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SOLIDIFICATION/STABILIZATION OF NONVALUABLE RESIDUE FROM WASTE PRINTED CIRCUIT BOARD ASSEMBLY

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ABSTRACT: The process of copper recovery from waste printed circuit board assembly (PCBA) has remained a large fraction of solid waste called "Nonvaluable Residue (NVR)". This residue is considered to be a hazardous waste because Pb, Cu, and Sb exceed the regulatory levels. Solidification/Stabilization (S/S) treatment technique is selected to improve waste characteristics before disposal of in hazardous waste landfills. In this study, a cement-based solidification/stabilization was used to treat NVR. Unconfined compression strength test (UCS) and toxicity characteristic leaching procedure (TCLP) were mainly used for physical and chemical characterization of the solidified/stabilized products. After curing for 28 days, the compressive strength and heavy metal leachability (Pb, Cu, Sb) were tested. The results showed that the compressive strength of blank sample was 20.75 MPa while compressive strengths of the solidified/stabilized NVR products were 7.36, 4.17 and 1.35 MPa for 20%, 30% and 40 wt% of NVR, respectively. All experimental mixture ratios satisfied the UCS requirements (0.35 MPa). In addition, the concentrations of Pb, Cu, and Sb in the TCLP leachate of all solidified/stabilized NVR products were lower than the limit value and the original waste. This study indicated that cement-based S/S treatment process was able to improve heavy metal immobilization and subsequently minimize potential environmental impacts in landfill disposal.

Keywords: Nonvaluable Residue (NVR), Waste Printed Circuit Board Assembly (PCBA), Heavy Metals, Solidification/Stabilization

1. INTRODUCTION

Nowadays the growing demand for technology and innovation has caused an immense amount of waste generation. Besides demand, one fact is that the lifespan of more products is decreasing; therefore, the large volume of waste stream is rapidly increasing. Waste electrical and electronic equipment (WEEE) or electronic waste such as computers, TVs, fridges, washing machines and cell phones is one of the fastest growing waste streams in many countries. According to the Department of Industrial Works report, in 2014 WEEE in Thailand generated over 20 million units, and had a trend to increase about 10% every year [1]. A main component in the electrical and electronic equipment (EEE) is printed circuit board assembly (PCBA) described as printed circuit boards mounted with various components such as semiconductor chips and capacitors. Although the proportion of PCBA is present only 3 to 6% of the WEEE total weight [2], [3], it has been discarded as waste in large amounts followed by an immense consumption of EEE products.

In general, the waste PCBA comprises about 40 wt.% metallic fractions (MF) and 60 wt.% non-metallic fractions (NMF) [4]. Several precious metals such as copper, gold, and silver are found in these wastes [5]. For nonmetallic fraction (NMF) the material compositions varies with the source and type of waste PCBA [6]. According to Yokoyama and Iji [7], the NMF consisted of glass fiber (65 wt%), cued epoxy resin (32 wt%), and impurities, e.g., copper and solder. The major economic force for recycling waste PCBA is the value of the MF, especially copper, gold, and silver [6]. At present, Thailand can recover only copper from waste PCBA [8]. The process of copper recovery from waste PCBA has remained a large fraction of solid waste residues. In this study, so called "Nonvaluable Residue (NVR)," which contains a variety of metals, e.g., gold, silver, lead and nickel and other toxic substances, including Brominated Flame Retardants (BFRs), could contaminate and is consequently harmful to the environment and humans. Most hazardous/ industrial solid wastes are treated by combustion or secured landfilling. These waste management methods can cause enormous damage to the environment if not properly treated. The combustion of the NVR could cause the formation of highly toxic polybrominated dibenzodioxins and dibenzofurans while landfilling of the NVR would lead to secondary pollution caused by heavy metals leaching to the groundwater [4], [9]. Therefore, before disposing NVR as hazardous waste by landfilling, it must be stabilized and solidified.

The solidification/stabilization (S/S) is a widely accepted technology for the immobilization of hazardous substances before their disposal such as heavy metals contained in waste. Cement solidification/stabilization is one of the most popular S/S techniques due to its low cost and wide availability [10], [11]. As can be found in other studies, the cement-based S/S is used to immobilize heavy metals in different waste types, for example, Pb and Zn in metallurgical dust [12], Cu, Zn and Ni in plating sludge [13], and Ba in sludge [14]. To date few studies have been conducted on the solidification/stabilization of electronic waste or waste PCBA. To reduce the leachability of the heavy metals contained in NVR and minimize the potential of environmental impacts, this paper aims to study the efficiency of the stabilization and solidification of heavy metals contained in NVR from the waste PCBA using Portland cement.

2. MATERIALS AND METHODS

2.1 Materials and Sample Preparation

The powder material of NVR carried out in this study was obtained from the electronic waste recycling plant in Thailand. This powder remained from the copper recovery process of waste printed circuit board assembly using mechanical and physical methods. The PCBAs were mainly dismantled from waste televisions and computers from a wide range of models and manufacturers. These derived PCBAs were single-sided boards with single-sided layer of copper. According to the recycling process using mechanical and physical methods of this plant, the size of PCBA was reduced by primary and secondary roll crushers and rod mill, respectively. After that, copper was separated from the material using a shaking table. PCBA scrap from the shaking table was divided in three parts: head (high density, medium (medium density), and tail parts (low density). A large fraction of fine particles coming from the tail part was NVR, waiting for further treatment and disposal. This NVR material was collected and used in this study.

In this study, the NVR powder was used to replace ordinary Portland cement (OPC) at a rate of 0, 20, 30 and 40% by weight of the binder. All four mixtures used a water to cement ratio of 0.75, and the ratio of sand to cement was 2.75. Each mix proportion was simply blended in a mechanical mixer and was cast in steel cubical molds at the dimension of 5x5x5 cm. Each mixture gave three cubical samples. After casting for 24 hours, the samples were removed from the molds and cured in water for 28 days. After curing 28 days, the cubical samples were ready for further analyses, e.g., unconfined compressive strength. For X-ray diffraction analysis, all blank samples and solidified/stabilized products had to be crushed to powder before the process of analysis.

2.2 Methods of Analysis

The chemical composition of the NVR powder was analyzed by X-ray fluorescence (XRF) and particle size of NVR was measured using laser particle size analysis (Mastersizer). Moreover, the crystalline phases and microstructures in the blank sample and solidified/stabilized NVR products were identified using X-ray diffraction (Rigaku) and scanning electron microscopy (Hitachi SU8030).

2.2.1 Unconfined compressive strength analysis

The compressive strength of solidified/stabilized products was tested in accordance with ASTM C109 [15]. After curing 28 days, three cubical samples of each mixture were tested using the unconfined compression machine (ADR-Auto V.2.0, ELE International) and average value of compressive strength was reported.

2.2.2 Toxicity characteristic leaching procedure (TCLP)

The metal leaching of solidified/stabilized NVR products at curing time for 28 days was assessed using the toxicity characteristic leaching procedure as defined by the U.S. EPA [16]. The sample was crushed to reduce the particle size to less than 9.5 mm. The crushed sample was extracted using acetic acid solution (pH 2.88$\pm$0.05) at a liquid to solid ratio of 20:1. The extraction vessels were rotated in an end-over-end fashion at 30$\pm$2 rpm for 18$\pm$2 h. The leachate was filtered through a 0.8 µm membrane filter to remove suspended solids and was used to analyze Pb, Cu and Sb present in the leachate by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) following the method 3010 [17].

3. RESULTS AND DISCUSSION

Fig. 1 shows the particle size distributions of ordinary Portland cement and NVR. The particle size analysis showed specific surface area was 1.17 m^2/g of OPC and 0.28 m^2/g of NVR. The mean particle size of OPC and NVR was approximately 21 µm and 208 µm, respectively. In addition, 90% of OPC and NVR particles size were smaller than 48.7 µm and 475 µm, respectively. The results of the particle size analysis showed that the actual fineness and specific surface areas of OPC were much more than the NVR powder. This indicated that the reaction of NVR powder could occur slowly when compared with the reaction of cement powder. The result of chemical compositions of the NVR in this study is presented in Table 1. It is obvious that the highest concentration was bromine (Br). Many heavy metals were found in NVR powder; with the highest concentrations being Pb, Sn, and Cu, in order. According to Thailand Notification of the Ministry of Industry B.E. 2548 (2005) on Disposal of Wastes or Unusable Materials [18], any waste or unusable material that contains or contaminates hazardous materials or exhibits hazardous characteristics including flammable, corrosive, reactive, toxic or having the specified constituents equal or exceeding the Total Threshold Limit Concentration (TTLC) as listed in the Annex 2, is defined as “Hazardous Waste”. The results of chemical compositions of NVR powder in Table 1 show that the concentration of Pb, Cu and Sb exceeded the limit values. Therefore, the NVR powder in this study was identified as a hazardous waste.

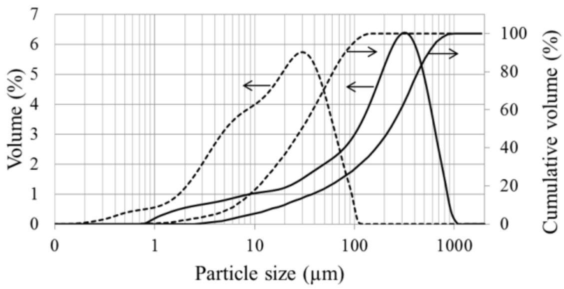

Fig. 1 The distribution of NVR particle size Dashed line: OPC and solid line: NVR

According to many other studies on the improvement of the quality of concrete in terms of strength, durability, and cost reduction, many waste products from natural and industrial process, e.g., silica fume, pulverized fuel ash, blast furnace slag, bagasse ash, rice husk ash, and sheanut shell ash, have been tested and are suggested to be pozzolanic materials or having pozzolanic properties that can be used in concrete paste and mortar [19]-[21]. Pozzolan is defined as a material with an amorphous siliceous or siliceous and aluminous content that reacts with calcium hydroxide in the presence of water to form cementitious hydration products [22]. Based on the ASTM C 618 standard [23] and related research [20], [21], a good pozzolanic performance is likely to contain high SiO_2 or SiO_2+Al_2O_3 or SiO_2+Al_2O_3+Fe_2O_3 content, at least 70 wt%. As seen in Table 1, among all oxide compounds, the presence of Al_2O_3, SiO_2, and Fe_2O_3 is low. Hence, the NVR powder from waste PCBA of this study was not a potential pozzolanic material. This may result in the worst performances of solidified/ stabilized cubes.

Table 1 Chemical compositions of NVR powder

Compositions	NVR	Regulation limit*
Elements (mg/kg)		
Br	32,800	n/a
Pb	12,300	1,000
Sn	12,100	n/a
Cu	11,800	2,500
Zn	3,250	5,000
Sb	2,760	500
Ba	2,730	10,000
Ni	966	2,000
Ag	164	500
Co	43	8,000
Oxides (%)		
Al_2O_3	9.62	
SiO_2	6.35	
Fe_2O_3	1.63	
CaO	0.97	
MgO	0.40	
SO_3	0.12	

Note: *Thailand Notification of the Ministry of Industry B.E. 2548 (2005) on Disposal of Wastes or Unusable Materials (Annex 2); n/a: not available

3.1 Unconfined Compressive Strength

The average compressive strength of solidified/ stabilized products compared with blank samples after curing 28 days is shown in Fig. 2. Blank samples (without NVR) exhibited compressive strength of 20.75 MPa while compressive strength of 20%NVR, 30%NVR and 40%NVR products were 7.36, 4.17 and 1.35 MPa, respectively. The results indicated that the percentage of NVR loading affected compressive strength. The compressive strength decreased when the amount of NVR increased. This was similar to several studies that investigated the effect of cement-waste ratio on compressive strength of solidified/ stabilized waste [19], [24]. According to Malviya and Chaudhary [25], the solidified products with a compressive strength less than 1 MPa were weak because they contained importantly less cementitious materials. In Fig. 2, compressive strength of all solidified/stabilized NVR products was more than 1 MPa. This indicated that all solidified/stabilized samples of this study were relatively strong.

Replacement of cement with NVR powder at the rate of 20 wt.% had the highest compressive strength when compared with 30 and 40 wt.% replacement. The decrease of cement proportion in the mixture causes a decrease of main products of the hydration reaction from Portland cement. This can be explained in that the main products of the hydration, calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$), are the main carriers of strength in hardened cement [19], [26]. This is in accordance with the following peaks of portlandite ($Ca(OH)_2$) by XRD analysis in Fig. 3.

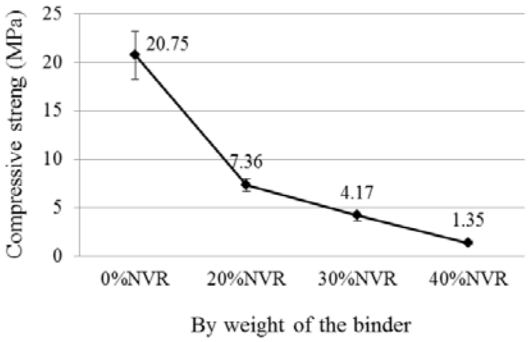

Fig. 2 Average compressive strength of solidified/ stabilized NVR products compared with blank sample

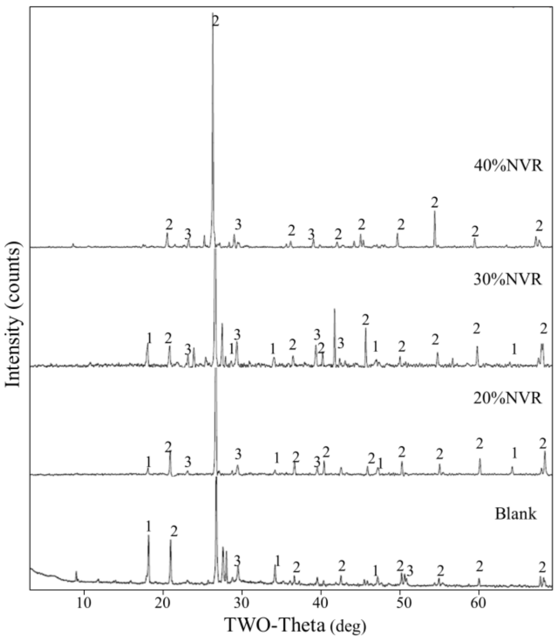

Fig. 3 XRD result for blank and solidified/stabilized products after curing 28 days; 1: Portlandite (Ca $(OH)_2$), 2: Quartz (SiO_2), and 3: Calcite ($CaCO_3$)

The XRD patterns of blank and solidified/ stabilized samples are shown in Fig. 3. Characteristic peaks of quartz (SiO_2), portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$), which can be found in mortar structure, are present in the XRD result. It can be seen that quartz (SiO_2) and portlandite ($Ca(OH)_2$) are major crystalline phases in blank samples. Similarly, XRD patterns also appear in solidified/ stabilized samples but the peak of portlandite ($Ca(OH)_2$) was lower when the NVR was added at a higher rate. The highest peak was SiO_2, which is found in all samples because SiO_2 is a main component of ordinary Portland cement and sand [10], and the NVR powder in this study. In addition, Scanning Electron Microscope (SEM) investigation illustrated another microstructure to improve strength development, called "ettringite", a small needle-like crystal, in both cement paste and NVR paste (see Fig.4). It is obvious that ettringite was formed and observed in cement paste more than in NVR paste. This confirmed less stiff and less durable solidified/stabilized NVR products in this study.

(a)

(b)

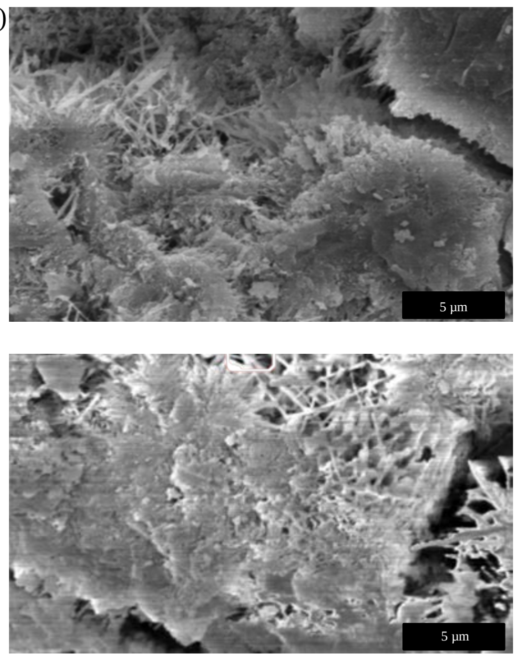

Fig. 4 SEM micrographs of samples at magnification of x10,000; (a) cement paste and (b) NVR paste

Moreover, all cubical samples containing NVR powder were observed to begin swelling and cracking during casting for 24 hours. (as seen in Fig. 5), and stopped afterwards. Regarding the swelling of those cubical samples, it was found that the height of these samples increased between 0.5 and 1.1 cm (or 10 to 22%) when compared with the blank sample. According to Aubert et al. [27], swelling and cracking can lead to loss of compressive strength for solidified/stabilized waste.

This can be explained in that the swelling and cracking resulted from air voids in solidified/ stabilized waste. In this study, 40% NVR powder replacement was the highest content that could be added in the mixture because it revealed a very poor performance of mortar setting. However, the compressive strength of all solidified/stabilized NVR products meets the U.S. EPA requirements of unconfined compressive strength at 0.35 MPa for disposed solidified/ stabilized waste in landfills [28].

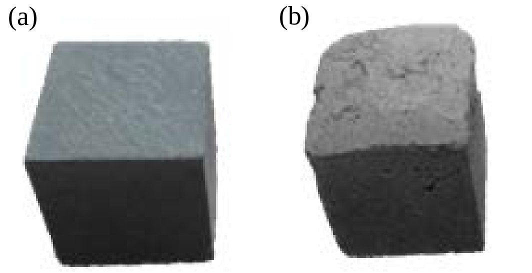

Fig. 5 Solidified/stabilized products; (a) blank sample and (b) solidified/stabilized NVR product

3.2 Toxicity Characteristic Leaching Procedure Test (TCLP)

TCLP test was generally used for chemical characterization of the solidified/stabilized NVR products, and to determine the efficiency of immobilization of heavy metals in the solidified/ stabilized products. In this study, Pb, Cu and Sb were selected as target substances for measurement because these heavy metals were detected at high concentrations in the original material and exceeded the regulation limits as mentioned above. Table 2 shows the metal concentrations in TCLP leachates of solidified/ stabilized NVR samples after curing for 28 days. The results showed that the concentration of Pb in the leachate of all solidified/stabilized NVR samples was lower than the limit value specified by the standard of the U.S. EPA [29]. This means that the cement-based solidification/stabilization technique is effective for immobilization of heavy metals in NVR powder. For Cu and Sb, the U.S.EPA does not specify in the TCLP leachate.

According to Ucaroglu and Talinli [24], when the amount of waste in the mortars increased, the heavy metal concentrations in leachate from the solidified/ stabilized products increased. In Table 2, it can be seen that the more amount of NVR in the mixture, the higher the level of Pb, Cu and Sb concentrations in the leachate extract, except Pb and Sb in the leachate from 40%NVR replacement.

4. CONCLUSION

The NVR powder from waste PCBA in this study was considered to be a hazardous waste because Pb, Cu, and Sb exceeded the regulatory levels, specified by Thailand Notification of the Ministry of Industry B.E. 2548 (2005) on Disposal of Wastes or Unusable Materials. This study primarily showed that the maximum amount of NVR powder that could be added in the mixture was 40% by weight of binder. After curing for 28 days, the compressive strength and heavy metal leachability (Pb, Cu, Sb) were tested. The results showed that all experimental mixture ratios satisfied the UCS requirements (0.35 MPa). Moreover, concentrations of heavy metals in TCLP leachates for all solidified/stabilized NVR products were below the regulation level specified by the U.S.EPA. It can be concluded that the cement-based solidification/ stabilization treatment technique is effective for immobilization of heavy metals in NVR powder from waste PCBA.

Table 2 Metal concentrations in TCLP leachates

Sample	Concentration (mg/L)		
	Pb	Cu*	Sb*
Regulatory limit	5	-	-
Blank	ND	0.13	ND
20%NVR	0.20	0.60	0.24
30%NVR	0.71	1.26	0.27
40%NVR	0.11	2.26	0.14

Note: * Not specified in the leachate from TCLP test by the U.S.EPA; ND: Not detected

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