

INVESTIGATE THE LIBERATION OF COPPER FROM WASTE PRINTED CIRCUIT BOARDS (PCBs)

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Abstract- Nowadays the waste PCBs increasing sharply proportionally the number of personal computers which is 5.7 million in 2005 and the predict amounts, it will be increase to 11.5 Million in 2010 (Unit Perancangan Ekonomi, 2006). From that figure it shows that, computer or Printed Circuit Board (PCB) which is one of the electric and electronic components may cause environmental problems during the waste management phase if it is not properly pre treated. Considering of the environmental problem, recycling of waste PCBs is an important subject not only from the treatment for waste but also from the recovery of valuable materials. The studies are focused on liberation size of copper in waste Printed Circuit Boards (PCBs). Waste PCBs sample were cut, dry crushed and ground down to assemble the criteria of liberation particle size of samples and sieved with the chosen size fraction. Samples were dissolved into aqua regia solution and analyzed with Atomic Absorption Spectroscopy (AAS) to determine the presence of valuable metals in solution that consists in samples. As well, light microscope was used to determine the degree of liberation of copper from PCBs particles. As the result it shows that Cu element (9.97%) is the highest metal composition in PCBs and it is very worth to recycle. At particles size 300 μm , it been seen from microscope that Cu particles start to fully liberated with metal and non-metal element.

Keywords: printed circuit board and liberation.

I. INTRODUCTION.

THE number of personal computers discarded globally has been increasing continuously year by year. Consequently, PCBs are the typical and fundamental component for all computers is also increasing sharply (Hall & Williams, 2007). Many studies have been carried out with regard to the recycling of waste PCBs with a view to recovering resources and at the same time preventing environmental contamination (Cui & Forssberg, 2003; Eswaraiah, Kavitha, Vidyasagar, & Narayanan, 2008; Mou, Wa, Xiang, Gao, & Duan, 2004; Takanori Hino et al., 2009; Yoo, Jeong, Yoo, Lee, & Kim, 2009). According to Veit et al. (2006) and W. J. Hall et al. (2007), the recycling of waste PCBs has now been recognized as a big challenge due consisted of a heterogeneous mixture of organic and metallic chemicals that contained plenty of toxic substances, such as brominated flame retardants (BFR), glass fibre, PVC plastic and heavy metals.

According to Zhang and Forssberg (1999), waste PCBs is proven to be recycling-worthy on the basis of materials composition. Overall, PCBs typically consist of 40% metallic, 30% plastic, and 30% ceramic elements, although their actual composition varies slightly depending on the specific class. The major metallic elements include copper (Cu), iron (Fe), lead (Pb), tin (Sn), nickel (Ni), aluminium (Al), and zinc (Zn). Precious metals such as gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) may also be present in very small quantities (Das et al., 2009; Hugo Marcelo Veit, Bernardes, Ferreira, Tenório, & Malfatti, 2006; Yoo et al., 2009; Zhang & Forssberg, 1999)

Waste PCBs can be considered as industrial ores, as the minerals contained are recovered, processed and reintroduced in the material production systems as industrial ores. Therefore, the principles used in classical minerals processing can be applied to describe the comminution and liberation of waste PCBs during separation and recovery process (Castro, Remmerswaal, Brezet, van Schaik, & Reuter, 2005; Wen et al., 2005). Liberation is obviously the core process in the mechanical pre-treatment. If such an aim is achieved, then not only is energy saved by reduction of

the amount fines produced, but any subsequent separation stages become easier and cheaper to operate. In practice complete liberation is seldom achieved, even if the sample is ground down to the grain size of desired particles. The particles of 'locked' gangue and further liberation from this fraction can only be achieved by further comminution. The "Degree of Liberation" refers to the percentage of samples occurring as free particles in relation to the total content. This can be high if there are weak boundaries between element of samples and gangue particles.

In respect of liberation in PCBs comminution products, a high degree is commonly reported. Zhang and Forsberg (1997) did extensive work on liberation of electronic scrap. In this work liberation of waste PCBs was studied. Basically, it is not energy intensive to unlock the associated materials such as ceramics, glasses and metals with different mechanical properties, depending on the locking regimes of materials involved. In general, materials locked through fastening, by screws, clinks and rivets, inserting, wrapping and packaging can readily be detached. Materials locked by means of coating, binding, welding and encapsulating are relatively difficult to be unlocked and materials locked by alloying and filling can not be liberated by mechanical means.

The "Degree of Liberation" refers to the percentage of samples occurring as free particles in relation to the total content. This can be high if there are weak boundaries between element of samples and gangue particles. Usually, however the adhesion is strong and during comminution, the various constituents are cleft across. This produces much middlings and a low degree of liberation involves directing the breaking stresses at the minerals crystal boundaries.

II. EXPERIMENTAL

Printed circuit boards (PCBs) were collected from obsolete or defective computers that are the largest source of the kind of waste. All the electronic devices such as resistors, capacitors, and inductors were removed from PCBs and feed into the crushing machine named MIKASA MACHINERY PTE.LTD MODEL 200. The comminution stage is a key step of physical process as the separation process and separation effect are subjected to degree of liberation result (Mou et al., 2004). The process in which the waste PCBs composition distribution in particles changes due to breakage is called 'liberation'. Comminution of waste PCBs begins at shearing process by shear shredder. Shearing of waste PCBs was carried out

repeatedly to produce particles of a given size distribution by sieving and sizing. The samples were sieved with the chosen size fraction using Ro-Tap Test Sieve Shaker for 30 minutes. Samples were dissolved into aqua regia solution and analyzed with Atomic Absorption Spectroscopy (AAS) to determine the presence of valuable metals in solution that consists in samples. Qualitative liberation measurement of the comminution waste PCBs was done by examining surface section of the sample in five size ranges fraction of $\leq 63\mu\text{m}$, $75\mu\text{m}$, $150\mu\text{m}$, $300\mu\text{m}$ and $600\mu\text{m}$. The degree of liberation is significant as it determines achievable selectivity. Complementary observations were done with stereo-zoom microscope, Nikon eclipse ME600 optical microscope and Jeol JSM 6460LA scanning electron microscope.

III. RESULTS AND DISCUSSION

After crushing at sufficient time, the particles of samples become finer and more liberate. Table 1 indicates the average contents of major metallic elements in the comminution waste PCBs with particle size classification. Most of the elements concentrated in finer fraction. The distributions of copper and lead clearly differ from those of aluminium, nickel, zinc, and iron. It can be seen that copper and lead were concentrated in the finer fractions of the shredded PCBs. The amount of copper in the fractions of size $\leq 300\mu\text{m}$ was about 73% based on the whole PCBs. This amount is equivalent to 60% of the total six amount of metallic elements contained in the fractions of size $\leq 300\mu\text{m}$. In terms of the metal composition, copper is the main metallic element present in PCBs and it very worth to recovery.

Particle size (μm)	Assay (%)					
	Cu	Fe	Ni	Zn	Al	Pb
1100	8.07	1.7	0.1	2.5	3.0	0.65
		1	0	0	5	7
600	21.4	1.8	0.2	2.1	4.5	1.66
	9	9	2	1	6	8
300	31.3	2.2	0.5	1.8	5.6	2.94
	5	2	0	0	9	5
150	23.5	0.4	0.3	0.3	1.9	4.31
	8	9	6	3	6	5
75	16.5	1.2	0.2	0.9	0.1	5.37
	3	1	7	1	7	3
63		1.9	0.1	0.3	0.6	8.01
	4.18	2	7	6	4	8
<63	2.53	3.1	0.1	0.1	0.3	9.75
		5	0	2	1	5

Table 1 : Average contents of major metallic elements in the comminution waste PCBs with particle size classification.

Comminution process was used to ensure that metal particles are physically liberated from waste PCBs before other separation processes take place. Subsequent to comminution process, the particles of waste PCBs become finer and liberate. At this point, an effective and efficient liberation is a crucial step due to significant heterogeneity and complexity of the materials present in waste PCBs. The liberation results were evaluated by the liberation degree of metals, which is defined as the ratio of free metal particles to the sum of free metal particles and locked metal particles. In this purpose, a combination shear and cutting type shredder was used for liberation of waste PCBs. According to Zhang and Forsberg (1999), the utilization of shear shredder in developing 'Intelligent Liberation' is a vital importance which is oriented towards obtaining materials particles suitable for subsequent separation.



Figure 1: Distribution of comminution fines waste PCBs in five size ranges fraction

In Fig 1 shows the distribution of comminution waste PCBs after sieving process using stereo zoom microscope at 2.0X magnification. It can be seen that in fractions $\leq 600\mu\text{m}$, the metallic particles particularly copper have achieved approximately complete liberation. An alternative approach was analyzed by means of grain counting that used by Zhang and Forsberg (1997). It is found that the metallic particles below 2mm achieve almost complete liberation. Copper

perform as point of reference due to a major metallic element in PCBs and have reddish colour contrast to other metal particles. According to Wen et al. (2005), good liberation of copper is prerequisite to the downstream separation process. However, as shown obviously in Fig. 1(a), copper particle at fraction $600\mu\text{m}$ has accomplished poor liberation due to the presence of copper particle associated with solder resist. PCB solder resist is a permanent epoxy resin based coating applied to

PCBs during the manufacture of the bare board. A solder resist encapsulates and protects all of the surface features of a printed circuit board except the specific areas where it is required to form solder joints. Generally, solder resist green in colour, other popular colours are normally available are red and blue.

In Fig. 1(b), the metal, in particular copper, are concentrated in coarser fraction ($\geq 300\mu\text{m}$). Commonly, metallic materials department to the coarser fractions as metallic materials are generally ductile and do not shatter into finer fractions during comminution process. The general morphology shows the metallic particles are present in very random shapes, indicative of shearing force from shear shredder. The glass fibres remain distinctly fibrous and have an elongated form of particles. On the other hand, the glass fibres notably produce particles well above the particle size $\leq 150\mu\text{m}$ in fraction as shown in Fig. 1(c), (d) and (e) (H. Veit, de Pereira, & Bernardes, 2002).

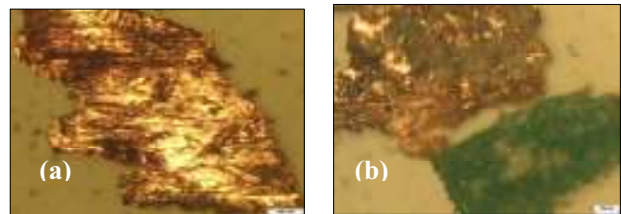


Figure 2: Copper particles at size fraction $150\mu\text{m}$ (a) liberated particle at 400X magnification (b) unliberated particle at 400X magnification.

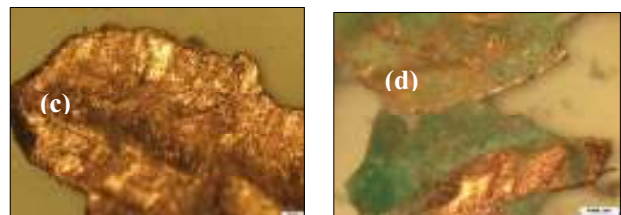


Figure 3 : Copper particles at fraction $300\mu\text{m}$ (a) Liberated particle at 400X magnification (b) Unliberated particle at 160X magnification

Fig. 2 and Fig. 3 illustrate the optical micrographs of the copper particle fraction $300\mu\text{m}$ and $150\mu\text{m}$. It is easy to obtain liberation of the composites present in PCBs, due to lower interfacial bonds when compared natural ores. Basically, it is not energy intensive to unlock the associated

materials such as ceramics, glasses and metals with different mechanical properties, depending on the locking regimes of materials involved. In general, a material locked through fastening, by screws, clinks and rivets, inserting, wrapping and packaging can readily be detached. Materials locked by means of coating, binding, welding and encapsulating are relatively difficult to be unlocked and materials locked by alloying and filling can not be liberated by mechanical means (Zhang & Forssberg, 1999)

In respect of liberation, Fig. 2(a) and 2(a) above it shows that, almost total liberation of Cu particles; however in Fig 2 (b) and 3 (b) indicates copper particles still be found associated with greenish resin of solder resist. It was established that composite or unliberated particles still found persist at this size range although not very abundant. Almost all the particles in both fractions are unlocked, but unliberated particles could still be found. For the finest particle size ($\leq 75\mu\text{m}$), it is not possible to observe liberation in the optical microscope. However, according to Das et al. (2009), a glance at similar data of previous size classes reveals that there should not be any interlocking in this fraction.

SEM analysis provided a more qualitative assessment of the liberation significant. A close up on composite and alloy particle is shown in Fig. 4 to 7. The primary purpose here is to establish whether or not unliberated particles still exist at comminution fines size fraction. Particle make up in the comminution fines waste PCBs has important implications in beneficiation planning. As shown in Fig. 4, at fines fraction $75\mu\text{m}$, there still exist unliberated particle which appears as copper trace unliberated from solder, glass fibre or metallic alloys (Ogunniyi et al., 2009).

In order to increase degree of liberation, waste PCBs need to be broken as fine as possible by extensive comminution. As been notify by Wen et al. (2005), the metals liberation degree of PCBs increases to 100% with decreasing particle size. From liberation point of view, complete liberation is seldom achieved even the waste PCBs ground down to the grain size of desired particles. Further liberation can only be achieved by further comminution. However by decreasing particle size, energy costs substantially increase, and it becomes more difficult to separate particles. Besides, there are some types of joints cannot be destroyed by shredding. According of Castro et al (2005), the unliberated particles could be present in physical joints and chemical joints. In physical joints, the components are fixed together due to the geometry of the joining elements and tend to be more significant in the larger size fraction. Chemical

joints are produced due two materials are joined chemically by inter-atomic or inter-molecular forces between the two materials and tend to be more significant in the smaller size fraction. Additionally, the chemical joints are not destroyed by shredding, once the smallest size class attained is still enclose the typical joint dimensions (Castro et al., 2005).

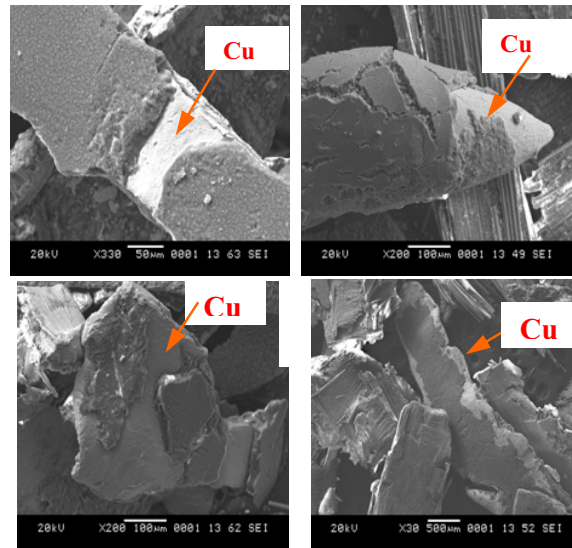


Figure 6: Unliberated copper particle at size fraction $150\mu\text{m}$.

Figure 7: Unliberated copper particle at size fraction $600\mu\text{m}$.

As the conclusion, we can say that the liberation particles can only be achieved by comminution process. Physical analysis using optical microscope approved particles with size $\leq 300\mu\text{m}$ is higher degree of liberation of copper element compared to particles with size 1.1 mm and $600\mu\text{m}$. By chemical analysis using AAS showed element of copper was higher than the other elements of metal contained in printed circuit boards.

ACKNOWLEDGEMENT

This study has been supported by the FRGS grant No. 9003-00064.

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