LEACHING BEHAVIORS OF HEAVY METALS ON PETROLEUM SLUDGE WASTE TREATMENT BY USING SOLIDIFICATION/STABILIZATION (S/S) METHOD WITH PALM OIL FUEL ASH AS PARTIAL CEMENT REPLACEMENT

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ABSTRACT

In Malaysia, petroleum is the most important source of energy which also producing hazardous waste called sludge. Petroleum sludge is referring to the waste containing mixtures of high concentration of hydrocarbons and accumulated heavy metals which being recognized as a hazardous waste. Without improper disposal or insufficient treatment, it can pose serious threats to the environment and human health. To solve these problems, there is a method has been developed for the treatment of petroleum sludge namely the solidification/stabilization (S/S) method. S/S method mainly based on the encapsulation of the pollutants within matrices using the cement. Tremendous research has been carried out using the ash from different sources in the S/S method as environmentally-friendly solutions. It replaces cement with a high pozzolonic characteristics binder that could encapsulate the pollutants better. Therefore, this study is an attempt to treat the Malaysian petroleum sludge (PS) by the incorporation of different percentage of palm oil fuel ash (POFA) to replace ordinary portland cement (OPC) in S/S method. The leachability of the samples was determined by Synthetic Precipitation Leaching Procedure (SPLP), Toxicity Characteristics Leaching Procedure (TCLP) and Static Leaching Test (SLT). The results were compared with United States Environmental Protection Agency (USEPA) standards. The heavy metals in PS, POFA and OPC were determined using X-ray Fluorescence (XRF) meanwhile dissolved heavy metals using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Addition test such as compressive strength test, density test and water absorption test were conducted on S/S matrices. The recommended percentage of POFA incorporation was 10% into 30% of PS with leachability complies to USEPA standard except for Ni and Cr. It performed better in physical and mechanical properties. SPLP leaching test results for PS mix OPC showed at 28th day curing, the highest leaching was 15.2 mg/L (Cr; 40% PS) meanwhile for PS mix OPC and POFA was 14.2 mg/L (Cr; 30% PS). The results showed that the full utilization of S/S matrices obtained the highest compressive strength up to 30.1 MPa. Meanwhile, the lowest 0.71 MPa was above the limit of 0.35 MPa. The long term leachability results also showed that all findings were below the USEPA standard. On 95th day curing was the recommended time after treating the S/S matrices to be disposed into landfill. Therefore, POFA can be an alternative low cost material that supports an environmentally friendly disposal method and also enhances the petroleum sludge treatment performance.
ABSTRAK

Di Malaysia, petroleum adalah sumber tenaga yang paling penting dan ianya juga menghasilkan sisa berbahaya yang dikenali sebagai enapcemar. Enapcemar petroleum merujuk kepada campuran yang mengandungi hidrokarbon pada kepekatan yang tinggi dan logam berat terkumpul dan ianya di iktiraf sebagai sisa berbahaya. Tanpa pelupusan yang tidak betul atau rawatan yang tidak mencukupi, ia boleh menimbulkan ancaman serius kepada alam sekitar dan kesihatan manusia. Untuk menangani masalah ini, terdapat satu kaedah yang telah dibangunkan untuk rawatan enapcemar petroleum iaitu pemekalan / penstabilan (S / S) kaedah. Kaedah S / S ialah pengkapsulan bahan pencemar kedalam bentuk matriks menggunakan simen. Banyak penyelidikan telah dijalankan dalam kaedah S / S dengan menggunakan abu dari sumber-sumber yang berbeza sebagai penyelesaian mesra alam. Ia menggantikan simen dengan ciri-ciri pozzolonic yang tinggi sebagai pengikat merangkumi bahan pencemar yang lebih baik. Oleh itu, kajian ini adalah satu percubaan untuk merawat enapcemar petroleum Malaysia (PS) dengan menggabungkan peratusan yang berbeza abu bahan api kelapa sawit (POFA) bagi menggantikan simen portland biasa (OPC) dalam kaedah S / S. Maka kepekatan bahan cemar sampel ditentukan dengan Synthetic Precipitation Leaching Procedure (SPLP), Toxicity Characteristics Leaching Procedure (TCLP) dan Static Leaching Test (SLT). Keputusan dibandingkan dengan piawaian United States Environmental Protection Agency (USEPA). Logam berat dalam PS, POFA dan OPC ditentukan menggunakan X-ray Fluorescence (XRF). Sementara itu kepekatan logam berat diuji menggunakan Inductively coupled plasma mass spectrometry (ICP-MS). Ujian tambahan seperti ujian kekuatan mampatan, ujian ketumpatan dan ujian penyerapan air yang dijalankan ke atas matriks S / S. Peratusan POFA yang disyorkan adalah 10% kedalam 30% PS dengan mematuhi piawaian USEPA kecuali Ni dan Cr. Ianya mempunyai sifat fizikal dan mekanikal yang memuaskan. Keputusan ujian kepekatan bahan cemar menggunakan SPLP untuk campuran PS dan OPC menunjukkan pada hari ke 28 pengawetan, pelepasan tertinggi adalah 15.2 mg/L (Cr; 40% PS) sementara dalam campuran PS dengan OPC dan POFA adalah 14.2 mg/L (Cr; 30% PS). Keputusan menunjukkan bahawa penggunaan penuh matriks S / S diperolehi kekuatan mampatan tertinggi sehingga 30.1 MPa. Sementara itu, 0.71MPa ialah yang terendah namun melebihi had 0.35 MPa. Keputusan juga menunjukkan bahawa kepekatan bahan cemar bagi ujian jangka masa panjang adalah di bawah USEPA. Hari ke 95 pengawetan adalah masa yang disyorkan selepas merawat matriks S / S untuk dilupuskan ke tapak pelupusan. Oleh itu, POFA boleh menjadi bahan kos rendah alternatif yang menyokong kaedah pelupusan mesra alam dan juga meningkatkan prestasi rawatan enapcemar petroleum.
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<td>±</td>
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<td>Tolerance or range of values</td>
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<td>µm</td>
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CHAPTER 1

INTRODUCTION

Petroleum sludge (PS) refers to the waste generated due to the storage of crude or any products containing the mixtures of high concentration of hydrocarbons accumulated with heavy metals such as copper (Cu), lead (Pb), iron (Fe), zinc (Zn), nickel (Ni), arsenic (As), chromium (Cr), and barium (Ba).

PS is identified as a hazardous waste under the Environment Protection Act and Hazardous Wastes Handling Rules, thus improper disposal or inadequate treatment of this sludge can cause alarming threats to the human health and the environment (Prakash et al., 2015). This sludge cannot be disposed in the landfill, even if it is free of hydrocarbons unless the sludge is totally remediated. This reason has triggered an intensifying attention in the recent years on the production of sludge during the petroleum refining process.

In Malaysia, petroleum is the most important source of energy. It is used for various applications including transportation, combustion, polymer industries, textile industries and other applications. Throughout the country, there are six petroleum refineries in operation (Malaysia Oil & Gas Report, 2016). Issues on PS are not only related to the human risks, but also to the degradation of the environment. Improper disposal and handling of PS may not only contaminate the soil but also lead to a serious threat to the groundwater.

Stabilization/solidification (S/S) method is not only fast but also an effective waste treatment technique (Yao et al., 2012). This treatment is one of the encapsulation methods that have been mainly used for hazardous waste treatment. In the recent years, tremendous researches have been carried out using the ash from different sources in the S/S method as an environmentally friendly solution to replace
the cement since ash is known as a good binding material with high pozzolanic characteristics. In Malaysia, palm oil fuel ash (POFA) is the most copiously produced waste materials, which is extensively produced from the palm oil industry by burning the empty fruit bunches, fiber, and palm oil shells (Kroehong et. al., 2011).

The POFA innovation in structural science has received much recognition mainly because it can be abundantly accessed and has low remunerative commercial value. A large growing literature has also shown that POFA has been utilized as a supplementary cementitious substance in manufacturing high-strength concrete in the recent decade (Islam & Islam, 2010; Anastasiadou et al., 2012; Kroehong et al., 2011). Therefore, the utilization of POFA in S/S method provides a sustainable solution towards the environment rather than being simply disposed in the landfill.

1.2 Problem statement of the study

Petroleum sludge (PS) generated from the petroleum industry in Malaysia is categorized as Scheduled Waste under Environmental Quality Act, 2005 that requires special handling and disposal method. A higher amount of PS generation is commonly related to a bigger refining capacity (Ling & Isa, 2006). For every 500 tons of processed crude oil, it has been approximated that one ton of PS waste is produced. In particular, throughout Malaysia, there are six petroleum refineries, which yield to enormous quantities of sludge that must be disposed.

Different virulent impacts caused by the heavy metals can be originated from the disposal of PS in the environment. Since they are genotoxic to people and other ecological receptors, nearly all heavy metals have a total impact with a specific hazard which develops into a major concern. Moreover, after remaining within the earthly environment for a prolonged period of time, heavy metals may appear to resist the process of desorption as well as the degradation.

In order to overcome these problems, few methods have been instigated for the treatment of PS. For examples, incineration, oxidation treatment, land treatment and
bioremediation. Even though these methods of treating the sludge are somehow effective, the problems of contamination, odor, and fire hazard still exists.

Due to these reasons, recent studies have successfully solved the problems by using the S/S method, which is mainly based on the encapsulation of the pollutants within matrices using the cement material. However, some disadvantages of this method include the high cost of the cement and the claim regarding the ordinary Portland cement (OPC) usage as the only binder in S/S method is ineffectual in immobilizing few common organic and inorganic contaminants.

Incorporation of different types of ash as cement replacement has become the focus of study (Yin et al., 2006; Zhang et al, 2011; Rozumova et al., 2015; Kroehong et al., 2011). Tremendous researches have been carried out using the ash from different sources in the S/S method. It’s been used as environmentally friendly material to replace the cement since ash is known as a good binder with high pozzolanic characteristics that could encapsulate the pollutants better besides it costless waste rather than purchasing OPC.

On the other hand, palm oil plantation produces waste called palm oil fuel ash in huge quantities. This replacement method can decrease the cost by using free disposal material from 3.4 million hectares palm oil plantations all over Malaysia. OPC is good in binding material together, however adding pozzolanic materials contribute to the strength development besides the cost of ash usually free as it part of waste.

Therefore, the aim of this study is to treat the Malaysian petroleum sludge by incorporating the palm oil fuel ash (POFA) as a replacement of the cement in S/S method. In addition to that, this study provides a sustainable solution by decreasing the sludge treatment cost by utilizing POFA to replace cement as well as providing costless materials for S/S method that may lead to construction applications.

1.3 Objectives of the study
This study aims to treat and encapsulate petroleum sludge (PS) using an S/S method with the implementation of POFA as a binder. The specific objectives of this study are stated:

1) To investigate the heavy metals concentration in petroleum sludge, palm oil fuel ash, and ordinary Portland cement.
2) To determine OPC and POFA mixture of short-term leaching behavior and compressive strength for S/S matrices.
3) To examine PS, OPC and POFA mixture of short-term leaching behavior and compressive strength of the S/S treatment method.
4) To execute the long-term leaching behavior (Static Leaching Test) for optimum S/S matrices and S/S treatment method matrices.

1.4 Scope of work

This study consists of four stages, namely (i) quantification of the heavy metals concentration in petroleum sludge, palm oil fuel ash, and ordinary Portland cement (ii) determination of short-term leaching behaviors of S/S matrices, (iii) identification of short-term leachability behaviors of S/S treatment method matrices and (iv) execution long-term leaching behavior (SLT) for optimum matrices.

The first stage involves the determination of heavy metals concentration in raw materials such as petroleum sludge (PS), palm oil fuel ash (POFA) and ordinary Portland cement (OPC). Various types of experiment are conducted to determine the heavy metals concentration in PS, POFA, and OPC. An experiment of X-Ray Fluorescence (XRF) is done to determine the heavy metals concentration and the chemical composition of OPC and POFA whereas the experiment for PS is conducted by the Kualiti Alam Sdn Bhd using the method of USEPA SW 846 6010 B.

The second stage is the designation of S/S matrices mixture to enhance the S/S method with incorporation of POFA as a partial cement replacement. This mixture design aims to maintain the hazardous substances inside the matrices and enhance
the immobilization of the toxicity from leaching out. The main component in this stage is to determine the ratio of OPC to be mixed with POFA using S/S method. Thus, the formulation of S/S matrices by using a predefined mold with different percentages of OPC and POFA is tested for its short-term leachability behaviors called the Synthetic Precipitation Leaching Procedure (SPLP). The compressive strength test is also conducted on the S/S matrices. Next, all the results are compared with the BS standard on the standard solid cement cube and landfill minimum disposal strength.

The third stage is about the S/S method as a treatment for petroleum sludge (PS). The short-term leachability test is executed to determine the heavy metals concentration of the PS mixed with POFA and OPC after the encapsulation. The leaching test methods, the Toxicity Characteristic Leaching Procedure (TCLP) and SPLP used on crushed matrices are short-term tests. After that, the results from these tests are compared with the USEPA standard. The compressive strength test is also conducted on S/S treatment method matrices. All the results from the compressive strength test are then compared with the BS standard on standard solid cement cube and landfill minimum disposal strength.

The final stage is to investigate the leachability behaviors in a long-term period for the optimum S/S matrices and S/S treatment. The leachability test, namely Static Leachate Test (SLT) is conducted on the solidified matrices. The results are then compared with the USEPA standard.

1.5 Significant of study

The findings from this study provide a fundamental information on a method to eliminate the enormous quantities of PS from the environment in a sustainable way and reduce the adverse effects of this sludge by encapsulating it within predefined matrices using the S/S method and also utilizing the POFA as a cement replacement. In petroleum industries, the PS generated can cause a serious pollution to the environment if it is not being taken care of. Thus, this study provides important information about the PS treatment in a sustainable manner by minimizing its pollutants to the environment.
The potentials of the POFA as a cement replacement are its low-cost effective material in the S/S method through its performance of the leachability behavior and the POFA properties could yield a very useful knowledge towards the feasibility of its usage. Furthermore, the findings of this study have helped in reducing the disposal of PS and POFA as well as providing a potential secondary raw material in different applications.

Due to the increasing of cement price year by year, this study provides a new knowledge about the effectiveness of POFA utilization as a cement replacement in PS matrices using S/S method. It also generates a new potential product that is sustainable in terms of materials used. The matrices generated using waste called PS with enhanced strength using POFA as partial cement replacement to OPC. This matrices could be used as sustainable alternative material in construction and other area.

CHAPTER 2

LITERATURE REVIEW
This chapter elaborates the study in detail on raw materials, namely petroleum sludge (PS), palm oil fuel ash (POFA), and ordinary Portland cement (OPC) using a remediation method known as solidification and stabilization (S/S) method.

The discussion begins with the characteristics, compositions, sources, and the adverse impacts of PS, POFA, and OPC. It is then followed by the elaboration of sludge remediation methods and finally S/S method as well as its applications.

2.2 Introduction, sources, and adverse impacts of raw materials

In this section, all sources of the raw materials such as petroleum sludge (PS), palm oil fuel ash (POFA) and ordinary Portland cement (OPC) are recognized and the adverse impacts of each material are described.

2.2.1 Introduction of Petroleum Sludge (PS)

According to Ling and Isa (2006), petroleum is primarily utilized for generating fuel oil and petrol which are essential "primary energy" sources. Energy-rich fuels (petroleum-based fuels) such as petrol, diesel, jet, heating, and liquefied petroleum gas are the products from the conversion of a total of 84% by volume of the hydrocarbons exist in petroleum.

During petroleum production, the hazardous wastes generated may comprise waste water, drilling fluid, and bottom tank sludge. Wang et al. (2012) defined sludge as a general term used to elucidate the residual deposited at the base of the tanks and other types of storage vessels. The capacity of a refinery dictates the volume of petroleum sludge generated, the bigger the refining capacity the larger the production amount of petroleum sludge (Wang et al., 2012).

As mentioned by Bayoumi (2009), there are many factors affecting the characteristic of sludge such as the immense diversity in the quality of crude oils, the
dissimilarities in the processes done in the oil-water separation, the leakages during the industrial operations as well as the mixing with the existing oily sludge.

TERA (2008) stated that due to the high viscosity and the hazard of the sludge, it is difficult to be hydrated. Most of the oil sludge elements have been recognized to be cytotoxic, mutagenic, and potentially carcinogenic (TERA, 2008; Sidney, 2008; Bayoumi, 2009). PS is made of water in oil emulsion and suspended solids as indicated by TERA (2008). The sludge primarily comprises about 55.13% of water, 9.25% of sediments, 1.9% of asphaltenes, 10.5% of wax and 23.1% of light hydrocarbons (Asia et al., 2006).

There are many reports over the years that PS contains volatile organic carbons and semi-volatile organic carbons that are genotoxic (Mishra et al., 2005; Prakash et al., 2015). The oil from the pyrolysis is basically composed of Polycyclic Aromatics Hydrocarbons (PAH) such as naphthalene, acenaphthylene, phenanthrene, fluoranthene, benzo[a] anthracene, benzo[fluoranthenes, benzo[pyrenes, indene[pyrene, benzo[ghi]perylene, and anthanthrene (Dominguez et al., 2003).

2.2.1.1 Sources of Petroleum Sludge (PS)

Petroleum sludge (PS) has been categorized by the United States Environmental Protection Agency (USEPA) as a hazardous organic complex (USEPA, 1997; Prakash et al., 2015). In the industry of petroleum, a huge quantity of oily wastes generated at both the upstream and downstream operations is called sludge. Among the processes involved in the upstream operation includes extracting, transporting, and storing crude oil. On the other hand, the downstream operation can be referred as the crude oil refining process (Islam., 2015).

Sludge is produced by refining the crude oil and the excess deposited at the bottom of the crude tank is scraped. According to Petronas personnel, there are more than ten tanks of sludge produced daily by refinery waiting to be disposed.

Ubani et al. (1999) indicated in their research that in the upstream operation, the slop oil at oil wells, crude oil tank bottom sediments and drilling mud residues are among the related sources of oily sludge. Moreover, according to Dindar et al. (2013), a diversity of sludge sources present in the downstream process such as the
slop oil emulsion solids, residues from oil/water separator, sediments at the base of the storage tanks, heat exchanger bundle cleaning sludge and surplus activated sludge from on-site wastewater biological treatment plant.

There are few factors affecting the sludge quantity generated from petroleum refining processes such as crude oil properties in terms of density and viscosity, refinery processing scheme, oil storage method, and most significantly, the refining capacity (Mishra et al., 2005). A bigger refining capacity is usually interrelated with a huge quantity of sludge generation.

Every 500 tons of processed crude oil has been approximated to generate one ton of oily sludge waste. It is estimated that more than 60 million tons of sludge can be produced every year and more than 1 billion tons of sludge has been accumulated worldwide (Mishra et al., 2005). As studied by Prakash et al. (2015), it is also anticipated that the increasing demand in refined petroleum products globally would lead to the escalating amount of the total sludge production.

2.2.1.2 Adverse Impacts of Petroleum Sludge (PS)

Sidney (2008) in her study revealed that crude oil sludge is a recurrent issue leading to corrosive effect and depletion in oil storing capacity. Sludge is an oxidized product or a chemical compound resulting from the oxidation of the hydrocarbons in the oil, forming insoluble materials, mostly organic in nature, such as dirt, grit, tank rust-scale, and other equivalent materials (Prakash et al., 2015). Conventional practices in dumping oil sludge have resulted in significant effects on the environment and humans. Around the globe, there are thousands of pits that are used as dumping sites for sludge (Prakash et al., 2015). Sludge dumped at these sites contaminate the groundwater by leaching through the soil and the contaminated soil migrated due to dust weathering.

Light hydrocarbons evaporated from these sites caused the contamination of air which added to greenhouse gases. Finding new sustainable technologies would permit the diminution of sludge dumping and environmental issues associated with it as eloquently stated by Asia et al. (2006).
This current issues faced by Petronas Refinery are the removal of sludge which required a high cost. The economic effect involves the cost of sludge removal and disposal, where the greater expenses required for the disposal fee of the environmentally-unfriendly material (Johnson et al., 2015).

Bojes and Pope (2007) stated that sludge contaminants are able to enter the environment because of the human activities which includes improper treatments and management, deliberate dumping, transportation, storage, and landfill disposal. The long-term exposure towards human is associated to the renal dysfunction.

The presence of heavy metals in sludge may have deleterious effects on the hydrocarbon oxidizer in decomposing. These high concentrations of heavy metals cause the sludge to be harmful towards the environment and the organisms need to discover remedies for the environmental protection (Asia et al., 2006).

2.2.2 Introduction of Palm Oil Fuel Ash (POFA)

The huge generation of palm oil in Malaysia has made Malaysia end up to be the second biggest palm oil producer globally in 2010 where 18.6 million metric tons of oil palm has been generated (Subramaniam et al., 2008).

This study uses the palm oil fuel ash (POFA) as a binder encapsulated with petroleum sludge (PS) to reuse and repurpose it. POFA has an exceptionally constrained utilization for other purposes since it does not contain adequate supplements to be utilized as fertilizers. Consequently, it is usually dumped into the open fields close to the palm oil industrial facilities, hence leading to environmental pollution and health hazards (Kroehong et al., 2011). In order to rectify these issues, a few studies are carried out to determine the feasibility of utilizing POFA as construction materials.

One of the industries that can utilize the palm oil wastes is the construction industry. Recently, many researchers have conducted various studies on the use of a recycled material as recycled aggregates and pozzolans since pozzolans contains silica oxide which can react with calcium hydroxide (Ca(OH)₂) during the hydration process (Abdul Munir et al., 2015).
In addition, by using POFA as a cement replacement, masonry block would be affordable since POFA is a free material. The greater the percentage of cement replacement, the lower the cost of the masonry block produced (Rahman et al., 2014). The price of the material cost affects the cost of the masonry block. Therefore, since cement masonry block cost is expensive, it is encouraged to use the recycled materials to replace the cement in order to obtain cheaper masonry block. Thus using POFA as replacement would reduce the cost of cement used.

These findings offer many advantages with respect to environmental management. In the meantime, huge amount of POFA being discarded in the landfill can be reduced. In addition, the utilization of low cost industrial agricultural waste could lead to a reduction in production cost. POFA has been employed in numerous applications. For instances, as the raw material for geopolymer composite, wastewater treatment, cement replacement in the production of concrete, and air purifier in cleaning atmospheric contaminants (Dahlan et al., 2007).

2.2.2.1 Sources of Palm Oil Fuel Ash (POFA)

Regarding the environmental contamination, palm oil industry has started to look for an effective solution for this huge amount of waste can be utilized. The utilization of waste produced by the palm oil industry as a composite material not only enhance the sustainability, but also solve the huge issues on waste problems. The abundantly produced waste from the palm oil industry has led to criticism. The wastes such as palm fibers, nut shells, palm kernel, and empty fruit bunches are the solid wastes obtained from the oil extraction in palm oil processing. Kroehong et al. (2011) analyzed that the production of these ashes is estimated more than 4 million tons per year in Malaysia only. This waste is not reused and mostly disposed into the landfills which lead to several environmental problems (Kroehong et al., 2011).

Furthermore, after incinerating these wastes, two kinds of POFA are produced which are boiler ash (BA) and POFA. BA is obtained from burning the palm fiber and kernel shells in the boiler where it comprises of clinkers and ash (Kroehong et al., 2011). Meanwhile, as a by-product of a power plant, POFA creates
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