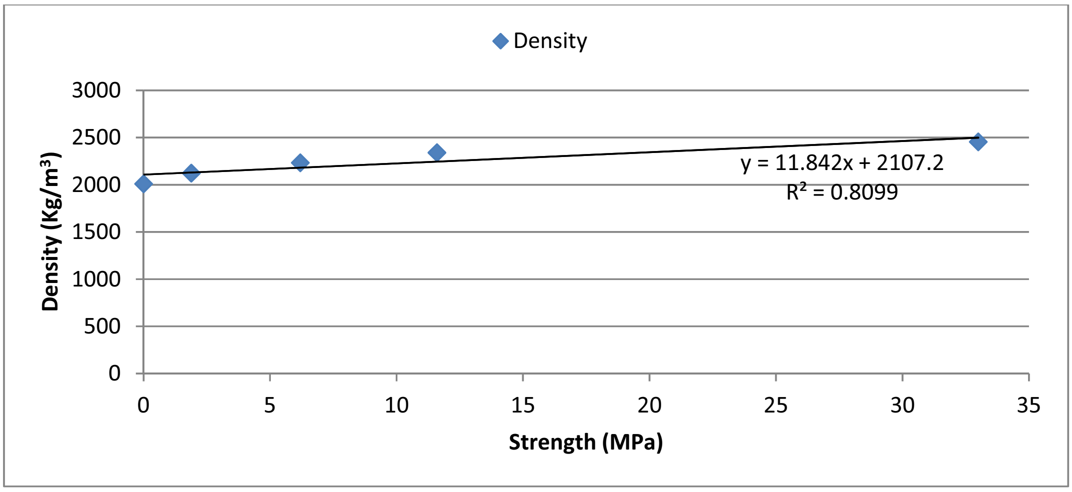

Figure 2: Relationship between compressive strength and density of PS mix OPC at 28 day

The results in Figure 3 show the leaching of heavy metals in mixture and zinc (Zn) shows the most leaching which more than 5ppm. Other heavy metals such as copper (Cu), lead (Pb), arsenic (As) and barium (Ba) leaches below than 5ppm except for 40percentage of PS for Cu and BA. These heavy metals leaching is not exceeding the USEPA standard.

For the leaching test, addition of PS in the mixture was increasing the leaching of heavy metals. For the lowest leaching concentration of heavy metals is As from 0.156, 0.392, 0.67, 0.825 and 0.846 in ppm respectively. For the highest leaching concentration is Zn from 6.57, 18.7, 19.44, 21, and 22 in ppm respectively.

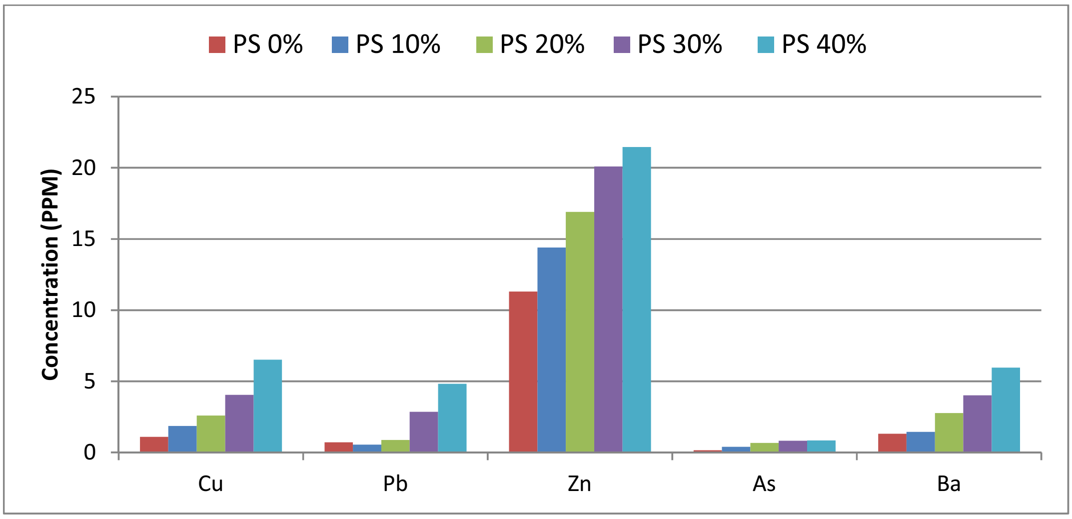

Figure 3 : 7th day curing Graph for PS + OPC : Leachibility (SPLP)

Figure 4 shows data for leaching behaviors at 28th day of curing. It shows the same pattern on the 7th day of curing where results showed decrement from the 7th day of curing as 28th day curing are mature phase for S/S matrices.

Meanwhile the heavy metals concentration shows reduction in value where clearly can be seen at Zn where 6.57 to 0, 18.7 to 0.172, 19.44 to 0.234, 21 to 0.585, 22 to 0.78 in ppm from the 7th day to 28th day curing respectively. Other heavy metal shows reduce below than 3ppm from 5ppm and comply to USEPA standard.

The results for heavy metals leaching were increased as the percentage of PS increase. This due to reduction of OPCpercentage in the mixture, proven by [2] research where OPC added as a binder and the concentration of heavy metals were reduced. For leaching test (SPLP) heavy metals decreasing as the s/s matrices more mature at 28th day of curing. These due to the percentage of PS and OPC binding together can trap more heavy metals at mature phase. Based on Table 2 shows the highest

For compressive strength test, results shows as the percentage of PS increase the strength decreasing. Thus increasing of the PS percentage into the mixture interferes the strength due to the material and physical character of the PS itself. For s/s matrices to be disposed into landfill, minimum limit requirement is 0.35MPa and thus the maximum PS percentage addition chosen is 30 percentage where when it mix with OPC at mature phase, it achieve 1.89 MPa.

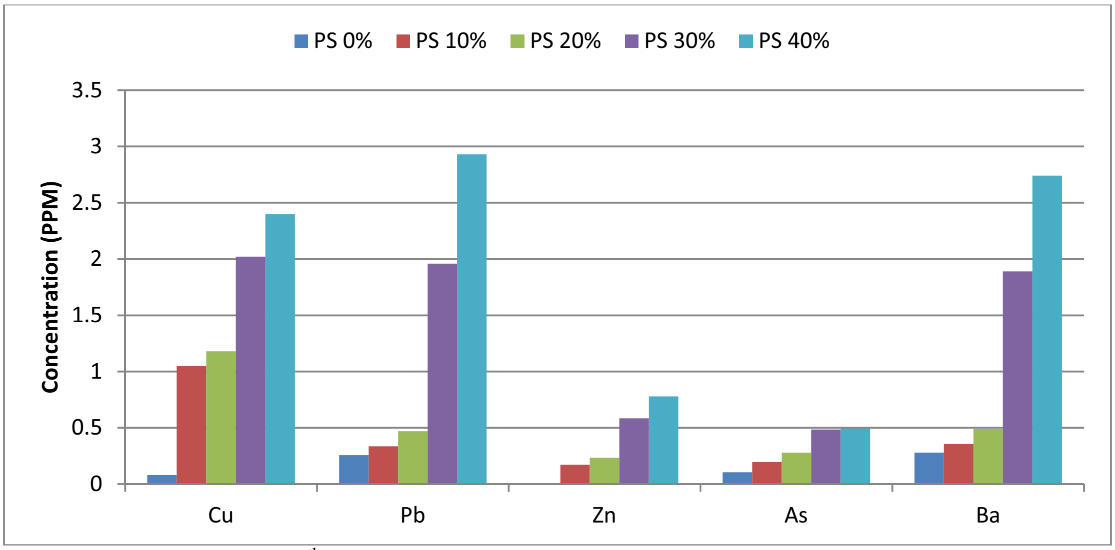

Figure 4 : 28th day curing graph for PS + OPC : Leachibility (SPLP)

4 Summary

As a conclusion, addition of petroleum sludge into the mixture decreases the strength of matrices up until 30percentage addition of petroleum sludge can be examine by compressive strength test and also comply with minimum strength of landfill disposal strength. In addition, the concentration of heavy metals at 28 days is lower than that at 7th days due to long hydration days increased bonding reaction between metals and binder and the heavy metals concentration were below USEPA standard. .Therefore, the petroleum sludge could be treated using s/s matrices and also enhance the method of disposal this hazardous sludge.

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