Non-destructive characterization of mechanically processed waste printed circuit boards - particle liberation analysis

Akira Otsuki, Luc de La Mensbruge, Andrew King, Silvia Serranti, Ludovica Fiore, Giuseppe Bonifazi

► To cite this version:

Akira Otsuki, Luc de La Mensbruge, Andrew King, Silvia Serranti, Ludovica Fiore, et al.. Non-destructive characterization of mechanically processed waste printed circuit boards - particle liberation analysis. Waste Management, 2020, 102, pp.510 - 519. 10.1016/j.wasman.2019.11.006 . hal-03488899

HAL Id: hal-03488899

<https://hal.science/hal-03488899>

Submitted on 21 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution - NonCommercial| 4.0 International License

**Non-destructive characterization of mechanically processed
waste printed circuit boards - particle liberation analysis**

Akira Otsuki^{1,2*}, Luc De La Mensbruge¹, Andrew King³, Silvia Serranti⁴, Ludovica Fiore⁴,
Giuseppe Bonifazi⁴

¹ Ecole Nationale Supérieure de Géologie, GeoRessources UMR 7359 CNRS, University of
Lorraine, 2 Rue du Doyen Marcel Roubault, BP 10162, 54505 Vandoeuvre-lès-Nancy, France

² Waste Science & Technology, Luleå University of Technology, SE 971 87 Luleå, Sweden.

³ Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, BP 48 91192 Gif-sur-Yvette Cedex,
France

⁴ Dipartimento di Ingegneria Chimica Materiali Ambiente, La sapienza - University of Roma,
Via Eudossiana, 18 00184 Rome, Italy

*Corresponding author: akira.otsuki@univ-lorraine.fr

Abstract

This work aimed to develop and propose methods for evaluating the metal degree of liberation to characterize the metal deportment/concentration and liberation/association of mechanically processed waste Printed Circuit Boards (PCBs) that hold the complex and heterogeneity structure and metal distribution/association. Waste PCBs passed through a series of mechanical processing (i.e. comminution, sieving) for the metal recovery were characterized to understand and to evaluate the metal distribution and degree of liberation of the metals in order to optimize the comminution process, avoiding excessive fine particle production. The characterizations were performed at laboratory scale, as well as utilizing large scale experimental facilities, i.e. a portable X-Ray Fluorescence (XRF), micro-XRF and Synchrotron X-Ray Tomography. The proposed methods confirmed that metal liberation was very high in the fine size fraction (0.125-0.350 mm) while many locked particles were identified in the coarse size fraction (0.350-0.500 mm). Such results were analyzed and were discussed in order to better understand metal deportment/concentration behaviors. The advantages and disadvantages related to the different characterization approaches were identified and discussed in this paper, as well as their methodological developments in a waste PCBs' mechanical processing perspective.

Keywords:

Metal deportment/concentration; liberation; elemental analysis; micro X-ray fluorescence; synchrotron; tomography; recycling

1. INTRODUCTION

Waste Electrical and Electronic Equipment (WEEE) is one of the fast-growing waste categories in the European Union, with the growth rate of 3-5 % per year (Eurostat, 2018). It is about 3 times higher than the rate of municipal waste. This is the result of massive production of the WEEE and its market expansion based on the technological progress.

PCBs are the fundamental components of any Electrical and Electronic Equipment (EEE); they represent about 3 wt% of the total electronic waste but they contain precious metals such as gold, silver and palladium as well as base metals such as copper (Kaya, 2016). Thus, there is a huge need and potential for recovering valuable materials from WEEEs. Generally, PCB recycling, finalized to recover metallic fractions includes three stages: the process starts with the pre-treatment which include composition analysis and selective disassembly (Kaya, 2016). Then PCBs are reduced in size through mechanical / physical processes such as shredding, crushing, pulverizing and screening (Duan et al., 2015; Ogunniyi et al., 2009; Wen et al., 2005; Zhao et al., 2004). Finally, chemical treatments are carried out (i.e. pyrometallurgical and hydrometallurgical processes) (Lister et al., 2014; Veit et al., 2006). However, their complex and heterogeneous structures (e.g. mixture of number of different metals, plastics, and ceramics in different sizes) and their variation with time, according to technological improvement as well as primary raw material exploitation strategies, lead to the technical difficulties and environmental issues for their effective pre-concentration stages to improve their recycling. One of the limitations is a lack of proper characterization method to quantitatively evaluate the distribution and liberation/association of different components that are spatially different/heterogeneous, without performing strong milling actions.

There are different categories of particle characterization that can be summarized in: destructive and non-destructive ones, as well as those based on imaging and image analysis (Otsuki et al., 2014). In both case, any information about elemental concentration/distribution or

similar information inside the particles, can be collected. Destructive methods are usually based on the preliminary sample dissolution into acid and the further measurement of the elemental composition by using a chemical method (e.g. atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry). Average values of the different metals, referred to a specific sample, is thus obtained.

Non- destructive methods, quick and easy to apply in terms of particle manipulation, can be directly applied without performing any acid digestion. Among them, the most commonly utilized method is X-Ray Fluorescence (XRF). This elemental analysis is based on measurement of the intensities of the X-rays emitted by secondary excitation. The primary beam irradiates the specimens exciting chemical elements to emit secondary spectral lines that have characteristic wavelengths for each element and intensities related to their concentration. Imaging and image analysis that are major point of this study can be performed with the particles immobilized into resin or mobile particles dispersed under the imaging equipment, such as optical microscope, scanning electron microscope. Following this approach, it is then possible to identify the particle liberations/associations that can be spatially heterogeneous. In this paper, we propose a couple of new solutions belonging to this latter approach, i.e. imaging based methods, using X-Ray based analytical devices.

All the analytical tests were carried out with the samples resulting from processing steps specifically set up to selectively concentrate and recover valuable metals from Printed Circuit Boards (PCBs). More specifically in this work we focused on discussing the applications of different non-destructive characterization methods (laboratory and large scale facility based) to study and understand the liberation and metal/non-metal deportment. Those methods can be applied in different stages of the beneficiation (milling and sieving in this specific case study), in order to enhance the metal recovery for recycling purpose.

The degree of liberation, indicating how much the target component is liberated from the non-

valuable components, is one of the most important factors to determine the successful enrichment of metals through the subsequent processes, such as physical separation and hydrometallurgical process (Koyanaka et al., 2006; Duan et al., 2009; Otsuki et al., 2014).

There are two major methods, both applied in the mineral processing sector, to analyze the degree of liberation of a component in a sample. They are area counting (e.g. Goodall et al., 2005) and particle counting (e.g. Abouzeid, 1990). The first method analyzes the surface area of target component/mineral according to the total surface area of the particles containing the target investigated. It has been utilized in the major liberation analyzers associated with the automated Scanning Electron Microscopy (SEM) systems. The current trend in the mineral liberation analysis is shifted towards the generation of large data sets through this automated SEM, such as MLA/QEM-SCAN (e.g. Goodall and Scales, 2007; Otsuki et al., 2014). This system was developed to analyze the liberation of minerals and have been attracting a lot of attention from both the industry and academic. However, it can be easily identified the potential “intrinsic” difficulty in its application to the analysis of complex electronic wastes due to the nature of samples, furthermore the associated analytical software is specifically designed and set up to analyze only minerals.

The second method, i.e. particles counting, analyzes the number of particles containing the target material liberated over the total number of particles containing the target material (Abouzeid, 1990). This approach can be associated with the computer aided optical microscopy. Both the previously mentioned approaches are 2D based. A 3D based analytical techniques can also be utilized, that is tomography proposed to apply in this paper for the determination of degree of liberation of mechanically processed PCB particles for the first time as far as the authors’ best knowledge.

Tomography is another characterization approach to apply. It is a non-destructive method to image the internal structure of an object by the irradiation of X-ray/neutron. The images of the

analyzed samples are thus displayed with different grey level tones depending on the constituting materials characteristics. Lin and Miller (1996) showed the importance of the determination of the degree of liberation through the evaluation of the volumetric mineral grade distribution, starting from the evaluation of the images (i.e. layers), exhibiting significant grey level differences, of particles constituted by dolomite and sphalerite. The same approach is difficult to achieve for particles resulting from the comminution of complex and heterogeneous electronic wastes. Printed circuits boards can be characterized due to the presence of several matrices/materials/elements (i.e. plastics, metals, alloys, etc.) presenting a different response to X-ray. Zeng et al. (2016) analyzed uncrushed printed circuit boards utilizing a 3D analytical approach based on the Cone Beam Computed Tomography. They worked on the contrast characteristics of the 3D images trying to identify the difference in chemical compositions, based on the differences in the grey levels. Their study did not allow to associate brightness (i.e. image grey level values and resulting voxels associated to the 3D reconstruction) to particles' compositions. On the other hand, this aspect is of great relevance to perform PCBs milled products (i.e. particles) composition determination and material/element deportment and liberation/association assessment as performed in this work for the first time.

Within the above outlined frame, this study analyzed the liberation of metals in comminuted PCBs by hammer mills, using (a) a bench top micro XRF mapping and performing elemental analysis by a portable XRF, (b) optical microscopy based imaging and (c) 3D reconstructed images obtained from Synchrotron X-Ray Tomography. The results of all the procedures were finally discussed with specific reference to the metal degree of liberation and different metal associations. The advantages and disadvantages of the three different methods proposed were also discussed as a summary of the work.

2. MATERIALS AND METHODS

2.1 Materials

Printed circuit boards (origin confidential) were comminuted through shredding and hammer milling followed by sieving. The shredder (Broyeurs-Compacteurs-Destructeurs, BLik) with six thick rotary blades, and equipped with a round sieve opening of 1 cm, was used to crush PCB particles. The hammer mills used were Broyeur Raymond (Laboratoire Stein et Roubaix; called HM1 in this article) with 12 hammers, 5 mm round sieve openings and approximately 630 cm³ free space inside and AR6539 (FORPLEX 00; called HM2 in this article) with 6 hammers, 1.5 mm round sieve openings, 10 cm mill diameter. Hammer milling has been reported as a selective liberation method for metals from PCBs based on the impact force applied through rotating hammers (e.g. Koyanaka et al., 2006; Otsuki et al., 2019-a; Otsuki et al., 2019-b). In this study, two size fractions (i.e. 0.125-0.350 mm, 0.350-0.500 mm) were selected based on our preliminary study identifying the significant difference in the degree of liberation in order to demonstrate the three different approaches to determine the degree of liberation (Eq.1; Abouzeid, 1990).

$$\text{Degree of Liberation} = \frac{N_{\text{unlocked}}}{N_{\text{unlocked}} + N_{\text{locked}}} \times 100 (\%) \quad (1)$$

Where ‘ N_{unlocked} ’, indicates the number of free particles of the metal of interest and ‘ N_{locked} ’ is the number of interlocked particles, either with other metals or with non-metallic fraction, i.e. plastics, glass and ceramics.

In this study, three different methods were performed in order to identify valuable materials for recovery and to evaluate the degree of liberation in two different size fractions. Finally, the results obtained were compared. The three methods are: micro XRF (sections 2.2.2 and 3.2), optical microscopic analysis (sections 2.3 and 3.3), tomography (sections 2.4 and 3.4). Also, a square piece cut off from the uncrushed PCB was used to analyze the elemental composition

prior to the comminution. X-ray fluorescent (XRF) analysis was applied to evaluate the elemental composition of the uncrushed and crushed PCBs.

2.2 Methods

2.2.1 Elemental analysis: portable XRF

XRF measurements for crushed PCB particles and uncrushed PCB characterization were performed with the portable XRF machine (Niton XL3t GOLDD+, Thermo Scientific) in-stand where the analyser was locked on a stationary stand and remotely operated through a connected PC. The Mining Cu/Zu testing mode equipped the full fundamentals parameter algorithm was used and the measurement duration was 120 s / point. Particles were put into a plastic container with X-ray thin film (TF-160-255, MYLAR, Port St. Lucie, FL, USA) window facing the X-ray beam and they were measured to have the elemental composition. The minimum 5 points from each sample were measured while their average and 95% confidence interval were calculated. For the uncrushed PCB, 20 different points were measured while their average and 95% confidence interval were also calculated.

2.2.2 Elemental analysis: Micro XRF

Micro X-Ray Fluorescence (micro-XRF) can be used to analyse both qualitative and quantitative composition of samples and allows high sensitive and non-destructive analysis of elemental composition (Bruker, 2010). In this study, chemical composition and element distribution were obtained using a Bruker M4 Tornado micro X-ray-fluorescence with a Rhodium filament. The applied measurement conditions for the analyses were: pixel time 6 ms/pixel, high voltage 40 kV, anode current 500 μ A, step size 50 μ m, and cycles 2. Micro-XRF was applied to obtain the chemical maps of the PCB samples. With the M4 Tornado software, these results can be presented as element distribution maps with element intensities in

false colors. Using micro-XRF to produce element maps is a potentially way of determining the elements present and their distribution in the sample.

2.2.2.1 Sample preparation

The micro-XRF analysis was carried out for uncrushed PCB in order to obtain the complete mapping. Crushed PCB particles were gently mixed and a small portion was dispersed on a plexiglass support. In some cases, overlapped particles were manually separated by using a spatula. To avoid particle dispersion and their movement during acquisitions, the plexiglass support was lined with a transparent film (Supplementary Figure 1). At the end of this sample preparation procedure, the micro-XRF analysis was performed to evaluate the elemental composition.

2.2.2.2 Particle counting

The ImageJ, 64-bit version Java 1.8.0_112 (70MB), was used for particle counting. The manual counting method was used by the "Cell counter" plug-in (Plugin - Analyze - Cell Counter). This plug-in consists of increasing the number of particle as they are selected by the user. For example, Figure 1 shows the procedure used to calculate the number of particles present in the samples analysed.

Fig. 1 goes here.

2.3 Optical microscopic analysis

A binocular optical microscope was used to capture images for their analysis to perform the liberation analysis of mechanically processed PCB particles. The optical microscope (Nikon SMZ 1000 with the eyepieces C-W10xB/22 Nikon) with objective lens (Plan Apo 1xWD70,

Nikon) was used. It was connected to a PC with the digital camera head (Digital Sight DS-Ri1, Nikon) to save images as digital data. The light source was given by using KL 1500 LCD SCHOOT. The details of the analysis will be given in the following sections.

2.3.1 Sample preparation

The aim of optical microscopic observation was to count metal, non-metal, and locked particles and total number of particles by observing representative samples of the crushed PCB particles, and to calculate the degree of liberation. The comminuted sample stored in a plastic container was gently mixed, its small portion was taken, and gently dispersed on a glass petri dish to aim one particle layer without overlapping. In addition, if necessary, overlapped particles were manually separated by using a spatula prior to the commencement of image acquisition. Then, particles are ready to observe under the microscope.

The optical microscope was focused on particles and start taking images. A series of images of the sample was taken aiming to capture approximately 1000 particles and build a map of particle images. The particle numbers were aimed to count enough number of particles to achieve a statistically representative analysis.

2.3.2 Particle counting

Images taken at different spots of a sample were merged, and the number of aluminum, copper and other type of metallic particles (e.g. alloys) were counted with the software ImageJ after the analysis preparation steps being introduced in the following sections.

The aim of this work is to evaluate the degree of liberation of metal particles; thus, the composite particles (e.g. plastic-metal composite) were considered as locked particles. The direct use of the image analysis software to process a raw image could not be achieved. The ImageJ software can recognize the shape, the brightness and the color of the particles. Thus, for example, a composite of three particles is defined as 3 separated particles according to the

software regardless the fact that they are locked. Such analysis is inappropriate and its correction was necessary. In addition, the contrast between particles and the background was not very high. Black plastics coexisted with white and clear white plastics; thus, a black or a white background cannot help to improve the contrast of all the particles. Supplementary Figure 2 shows the optical microscopic images of crushed PCB particles in 0.125-0.350 mm size fraction. The other graphic software (Inkscape) was used to manually identify individual particles prior to particle counting.

To solve the problems of the direct analysis with the ImageJ, small dots with different colors were plotted on top of each image (Figure 2 (a)) with another software Inkscape to identify the particles before counting with the ImageJ. Different colors were assigned to the different types of particles (e.g. metals, plastics) and their liberations/associations (i.e. liberated, locked). Then, the number of particles can be counted directly by using the ImageJ software upon keeping the dots with applying a white background.

Each image was binarized using the ImageJ software. The color of the particles and their shape can then be easily identified.

Inkscape allowed to combine all the images into one file and to build the entire surface to study (Figure 2 (b)). The same particles between different images were identified and counted only once with this method. Plastic particles were identified in pink dots while metallic particles were given in red dots. Lines were also drawn to limit the surface to study when the same particles were observed in different images.

Fig. 2 goes here.

2.4 Tomography

The images resulting from tomographic analysis showed as the color of plastic particles vary

between black and grey while metallic particles are seen much more bright. The brightest particles in PCBs accounted for Cu. Stacks of 2D images can be used for 3D reconstruction; but this study worked on mainly 2D images with the use of neighboring images to capture the association of the particles situated in the specific 2D cross sections selected for this investigation. Measurements were made in Pisché beamline at synchrotron Soleil (King et al., 2016), a light beam dedicated to X-ray diffraction and tomography by absorption contrast at high level of energy (20-50 keV). This beam line allowed us to optimize the setting for improving the contrast between different particles utilizing the strong X-ray and variety setting options while our preliminary study by using a laboratory X-ray tomography machine showed the difficulty to achieve that objective due to its limitation for distinguish different particles by keeping a good contrast between different particles.

For the sample HM 2b (0.125-0.350 mm), 624 cross sectional images were made with the sample within a four centimeter high plastic tube. The aim is to analyse different layers of the sample and to realize the same work of particle counting as for optical microscopic observation.

2.4.1 Particle counting

The 624 cross sectional images were obtained as a continuous images of the sample. Then, the shape, structure and association of particles were observed and studied. Inkscape was used to identify metal and plastic particles with the same methodology applied to the optical microscopic image analysis. In average 250 particles were counted on each image (the diameter of circular section was 1 cm). Eight cross sectional images significantly separated each other were used to count more than 1000 particles for the representative analysis and describe the sample in order to avoid counting the same particles repeatedly from the neighboring images. They are the #1, 100, 200, 300, 400, 550, 600, and 624. The size of particles in the HM 2b sample are below 350 μm ; thus the gap of more than 20 images was enough to observe and count totally different particles. The #500 had many artefacts, and the measurement was thus replaced by the analysis of the

image #550. A typical image after the contrast optimization used for the analyses is given in Fig. 2 (c) with different color dots assigned to plastic (pink) and metal (red) particles shown in Fig. 2 (d).

3. RESULTS AND DISCUSSION

3.1 Portable XRF measurements

Supplementary Table 1 shows the results of XRF analyses of the crushed PCBs with the hammer mill (a) in comparison with the uncrushed PCB (b). The size of particles are in the range of 0.125-0.350 mm and 0.350-0.500 mm. The metals with the abundant concentrations were listed. The Cu is the major element (35% in uncrushed PCB) of this PCB that corresponds to the optical microscopic observations and agreed with literature (e.g. Ghosh, 2015), followed by Al and Si (Supplementary Table 1). Other metal elements are also detected; but it was hard to identify as liberated particles under the microscope due to the trace elemental concentration and the possible alloy formation. In this study, we focused on Cu and Al for the determination of their degree of liberation.

The uncrushed PCB contains nearly three times higher Cu than the crushed ones. This indirectly indicated that the Cu was successfully separated into other size fractions from the fractions of 0.125-0.500 mm. There was more than 30% of copper in the uncrushed PCB determined from the results of the 20 measurements in its different locations. The uncrushed PCB also contained 13% of sulphur while the crushed PCB contained much smaller than 1% (results not shown in Supplementary Table 1). This indicates that the rejection of sulphur from the size fractions studied and enrichment in other size fractions. On the other hand, the aluminium concentration in non-treated PCB was close to two times smaller than the one in the crushed PCB (1.6% to 3.1-4.5% in 0.125-0.50 mm). This means that the aluminium was enriched into the size fraction studied after the hammer milling, especially in 0.125-0.350 mm.

The elemental concentration in this uncrushed PCB varied: the 95% confidence interval of Cu was 4.95% while the one of Al% was 0.15 from the measurement of 20 different locations. Generally speaking, the elemental distribution within the uncrushed PCB is not homogeneous which agreed with the micro-XRF results shown in the section 3.2, and thus studying a series of different spots is required to have statistically representative results and capture the clear idea of their compositions. More discussion on the portable XRF results can be found in (Otsuki et.al, 2019-a).

3.2 Micro XRF measurements

3.2.1 Uncrushed PCB

Figure 3 shows the digital image and micro-XRF elemental mapping, indicating the element distributions of the uncrushed PCB. The micro-XRF analysis made it possible to identify the chemical elements and to associate them with their functions.

The copper (Cu, Figure 3 (c)) is the major element of this PCB due to its good characteristics of electrical and thermal conductivity. The superficial green layer of PCB is called solder mask. It is a thin layer of polymer, like a lacquer, which is applied in PCBs to protect against the oxidation and to avoid the formation of bridges between close welds (Mitzner, 2009). The solder mask contains silicon (Si, Figure 3 (f)), which is used to control the viscosity of the liquid welding mask before polymerization, barium (Ba, Figure 3 (d)) and sulfur (S, Figure 3 (f)), used as a flame retardant (Woolley, 2013). The serigraphy (letters, numbers and symbols) that identifies the components on the board, is made of titanium (Ti, Figure 3 (e)).

Fig. 3 goes here.

Other materials present inside the PCB are the ceramics; these possess insulating, semi-

conductive, superconductivity, piezoelectric and magnetic properties which made them fundamental materials for microchips and other components present in printed circuits. A ceramic material usually consists of a metallic element and a non-metallic element, such as SiO_2 or Al_2O_3 (Veit and Bernardes, 2015). In fact, Figure 3 (f) indicates the presence of silicon in the chips mounted on the board. In the assembly and interconnection of silicon chips, welding plays a crucial role. The soldering based on lead and tin (63% Sn and 37% Pb) are the classic connection material; Figure 3 (g) show the presence of tin (Sn) and lead (Pb) based solders used for the connection. The sample also contains the bromine (Br, Figure 3 (h)). Bromine is used as a flame retardant, in order to prevent the propagation of an accidental combustion in the electric circuits of electrical and electronic equipment. Noticeable and aligned Br concentration was identified. One can see the PCB producer's intention to segregate several different small equipment colonies to avoid the fire propagation to all the surface. About precious metals such as silver (Ag) and gold (Au), they are found in specific areas such as inside the microprocessor circuit and in contacts. Specifically, connector pins are made of gold and nickel alloy while the gold present in the microprocessor is pure (Figure 3 (j)).

3.2.2 Crushed PCB

The two different particles size classes (i.e. 0.125-0.350 mm, 0.350-0.500 mm) were analyzed, using micro-XRF based mapping in order to identify the alloys, the metals constituting the individual particles and thus the degree of liberation. The analysis showed that most of the metallic particles were weakly locked (<20-30% of particle surface) with plastic, glass fiber, or other metals, in different degrees. The majority of those composites contain small quantities of secondary element (e.g. Br in Cu host in Figs. 4 (b); Si and Ca in Al host in Fig. 4 (d)) that are hard to recognize under the optical microscope due to their small quantities and similar optical properties with the host material most of the cases. Degree of liberation varies with the type of elements (i.e. Cu, Al, other metals) and particle size. Figure 4a, 4b, 4c and 4d show some locked

and unlocked Cu and Al particles identified in the sample HM2b (0.125-0.350 mm). In general, the combination of micro-XRF mappings and stereomicroscope images can help a good identification of liberation/association of metallic components with the PCB particles mechanically processed.

Table 1 summarizes all the results of the analyses carried out on the size fraction 0.125-0.350 mm (HM2b) by using the combination of stereomicroscope images and micro-XRF mapping. The results indicated that the population of unlocked Al particles (1.88%) were twice of the one of Cu (0.94%), out of 319 particles counted, and the degree of unlocked Al particles (86%) was higher than Cu (30%). Their degree of liberation will be further discussed, together with the results of the coarser size fraction (0.350-0.50 mm).

Fig. 4 goes here.

Figures 4e, 4f, 4g and 4h show some locked and unlocked copper and aluminium particles identified in the sample HM2a (0.35-0.50 mm). Although the trend is similar with the fine size (0.125-0.350 mm, Figures 4 (a)-(d)), the analysis showed that composite particles were strongly locked (<60-70% of particle surface) with plastic, glass fiber, or other metals, in wider range of locking degrees (10-70%) than the fine size fraction (10-30%, Figures 4 (a)-(d)). Also, more elements are associated with the host metallic element (e.g. Cu with Al, Si, Ca, Fe, Cu and Br in Figure 4(f); Al with Si, Ca and Fe in Figure 4 (h)) than the ones in fine size fraction (e.g. Cu with Si, Ca and Br in Figure 4 (b); Al with Si and Ca in Figure 4 (d)). The results indicate as the fine grinding/communication enhances the liberation of Cu and Al from other elements.

Table 1 goes here.

Table 1 also shows the results obtained for the HM2a sample (0.350-0.500 mm). These show that the population of unlocked Al particles (1.20%) were the same as Cu (1.20%), out of 249 particles counted although their degree of liberation is smaller (15% Cu, 60% Al) than the ones in the fine size fraction (30% Cu, 86% Al in 0.125-0.350 mm) and will be further discussed together with the results of finer size fraction.

The combination of the stereomicroscope and the micro-XRF analyses showed that most of the metallic particles are locked with plastic, glass fiber and/or other metals. This analysis made it possible to determine the distribution of Cu and Al in the particles and therefore to evaluate their degree of liberation. As shown in Table 1, in the coarse size fraction (0.350-0.50 mm), the number of locked particles is higher than the fine size fraction (0.125-0.350 mm). Table 1 shows the degree of liberation of Cu and Al, calculated by using the results of the combination of stereomicroscope and micro-XRF mapping. Apart from Al in 0.125-0.350 mm (86%), the degree of liberation based on this particle counting method is generally low ($\leq 60\%$) as shown in the Table 1, since the detection of small quantities of other elements within the host metallic elements (Cu, Al) decreases the degree of liberation based on the particle counting. Area counting would increase the degree of liberation and the results could be more representative and useful, especially for the separation/process unit operations utilizing surface or bulk properties of materials of our interest (e.g. Cu, Al) for their selective recovery for recycling. The comparison between the particle counting and area counting is out of focus of this paper and will be published in a separate paper.

3.3 Optical microscope analysis

Table 2 shows the results of particle analysis of the HM2b sample with the size fraction 0.125-0.350 μm with the optical microscope. The 18 images were recorded after spreading the particles on a glass surface. In each image, the number of liberated/unlocked and locked copper, aluminium, other metals (e.g. alloys) particles were counted. Then, the percentage of the copper,

aluminium and total metal were calculated for each image and summarized to capture all the information for the entire surface. The results indicated the Cu 1.66%, Al 4.15% were presented as unlocked particles out of 1326 particles counted.

The efficiency of hammer milling to liberate metals was determined by calculating the degree of liberation of main metals, i.e. Cu, Al, alloys. The results showed a high degree of liberation reaching 85% of Cu, 90% of Al bearing particles. Thus, in total 89% of metal particles were liberated in this size fraction after the hammer milling. The precision of the value could depend on the operator. S/he has to identify the locked particles by differences in shape, contrast, brightness and color of the particles within the grains. Then, there are potentially three major source of errors: (1) a size of the plastic or the metal locked in the grain can be relatively small to be distinguished under the optical microscope that aims to capture many particles for a representative measurement; (2) the contrast between copper and black plastic particles is huge and could hinder those plastic particles; (3) 2D image observation that could be difficult to identify whether particles are locked or liberated but simply overlapped or attached by the electrostatic forces. The 3rd issue can be addressed by using the 3D information extracted from tomographic images and applied in this study. Therefore, there has to be a good balance between the number of particles counted and the image quality of the particles. In addition, a proper dispersion of individual particles without overlapping each other is significantly important.

Table 2 goes here.

The HM2a sample containing coarser particles (0.350-0.500 mm) was also analyzed in order to compare the results with the finer size fraction (0.125-0.350 mm, Table 2). Over 28 images taken, 1234 particles were counted and analyzed. Almost all the copper particles were locked

with plastic or other metals (aluminum, alloys). Also, for aluminum particles or other metals (e.g. tin, alloys), the degree of liberation was low. It means that the size reduction through the hammer milling was not sufficient in this size fraction. Less than 15% of the copper was liberated while 53% of aluminum did. In general, the degree of liberation of metals was 45% that was significantly lower than the value obtained by the finer size fraction (89% in 0.125-0.350 mm). The above mentioned trend observed by the optical microscopic image analysis is similar with the results obtained by the combination of the stereomicroscope and micro-XRF imaging although their degree of liberation is higher (85% Cu and 90% Al in 0.125-0.350 mm in Table 2) than the latter combination (30% Cu and 86% Al in 0.125-0.350 mm in Table 1). This can be due to the different nature of the two methods applied, as mentioned in the previous sections, especially in terms of recognition of composite particles.

3.4 Tomographic image analysis

Total 2050 particles were counted over the images of the HM2b (0.125-0.350 mm) crushed sample. Approximately 250 particles were identified in each image. The challenge was associated with the contrast of each image to identify the dark plastic particles. Some particles seen as isolated in one cross sectional 2D image can be locked with other particles. Thus, the neighboring images were also checked to identify whether they are really isolated or not, with the utilization of the 3D information to track the whole surface of the particles. By knowing such potential errors and utilizing 3D option, the degree of measurement errors kept low with respect to the total number of particles counted in each image. Table 3 contains all the measurement results of particle analysis of the HM2b sample with the size fraction 0.125-0.350 mm with the tomographic images.

Through the analyses of tomographic images, it was rather difficult to distinguish the different types of metals due to the small difference in their grey levels. Thus, only the liberation of the

total metal particles (bright particles in tomographic images) was determined. This is different from the case of Lin and Miller (1996) who studied only two mineral components that have the significant grey level difference indicated by the complete spectra isolation. The liberation % of metal was 80.26% for 152 particles. The value is close to the one identified with the analysis of the optical microscopic images (89%), but away from the one obtained with the micro-XRF analysis (54%). With tomographic images, the identification of the nature of particles is rather limited with the grey scale difference given in the tomographic images due to the limited access to the different range of colors associated with them. On the other hand, utilizing both the grey level and shape of the particles can help us the particle composition. For example, the shape of cable for the brightest particle allows us to identify it as copper cables. With the micro-XRF mapping, the detection of small quantities (<20-30% of particle surface) of secondary elements in the host metallic particles (e.g. Br in Cu, Si and Ca in Al) made the degree of liberation by the particle counting method lower than the other two methods.

Table 3 goes here.

3.5 Comparison between the analyses using micro XRF and image analyses

The three methods provided the similar results in terms of the general trend (i.e. higher degree of liberation with fine particles than coarse particles) with some variation in the absolute values in the degree of liberation and some access limitation (i.e. synchrotron X-ray tomography). The micro-XRF results showed the lower degree of liberation values than the other two methods, by particle counting. This is due to the capability of micro-XRF to detect small quantities of secondary material(s) within the host Cu/Al particles while those secondary materials can be

hard to recognize due to their quantities and/or similar optical/physical properties with their host by using either optical microscope or tomography images.

In any of the three methods, the experimental work in the above-mentioned image analyses showed that the precision of the data and analysis could depend on the contrast and the resolution of the images. In addition, the preliminary knowledge about the nature of the sample (e.g. composition, association) would be of great help for the better analyses, as applicable to all the other analyses (e.g. electron microscopic analyses). Table 4 shows the summary of advantages and disadvantages of micro-XRF, optical microscopic and synchrotron tomographic image analyses for the mechanically processed PCB particles.

The light elements (for example the C present in the plastics) cannot be analyzed by micro-XRF because are weak absorbers and relatively strong scatterers of X-rays. During the optical microscopic observations, the presence of the different types of the color and brightness of particles prevented us from select the best background for all the particles in order to maximize the contrast. In tomography, the grey scale and the artifacts made difficult the identification of the light plastic particles seen as dark spots. Meanwhile, it was relatively easy to identify the locked particles with the both optical microscopic and tomographic images while the tomographic images allowed us see the entire structure of each particle using the 3D information captured.

Table 4 goes here.

4. CONCLUSIONS

The degree of liberation of mechanically processed PCB particles were analyzed by using the images obtained by three different methods, including the methodological developments, for the recycling oriented non-destructive characterization. The three methods were: micro-XRF, optical microscope, and synchrotron x-ray tomography.

The micro-XRF analysis provided the elemental distribution maps of the sample surface and associate them with their functions. It was possible to identify the materials (ceramics, metals, etc.) that are interesting for the material recovery, determine the distribution of the detected element and evaluate the degree of liberation of copper and aluminum in the PCB samples.

The analyses of tomographic images used mainly 2D cross sectional images but also 3D information to investigate whether particles were liberated or not in their whole surfaces. That is one of the major advantages over the analyses of micro-XRF and optical microscopic images. The other difference is that the utilization of color of the particles in the sample. Optical microscopic images can utilize the variety of colors to distinguish different particles while the tomographic images assign only the grey level difference that makes difficult to distinguish different particles with small grey level difference.

Although the similarities/differences among three methods were discussed, the common issues were also identified. The good knowledge of the sample would be of a great help for the operator to distinguish different particles and decide the particle liberation or locked. On the other hand, their accuracy could depend on the operator's judgment and knowledge about the sample to identify and distinguish different particles and the image resolution. The degree of liberation of metals determined by the optical microscope and tomographic image analyses were very close (81% with tomography; 89% with optical microscope), but different from the ones obtained through the micro-XRF mapping (54%) by the particle counting. In general, the metal particle liberation was very high in the fine size fraction while many locked particles were

identified in the coarse size fraction whose trend agreed with the anticipation.

Onsite sampling and measurement to evaluate the degree of liberation and processing performance tuning and the metal recovery performance prediction would be highly efficient and beneficial for recycling process in the future. In order to achieve those goals, next steps would be the application of the proposed methods to confirm their applicability to different materials as well as optimization and automation of the image analysis procedures.

ACKNOWLEDGEMENTS

The author would like to acknowledge the contribution from Ms. Lisa Gasser for sample preparation. A part of results in liberation analysis in this article was presented in Sardinia 2017. Tomography measurement was performed in synchrotron SOLEIL in using the beamline Psiché.

REFERENCES

- Abouzeid, A.Z.M. (1990). Mineral Processing Laboratory Manual, Trans Tech Publications, Clausthal-Zellerfeld, 23-27.
- Bruker (2010). Physical Principles of Micro-X-ray Fluorescence - M4 Tornado.
- Eurostat. <http://ec.europa.eu/eurostat/web/waste/key-waste-streams/weee>, accessed on 18/05/2018.
- Duan, C.L., Diao, Z.J., Zhao, Y.M., Huang, W. (2015). Liberation of valuable materials in waste printed circuit boards by high-voltage electrical pulses. *Miner. Eng.* 70, 170–177.
- Duan, C., Wen, X., Shi, C., Zhao, Y., Wen, B., He, Y. (2009). Recovery of metals from waste printed circuit boards by a mechanical method using a water medium. *J. Hazardous Materials* vol. 166, 478–482.
- Ghosh, B., Ghosh, M.K., Parhi, P., Mukherjee, P.S., Mishra, B.K. (2015). Waste printed circuit

boards recycling: an extensive assessment of current status. *J. Cleaner Production*, vol. 94, 5-19.

Goodall, W.R., Scales, P.J. (2007). An overview of the advantages and disadvantages of the determination of gold mineralogy by automated mineralogy. *Miner. Eng.*, vol. 20, 506-517.

Goodall, W.R., Scales, P.J., Butcher, A.R. (2005). The use of QEMSCAN and diagnostic leaching in the characterization of visible gold in complex ores. *Miner. Eng.*, vol. 18, 877-886.

Kaya, M. (2016). Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. *Waste Manag.* 57, 64-90.

King, A., et al. (2016). Tomography and imaging at the PSICHE beam line of the SOLEIL synchrotron. *Rev. Sci. Instrum.*, vol. 87, 093704.

Koyanaka, S., Endoh, S., Ohya, H. (2006). Effect of impact velocity control on selective grinding of waste printed circuit boards. *Adv. Powder Technol.* 17, 113-126.

Lin, C.L., Miller, J.D. (1996). Cone beam X-ray microtomography for three-dimensional liberation analysis in the 21st century. *Int. J. Miner. Process.*, vol. 47, 61-73.

Lister, T.E., Wang, P., Anderko, A. (2014). Recovery of critical and value metals from mobile electronics enabled by electrochemical processing. *Hydrometallurgy* 149, 228-237.

Mitzner, K. (2009). *Complete PCB Design Using Or CAD Capture and layout*. Elsevier Inc.

Ogunniyi, I.O., Vermaak, M.K.G., Groot, D.R. (2009). Chemical composition and liberation characterization of printed circuit board comminution fines for beneficiation investigations. *Waste Manag.* 29, 2140-2146.

Otsuki, A. Chen, Y., Zhao Y. (2014). Characterisation and beneficiation of complex ores for sustainable use of mineral resources: refractory gold ore beneficiation as an example. *Int. J. Soc. Mater. Eng. Resour.*, vol. 20, 126-135.

Otsuki, A., Gonçalves, P.P., Stieghorst, C., Révay, Z. (2019-a). Non-Destructive

Characterization of Mechanically Processed Waste Printed Circuit Boards: X-ray
 Fluorescence Spectroscopy and Prompt Gamma Activation Analysis. *J. Compos. Sci.*, vol. 3,
 54.

Otsuki, A., Gonçalves, P.P., Leroy E. (2019-b). Selective Milling and Elemental Assay of
 Printed Circuit Board Particles for Their Recycling Purpose. *Metals* vol.9, 899.

Woolley, M. (2013). Corrosives on a PCB: Finding the source. <https://www.edn.com>.

Veit, H.M., Bernardes, A.M., Ferreira, J.Z., Tenório, J.A.S., de Fraga Malfatti, C. (2006).
 Recovery of copper from printed circuit boards scraps by mechanical processing and
 electrometallurgy *J Hazard Mater*, vol 137, 1704-1709.

Veit, H.M., Bernardes, A.M. (2015). Electronic waste. *Recycling Techniques. Topics in Mining,
 Metallurgy and Materials Engineering*. Series Editor: Carlos P. Bergmann. Springer.

Wen, X., Duan, C., Jiao, H., Zhao, Y., Zhou, X., Song, S. (2005). Study on metal recovery from
 discarded printed circuit boards by physical methods. *Proceedings of IEEE International
 Symposium on Electronics and the Environment*, 121- 128.

Zeng, L., Yan, B., Wang, W. (2016). Contrast Enhancement Methods Based on Gray and Its
 Distance Double-Weighting Histogram Equalization for 3D CT Images of PCBs.
Mathematical Problems in Engineering Vol. 2016, Article ID 1529782.

Zhao, Y., Wen, X., Li, B., Tao, D. (2004). Recovery of copper from printed circuit boards.
Miner Metall Proc 21, 99-102.

Tables and Figures

Table 1. Metal and plastic particles counted using the stereomicroscope images and micro-XRF mapping, and calculated degree of liberation of metals in hammer mill products 0.125-0.350 mm (HM2b) and 0.350-0.500 mm (HM2a).

Particle size	Cu			Al			Total number of particles counted	% unlocked particles against total number of particles counted	
	Unlocked	Locked	Degree of liberation (%)	Unlocked	Locked	Degree of liberation (%)		Cu	Al
0.125 - 0.350 mm	3	7	30	6	1	86	319	0.94	1.88
0.350 - 0.500 mm	3	17	15	3	2	60	249	1.20	1.20

Table 2. Metal particles counted using the optical microscopic images, and calculated degree of liberation of metals in hammer mill products 0.125-0.350 mm (HM2b) and 0.350-0.500 mm (HM2a).

Particle size	Cu			Al			Total number of particles counted	% unlocked particles against total number of particles counted	
	Unlocked	Locked	Degree of liberation (%)	Unlocked	Locked	Degree of liberation (%)		Cu	Al
0.125 - 0.350 mm	22	4	85	55	6	90	1326	1.66	4.15
0.350 - 0.500 mm	10	59	14	46	41	53	1234	0.81	3.73

Table 3. Metal and plastic particles counted using the tomographic images. Sample HM2b (0.125-0.350 mm).

Image number	Number of particles		Total	% unlocked metal particles against total number of particles counted	Degree of liberation (%)
	Unlocked	Locked			
1	9	2	266	3.38	81.82
100	12	2	260	4.62	85.71
200	9	3	330	2.73	75.00
300	16	3	260	6.15	84.21
400	13	6	260	5.00	68.42
550	18	2	206	8.74	90.00
600	21	5	247	8.50	80.77
624	24	7	221	10.86	77.42
TOTAL	122	30	2050	5.95	80.26

Table 4. Advantages and disadvantages of micro-XRF, optical microscopic and tomographic image analyses for mechanically processed printed circuit board particles.

Micro XRF		Optical microscope		Synchrotron tomography	
Advantages	Drawbacks	Advantages	Drawbacks	Advantages	Drawbacks
Fast multi-elemental and non-destructive analysis. No need of sample preparation.	Light elements (Li, Be, B, C, N, O and F) are weak absorbers and relatively strong scatterers of X-rays, cannot be analyzed.	Particles can be directly manipulated to disperse under the microscope prior to the commencement of the image acquisition.	Results could depend on the operator's skill and knowledge about the sample.	Large number of particles can be imaged in a short period of time.	Difficulty to distinguish different metals using their differences in grey levels in the presence of many different components.
The creation of elemental maps was realized to check the chemical composition and its distribution/association.	The detection limit (LOD) for heavy elements is greater than 20 ppm.	Access to the full color range of the particles in the sample.	Time consuming; use of 2D image could be difficult to study overlapped particles and particle association in the vertical direction.	3D image acquisition to study the whole particle surface.	Resolution depending on the machine and setting.

670
671
672
673

674
675
676
677
678
679
680
681
682
683
684
685

Fig. 1. Particle counting using the "Cell counter" plug-in inside ImageJ environment.

686
687
688

689
690
691
692
693
694
695

Fig. 2. (a) Individual particles assigned with dots, and (b) combined images with the dots. Sample HM2b 0.125-0.350 mm. (c) A cross section of tomographic image after contrast adjustment and (d) dots assigned for particles. Sample HM2b 0.125-0.350 mm.

Fig. 3. Micro-XRF results of the analyzed uncrushed PCB: (a) source digital image and (b) corresponding total map showing investigated chemical elements. Distribution of (c): Cu, (d): Ba, (e): Ti, (f): Al, Si, S and Fe, (g): Sn and Pb, (h): Br, (i): Ca and (j): Ni, Ag and Au as an individual color map.

Fig. 4. Sample HM2b (0.125-0.350 mm): (a) unlocked and (b) locked copper particles observed with the stereomicroscope image and with the micro-XRF imaging; (c) unlocked and (d) locked aluminum particles observed with the stereomicroscope image and with the micro-XRF imaging. Sample HM2a (0.350-0.500 mm): (e) unlocked and (f) locked copper particles observed with the stereomicroscope image and with the micro-XRF imaging; (g) unlocked and (h) locked aluminum particles observed with the stereomicroscope image and with the micro-XRF imaging.

Supplementary materials

Supplementary Figure 1. Sample disposition inside the Bruker M4 Tornado.

Supplementary Figure 2. Optical microscope images combined for further process. Sample HM2b 0.125-0.350 mm.

Supplementary Table 1. Concentrations of the major elements identified by the portable X-Ray Fluorescence (XRF). The analysis is divided by size fractions and for the different hammer mills used (HM1 and HM2). The metal (wt.%) on the uncrushed PCBs is given at the bottom of the XRF analysis. The 95% confidence interval and absolute uncertainties for XRF and PGAA respectively are also given next to each metal% under the symbol of +/- [Adapted from (Otsuki et al., 2019)].

Mill	Size (mm)	Cu (%)	+/-	Fe (%)	+/-	Al (%)	+/-	Zn (%)	+/-	Si (%)	+/-
HM1	0.35–0.5	11.30	1.35	0.19	0.01	3.29	0.17	0.07	0.01	3.06	0.45
	0.125–0.35	3.91	0.58	0.33	0.02	3.27	0.16	0.14	0.01	4.46	0.35
HM2	0.35–0.5	4.16	0.30	0.24	0.01	3.10	0.26	0.15	0.05	4.11	0.32
	0.125–0.35	8.25	0.56	0.27	0.02	4.46	0.34	0.34	0.07	3.77	0.13
Uncrushed PCB		35.04	4.95	0.03	0.01	1.62	0.15	0.09	0.04	3.86	0.28