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VITRIFICATION OF PETROCHEMICAL SLUDGES CONTAINING HEAVY METALS

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ABSTRACT

Increasing amounts of petrochemical sludges that need to be disposed in a safe and economical way have become a very important issue in waste management. This study aimed to reduce leaching of heavy metals from petrochemical sludges using the vitrification method. The ashing temperature of 985°C was selected in preparing the ash of the dried sludge prior to the vitrification process at 1100°C to 1400°C. Scanning Electron Microscope (SEM), Thermogravimetric (TGA) and Toxicity Characteristic Leaching Procedure (TCLP) analyses were carried out on the vitrified samples. Some heavy metals namely Al, Au, Fe, Ni, Mn and Zn were found in the raw sludge. Results showed that the concentrations of Al and As decrease as the vitrified temperature increased. The vitrification method exhibited excellent output in immobilizing the transition metals leading to a reduction in environmental pollution caused by petrochemical sludge containing heavy metals.

1.0 Introduction

A petrochemical sludge is a residue produced from the refining process which mainly consists of hydrocarbon, heavy metals and some inert materials. The sludge is highly carcinogenic with, low allowable release concentrations and an ongoing accumulation in land/water ecosystems. Materials that show radioactivity, bio-concentration, flammability, reactivity, toxicity and carcinogenic characteristics were defined as hazardous wastes [1].

Treated petrochemical sludges were found to contain poly-nuclear aromatics PNAs which exhibit high organic partition coefficients, low vapour pressures, very low aqueous solubility, and a tendency to bio-accumulate in the natural environment [2]. The regulatory concentration limits for the 39 contaminants, as analyzed by the Toxicity Characteristic Leaching Procedure (TCLP), range from 0.008 mg/L to 400 mg/L [3]. Various studies on the composition and pore size distribution of petrochemical sludges [4], bio-sludge as an adsorbent resource [5, 6], land treatment of petrochemical wastes [7] and biodegradation of petrochemical wastes [8] have been carried out.

Increasing population, consumerism and industrial development have led to an increase in the quantities of hazardous and municipal solid waste (MSW) worldwide. Various thermal processes, including incineration, pyrolysis, melting or vitrification, have been proposed for treating these hazardous wastes prior to disposal; their aim is to destroy the organic fraction and convert the inorganic fraction into an inert silicate slag, or glass, that can either be advantageously reused, or harmlessly disposed of in an inert landfill [9]. Vitrification is a unique thermal treatment of wastes that has become widely used. It is a new approach for solid waste management as it has been proven to be the one of the most promising and low-cost methods for the stabilization of hazardous solid wastes. The process has been applied for various forms of urban, industrial and radioactive wastes [10].

Vitrification has a number of important merits such as large waste volume reduction, low cost application, negligible mass of by-products and the ability to produce marketable materials. The toxic elements and chemical substances can either participate in the formation of the glass network or be captured in the form of precipitates or crystals in the glass network. This study aims to establish a vitrification treatment by which heavy metal contents in a sludge is stabilized and transformed into a stable form.

2.0 Materials and Methods

2.1 Sample Preparation and Vitrification

In this study, the petrochemical sludge was taken from a PETRONAS (national oil company) refinery wastewater treatment plant located in Melaka, Malaysia. Volatile matters and fixed carbon content on dried basis were determined using a thermogravimetric analyzer (TGA) with a heating and cooling rate of 5^{o}C/min at 50 mL/min using N_2 as the inert gas for purging.

Prior to the vitrification experiment, these sludge samples were dried at 105^{o}C for 1 to 2 days. The ashing temperature was at 985^{o}C (Figure 1a). The sludge samples were heated using a furnace at heating rates of 5^{o}C/min and 10^{o}C/min for 16 hours. All samples were vitrified at temperature ranges from 1100 to 1400^{o}C in 2 hours with a constant rate of 5^{o}C/min, followed by a cooling stage until room temperature is achieved as shown in Figure 1b.

(a) **(b)**

Figure 1: Petrochemical Sludge:
(a) After Ashing at 985 ^{o}C; (b) After Vitrification at 1400 ^{o}C

2.2 Compositions and Metal Leaching of Slags

The concentration of metals in a solid sample was analyzed via acid digestion of the dried sludge according to US EPA method 3050B [12]. The content was evaluated using an Optical Emission Spectrometer (Perkin Elmer Optima 3700 DV) to determine the composition of the specimens. In this experiment, each sample was analyzed three times to ensure good reproducibility. In addition, a scanning electron microscope equipped with an EDX detector was used to study the texture and chemical elements present on the surface of the samples.

Table 1 shows the metal compositions in the raw sludge. The compositions of eight hazardous metals including Fe, Al, Mg, Au, K, Zn, Pb and Ni in ash were 349.40, 103.91, 41.47, 30.08, 25.82, 1.89, 1.89 and 1.66 mg/L, respectively. These compositions were roughly similar to those found by Lin *et al.*[5] and Brown *et al.*[8].

Table 1: Heavy Metals Concentrations of Raw Sludge and EQA Limits (mg/L)

Analyte	Fe	Al	Mg	Au	K	Zn	Pb	Ni
Average conc.	349.40	103.91	41.47	30.08	25.82	1.89	1.89	1.66
EQA standard	5.00	NA	0.20	NA	NA	2.00	0.10	0.20

**NA: not regulated*

3.0 Results and Discussion

From the study of the thermal behaviour of the ash, investigated by thermogravimetry analysis, the curve presented in Figure 2 was obtained. The moisture contents and the ash contents of the raw petrochemical sludges were determined by oven drying to constant weight and were found to be 78.25% and 56.9% (dry basis), respectively. The total weight loss determined by TGA is approximately 90.63%. Previous study by Lin *et al.* [5] shows that the sludge moisture contents were between 75 to 80%.

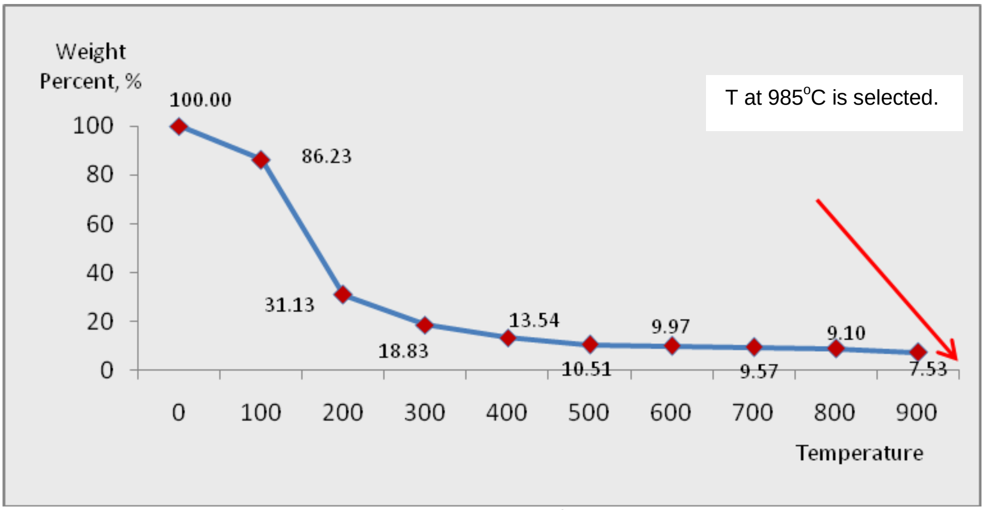

Figure 2: TGA Curves for Vitrified Sludge at 985°C

The TCLP results are shown in Table 2. The results revealed that all elements except As at vitrification between 1100 and 1350°C were within the EQA standard. The concentrations of Mn and Zn were found to decrease as the vitrified temperature increased. The results indicated that all leaching metal concentrations were below the EQA regulation standards, which were consistent with the results reported by Li *et al.* [5].

In general, chemical stability is consistent with the progressive formation of more compact and interconnected glass network structure [11]. As shown in Table 2, the concentrations in the vitrified sample were significantly lower than the metal concentrations in the raw sludge. Therefore, vitrification of petrochemical sludge waste resulted in the reduction of metal leachability.

3.1 SEM analysis

SEM images were quantitatively analyzed for vitrified samples in the temperature range of 1100 to 1400^{o}C at ashing temperature of 985^{o}C, as shown in Figure 3. It can be seen from Figure 3a, that the surface was uneven caused by many bubbles and holes that were given off during vitrification of the volatile organic compound.

As the vitrified temperature was increased to 1200^{o}C, more bubbles appear on the surface as shown in Figure 3b, which probably was caused by the release of air trapped in the melted sludge. The bubbles size decreased as the temperature increased. From the image in Figure 3c, it should be noted that some uneven surfaces were seen reflecting the contaminants. Figure 3d shows the surface at vitrification of 1350^{o}C that contains holes which can be seen in the image as a black dot. Figure 3e shows stable and smooth surface that yielded the most desired glass structure at a vitrification temperature of 1400^{o}C.

Table 2: Recovery Metals of Vitrified Sludge

Analyte	Concentration (mg/l)					EQA standard
	T=1100°C	T=1200°C	T=1300°C	T=1350°C	T=1400°C	
Ag	0.000	0.000	0.000	0.000	0.000	0.100
Al	6.261	7.075	0.836	4.019	3.119	NA
As	0.087	0.073	0.118	0.056	0.027	0.05
Au	0.702	0.701	0.712	0.705	0.709	NA
Cr	0.000	0.000	0.000	0.000	0.000	0.05
Fe	0.743	1.579	0.5	1.349	1.693	5.0
Mn	0.4	0.314	0.02	0.035	0.052	0.2
Ni	0.000	0.000	0.000	0.000	0.000	0.2
Zn	0.000	0.03	0.000	0.000	0.053	2.0

**NA: not regulated*

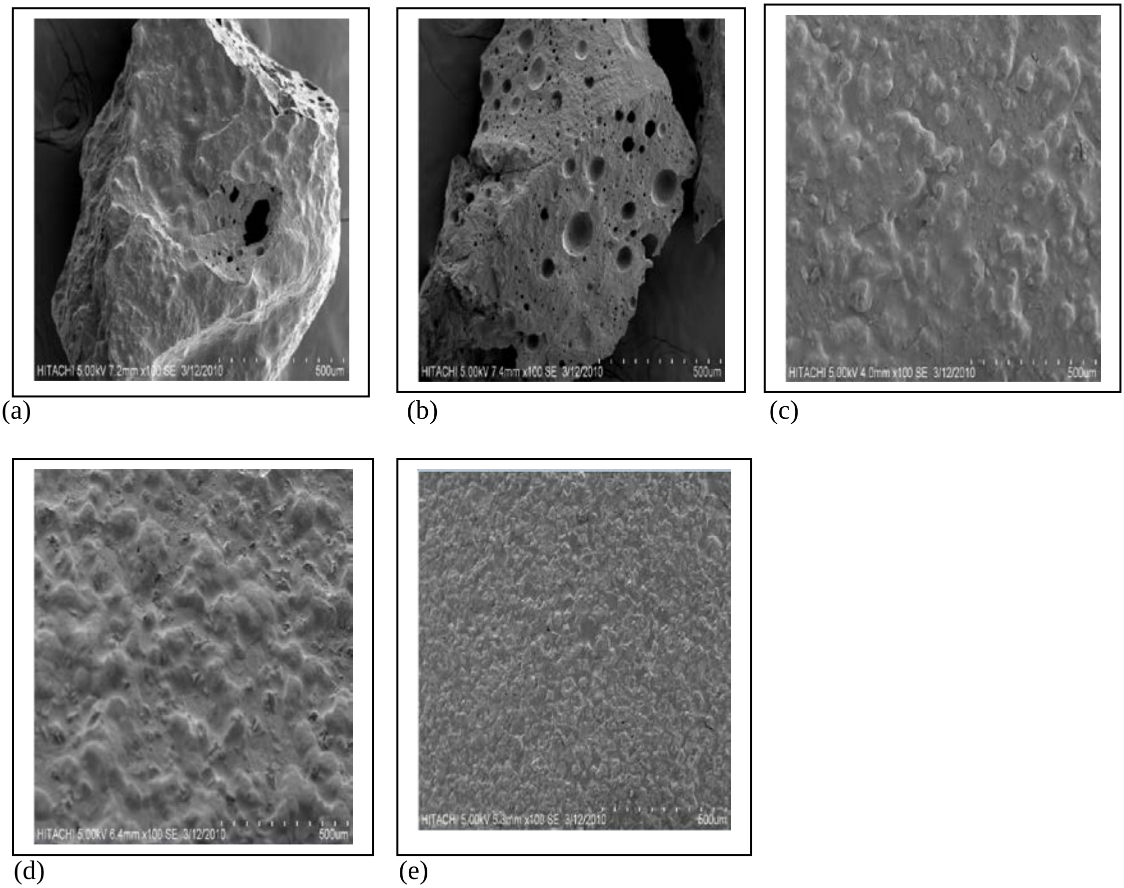

Figure 3: SEM Microphotograph at Magnification with Vitrified Temperature at (a) 1100^{o}C (b) 1200^{o}C (c) 1300^{o}C (d) 1350^{o}C and (e) 1400^{o}C

4.0 Conclusion

The ash content, moisture content and total weight loss of petrochemical sludges were found to be 56.9%, 78.25% and 90.63%, respectively. From the experiments, the solid residues obtained after vitrification treatments exhibited a considerably lower leaching of heavy metals contents than the raw petrochemical sludge with a smooth surface morphology obtained at a vitrified temperature of 1400^{o}C. It can be concluded that the vitrification process should represent a reliable, environmental friendly and safe solution for stabilizing and converting petrochemical sludges into useful products.

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