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# Selective recovery of copper from metal-rich particles in waste printed circuit boards by mechanical processing

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**Abstract:** This paper proposes a ball mill for the selective beneficiation of copper from metal-rich particles without any chemical treatment. Before ball milling, improved metal-rich particles were obtained through pretreatment including magnetic separation, crushing and separating. The effect of grinding time on the metal grade and recovery of copper (Cu), tin (Sn) and lead (Pb) was investigated. The results showed that there was a selective increase in Cu content in the concentrates during processing. In addition, Sn and Pb were enriched in tailings. Under optimum grinding cycles, the copper grade was beneficiated to 94.72 wt% from the initial 74.22 wt%, and its recovery rate was 86.78%. The content of tin and lead was increased to 28.27 wt% and 18.86 wt% from 10.13 wt% and 6.63 wt% in the by-products, respectively. The selective enrichment is due to the different plasticity and strengthening capacity of the components. The whole mechanical process is environmentally friendly, and the results will be useful for sustainable recycling of DPP.

**Keywords:** Cu; Selective beneficiation; Waste printed circuit boards (WPCBs); Ball milling; Waste recovery

**Селективне відновлення міді з частинок, багатих металом, у відпрацьованих друкованих платах шляхом механічної обробки.** *Yonglin Xu*

Пропонується кульовий млин для селективного збагачення міді з часток, багатих на метали, без будь-якої хімічної обробки. Перед обробкою кульовим млином були отримані поліпшені частинки, багаті на метали, шляхом попередньої обробки, включаючи магнітну сепарацію, дроблення і поділ. Було досліджено вплив часу подрібнення на сорт металу та вилучення міді (Cu), олова (Sn) та свинцю (Pb). Результати показали, що концентрація Cu селективно зростала під час механічної обробки. Крім того, концентрація Sn та Pb збільшувалася в порошку відходів. При оптимальних циклах подрібнення вміст міді збільшився до 94,72 мас.% від початкового 74,22 мас.%, а її ступінь добування склала 86,78%. Вміст олова та свинцю збільшився до 28,27 мас.% та 18,86 мас.% з 10,13 мас.% та 6,63 мас.% у побічних продуктах відповідно. Виборче збагачення було зумовлено різною пластичністю та здатністю до зміцнення компонентів. Весь механічний процес є екологічно чистим.

## 1. Introduction

Waste printed circuit boards (WPCBs) typically contain significantly higher concentrations of valuable metals than natural ores, recycling metals from WPCBs has received extensive attention in recent years [1-6]. The existing recycling processes for WPCBs involve physical, pyrometallurgical, hydrometallurgical, bio-metallurgical and hybrid processes [7-11]. Among the main recovery methods, physical and mechanical methods of pre-treatment of WPCBs are mainly used to prepare enriched and clean raw materials for further pyrometallurgical, hydrometallurgical or other types of purification processes [12, 13].

The physical and mechanical processes mainly include disassembly, shredding, and crushing to liberate metals and nonmetals. Thus, many metal-rich particles are obtained by further concentrating the metal contents [14-17]. Due to the multiple components and complicated compositions in a mixture of metal-rich particles, it is very difficult to separate different components completely by traditional physical separation, such as by density separation, magnetic separation or eddy current sorting [13, 14]. Generally, the different metals are mainly refined by smelting, chemical or hydrometallurgical processing, leading to high energy consumption and environmental issues [18]. Therefore, a more environmentally friendly and sustainable way to address the problem of metal-rich particles from WPCBs is urgently required.

Among other prevalent techniques, such as pyrometallurgical and hydrometallurgical processes, physical processing is admittedly the most environmentally friendly technique [9]. Previous studies showed that the grinding technique could enhance the selective grinding effect between ductile and brittle materials [19-22]. A swing hammer-type impact mill was used for grinding the PCBs, and a high-speed video camera was used to study the destruction process of the PCBs. It was found that the destruction of the ductile and brittle materials in the PCBs was totally different within the grinding chamber, which makes selective grinding possible between metallic and nonmetallic components in PCBs [19]. Verma H. R. et al. found that the copper content of +100 BBS (British Standard Specification) particles was higher than that of -100 BSS particles because the non-metals were crushed to a size below 100 BSS. Moreover, the morphology of copper, glass fibers and nonmetals were also quite different [23]. Yoo J. M. et al. enriched metallic components with mechanical separation processes, including milling, size classification and other physical separation techniques [14]. Arshadi M. et al. evaluated the content of different waste PCBs to enhance basic metal recycling and suggested that Cu, Ag and Sn were the most economical basic metals that should be recovered from PCBs [3]. Apparently, the aforementioned studies were mainly focused on improving the whole metal enrichment rate by removing nonmetals; however, reports on how to physically extract one kind of metal, namely, copper, from metal-rich particles are rare.

Ball milling is a material processing method with a high efficiency, simple operation, and a low cost [24]. The planetary ball mill is widely used in the field of powder metallurgy [25-27]. Through the rolling and collision between the grinding balls and the tank, the particles in contact with the milling balls are smashed or ground, thus reducing the surface activity and agglomeration and continuing the grinding process. Based on the various strengths and hardness of the different components in the metal-rich particles in WPCBs, it should be feasible to obtain interesting fracture characteristics. In contrast to the path for metallurgy methods, metal powders can be obtained by ball milling and directly applied for materialization, which results in a shorter regeneration path for the WPCBs. Hence, it is meaningful to study the various behaviors of different metallic WPCB particles during the ball milling process.

In this study, planetary ball milling was adopted for the first time to grind metal-rich particles of WPCBs to produce copper beneficiation. The effects of milling time on the selective beneficiation process were investigated. The Cu content and recovery rate after different milling cycles were studied, and optimized grinding conditions were proposed. To determine the phase evolution during the WPCB grinding process, material phases were identified in the feed particles, metal-rich concentrates and tailings. This study provides a novel environmentally friendly method to beneficiate copper from metal-rich WPCB particles and useful data for the efficient mechanical beneficiation of copper without toxic emission.

## 2. Experimental

### 2.1. Materials

The raw coarse particles from the WPCBs were collected from a local e-waste scrap recycling company (China Resources and Environment Co., Ltd). The average size was 5 ~10 mm. The total metal content in the WPCB particles was approximately 83 wt.%, and the residual 17 wt.% was composed of non-metal particles, including epoxy resins, plastics and ceramics.

### 2.2. Mechanical processing

A schematic diagram of the copper beneficiation process of the raw metal-rich particles from the WPCBs is shown in Fig. 1. The main stages comprised a pretreatment upgrade process (1st step) and selective beneficiation pro-

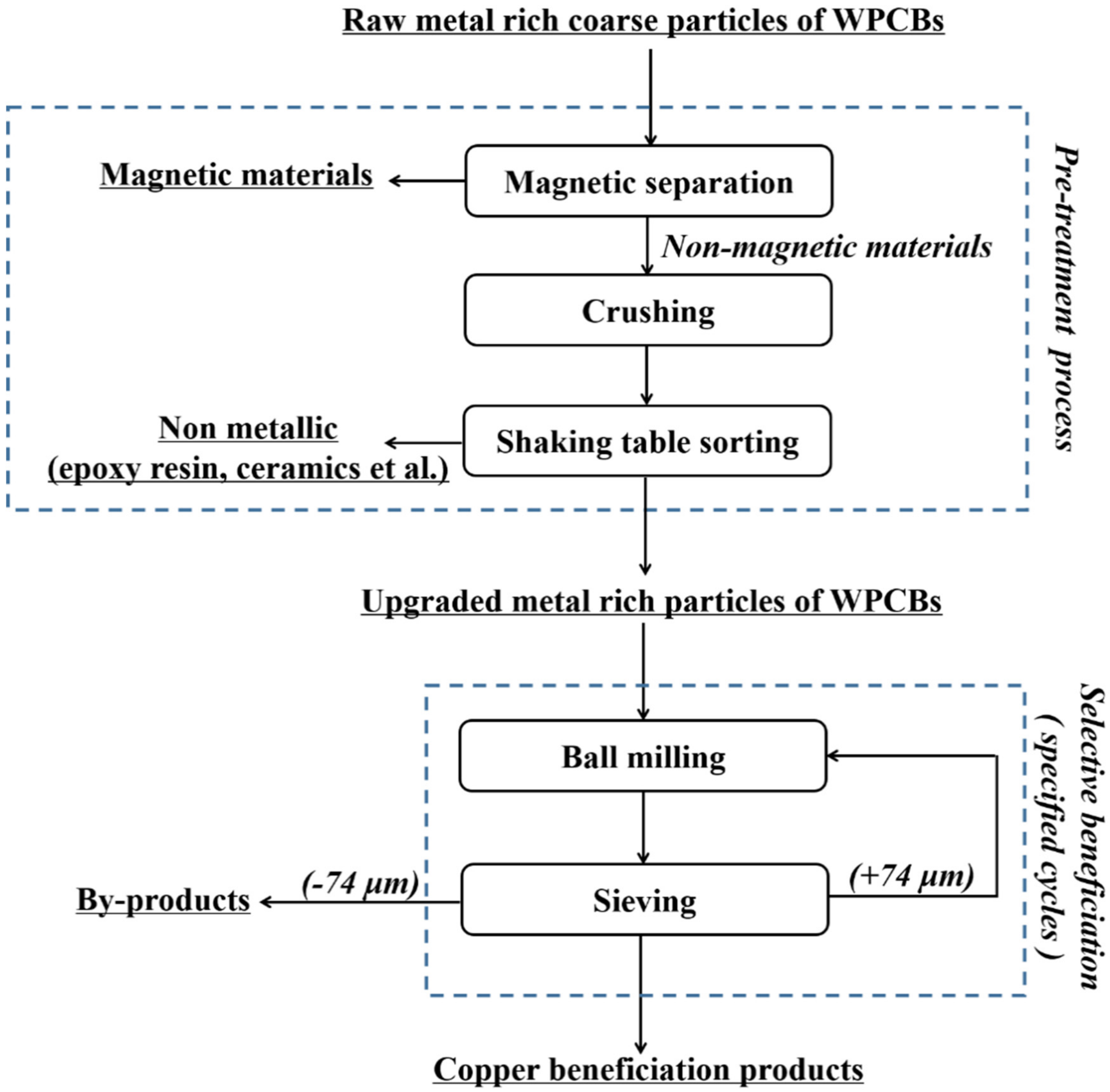


Fig 1. Flow chart of copper enrichment from unprocessed metal-containing particles of WPCB by mechanical processing

cess (2nd step) that involved cycles of ball milling and sieving.

There are three steps in the pretreatment process. First, a magnetic separator (CRIMM, Changsha Mining Research Institute, Changsha) was used to remove magnetic components. The constant magnetic field strength was 0.09 Tesla, and the working capacity of magnetic separation was ~ 460 kg per hour. Second, the nonmagnetic materials were shredded to less than 0.4 mm using a crusher (DF-50-A, Lin Da Machinery Co., Ltd. Wenling). Third, a water shaking table (6-S MX, Mingxin Metallurgical Equipment Co., Ltd. Shicheng) was used to remove most of the non-metallic particles by density separation. The shaking frequency was 6.3Hz, and the working capacity of shaking table separation was ~ 100 kg per hour. Thus, upgraded metal-rich particles were obtained.

In the second process, a high-energy planetary ball mill (QM-3SP4, Nanda Instrument Co., Ltd. Nanjing) and a 200 mesh screen were used for grinding and sieving the upgraded metal-rich particles. The grinding time was chosen as the decisive factor determining the total energy generated during ball milling; other grinding parameters were determined based on our previous experiments. The details are as follows: the rotation rate was 400 rpm, the mass ratio of the balls to the materials was 20:1, and the ball milling medium was deionized water. The upgraded metal-rich particles were mechanically milled for different cycles. After each cycle, the particles were separated

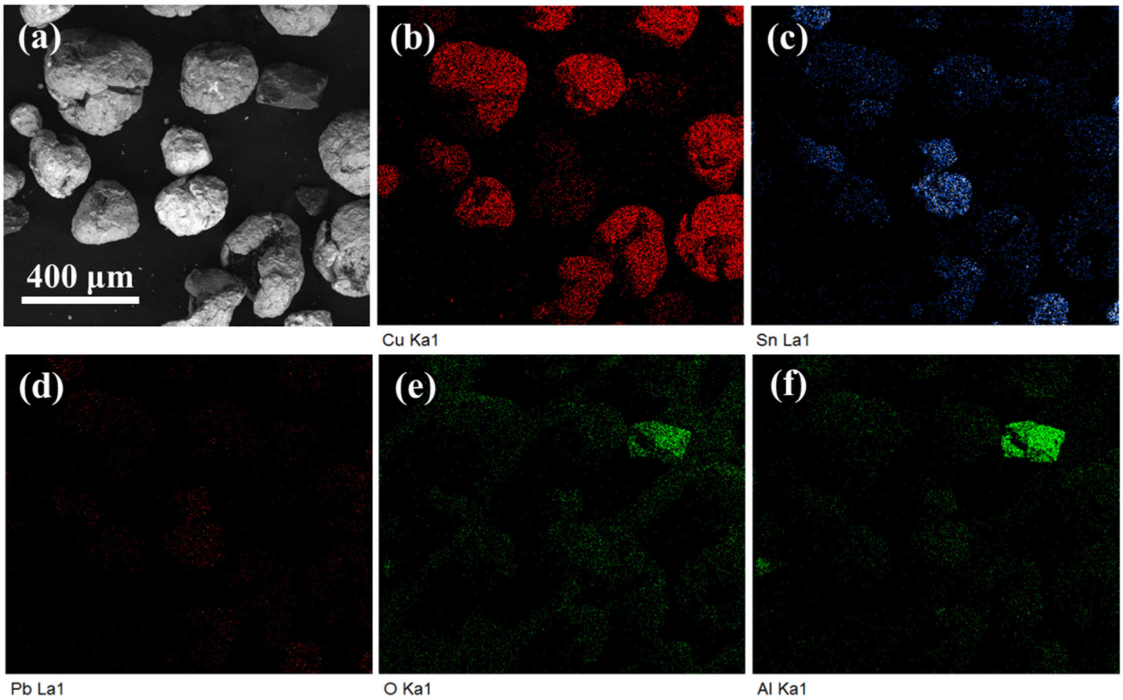


Fig 2. Morphology and element mapping of the particles after pretreatment: (a) SEM of the upgraded metal-rich particles and (b-f) distribution maps of the Cu, Sn, Pb, O and Al.

into two categories by sieving: concentrated particles (+74 µm or above 74 µm in diameter) and tailings powder (-74 µm or below 74 µm in diameter and also referred to as by-products in this study). The tailings were removed, and the concentrated particles were milled for the next cycle (milled for 1 hr during each cycle). The milling time was 1 hr, 2 hr, 3 hr, and 4 hr in this study.

### *2.3. Morphology and composition analysis*

Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) (Quanta 200) were used to detect the morphological characteristics of WPCB particles. The chemical composition of the upgraded metal-rich WPCB particles, concentrated particles and tailings powder from each cycle was investigated in the Guangdong Industrial Analysis and Testing Center. Since the particles were not homogeneous enough, the composition may unreliable if determined directly from the solid phase. Hence, the particles were first completely dissolved using aqua regia, and then, the acid insoluble components were cleaned using distilled water, vacuum dried, and weighed; this amount was recorded as the non-metallic content. The Cu content in the filtrate was determined based on the YS/T 521.1-2009 standard, and the contents of Sn and Pb were measured based on the GB/T 23942-2009 standard by inductively coupled plasma-atomic emission spectrometry (ICP-AES-JY ULTIMA-2). The balance was recorded as other metals. An analytical balance (Mettler Toledo ME204) was used to weigh the mass of the concentrates and tailings for the recovery rate calculation. In addition, the phases of both the concentrate particles and tailings powder obtained by each cycle were identified using X-ray diffraction (XRD, PANalytical X'Pert Pro) with Cu Kα radiation.

## *3. Results and Discussion*

### *3.1. The morphology and contents of upgraded metal-rich WPCB particles*

The raw coarse particles from the WPCBs were pretreated by magnetic separation, crushing and shaking table sorting to obtain upgraded metal-rich particles. Fig. 2 illustrates the morphology and the element mapping results of the upgraded metal-rich particles that were prepared and ready for ball-milling treatment.

According to Fig. 2, the main components in the WPCBs were Cu (Fig. 2b), Sn (Fig. 2c), Pb (Fig. 2d) and alumina particles (Fig. 2e and f). The metals mostly had a nearly spherical and ellipsoidal shape, while the alumina particles had a polygonal shape after pretreatment. Based on Fig. 2, the Cu, Sn and Pb contents in the upgraded metal-rich WPCB particles

Table 1. Average metal content in the upgraded metal-rich particles in the WPCBs

| Elements | Cu | Sn | Pb | Other metals | Nonmetals | Total |
|---|---|---|---|---|---|---|
| Content (wt.%) | 74.22 | 10.13 | 6.63 | 4.20 | 4.82 | 100 |

were determined. Considering that the mixture exhibited some inhomogeneity, the soluble method was adopted for chemical analysis, where 50 grams of the upgraded particles were completely dissolved using aqua regia, and the extracts were precisely analyzed by ICP-AES. The tests to determine the composition were repeated three times, and the deviation of each element was less than 1.5 wt.%. Moreover, acid-insoluble components were registered as nonmetallic. The average composition is shown in Table 1. The major metallic components of the upgraded metal-rich WPCB particles were copper (74.22 wt.%), tin (10.13 wt.%) and lead (6.63 wt.%).

### *3.2. Effect of the milling time on the yield of the concentrates and tailings in the WPCBs*

The upgraded metal-rich WPCB particles were mechanically milled for several cycles, and the mill time for each cycle was 1 hour (hr). After each cycle, the masses of the concentrated particles and tailings powder were weighed. The yield of concentrates $\gamma_c$ and the yield of tailings $\gamma_t$ were calculated based on Eq. (1) and (2):

$$\gamma_c = \frac{Q_C}{Q_O} \times 100\ \% \quad (1)$$

$$\gamma_t = \frac{Q_t}{Q_o} \times 100\% \quad (2)$$

where $Q_o$ is the weight of the original upgraded metal-rich particles of WPCBs, $Q_c$ is the mass of concentrates and $Q_t$ is the mass of tailings.

The effect of the milling time on the yield of the concentrate particles and tailings powder from the WPCBs is shown in Fig. 3.

It was observed from Fig. 3 that the tailings yield $\gamma_t$ increased with increasing milling time. However, the rate of the increase for each cycle was quite different. The $\gamma_t$ of the tailings was 20% after ball milling for the 1st hr, and it was 29%, 32%, and 58% after milling for the 2nd hr, 3rd hr, and 4th hr, respectively. Correspondingly, the relative tailings yield growth rates were 20%, 45%, 10% and 81% after the 1st hr, 2nd hr, 3rd hr, and 4th hr, respectively. In particular, when the milling time was increased

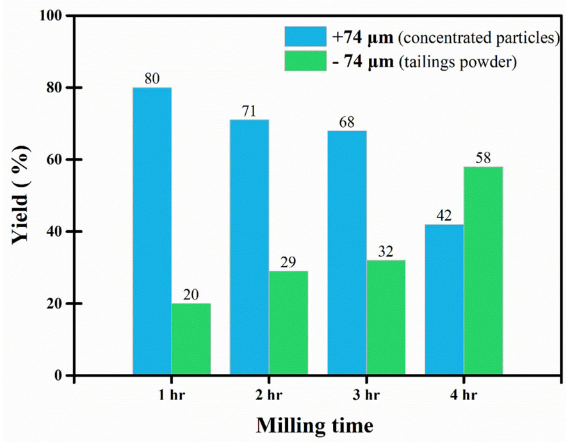


Fig 3. Effects of milling time on the yields of copper concentrate and tailings from the WPCBs (milled for 1 ~ 4 cycles.)

from 3 hr to 4 hr, the $\gamma_t$ of the tailing particles increased significantly because the particles were refined. This indicated that after a certain time of ball milling, the energy accumulated on the surface of the WPCB particles due to the collisions during the milling process exceeded the cohesion of the particles; this loss of cohesion led to the destruction of the WPCB particles and the formation of fine particles. Finally, only 42% of the concentrate materials were left after mechanical milling for 4 cycles.

### *3.3. Effect of the milling time on the grade and recovery of Cu, Sn and Pb in the concentrates and tailings*

The recovery rate of useful components is an important indicator of the efficiency of the sorting process. The higher the recovery rate, the more useful components are extracted during the enrichment process. The recovery rates $\varepsilon_c$ of the Cu, Sn and Pb in the concentrates were calculated based on Eq. (3), and the recovery rates $\varepsilon_t$ of the Cu, Sn and Pb in the tailings were calculated based on Eq. (4):

$$\varepsilon_c = \frac{\beta\gamma_c}{\alpha} \times 100\%\ , \quad (3)$$

$$\varepsilon_t = \frac{\vartheta\gamma_t}{\alpha} \times 100\%\ , \quad (4)$$

where α is the element grade of the upgraded metal-rich particles from the WPCBs, β is the element grade of the concentrate particles, υ is the element grade in the tailings and γ is the

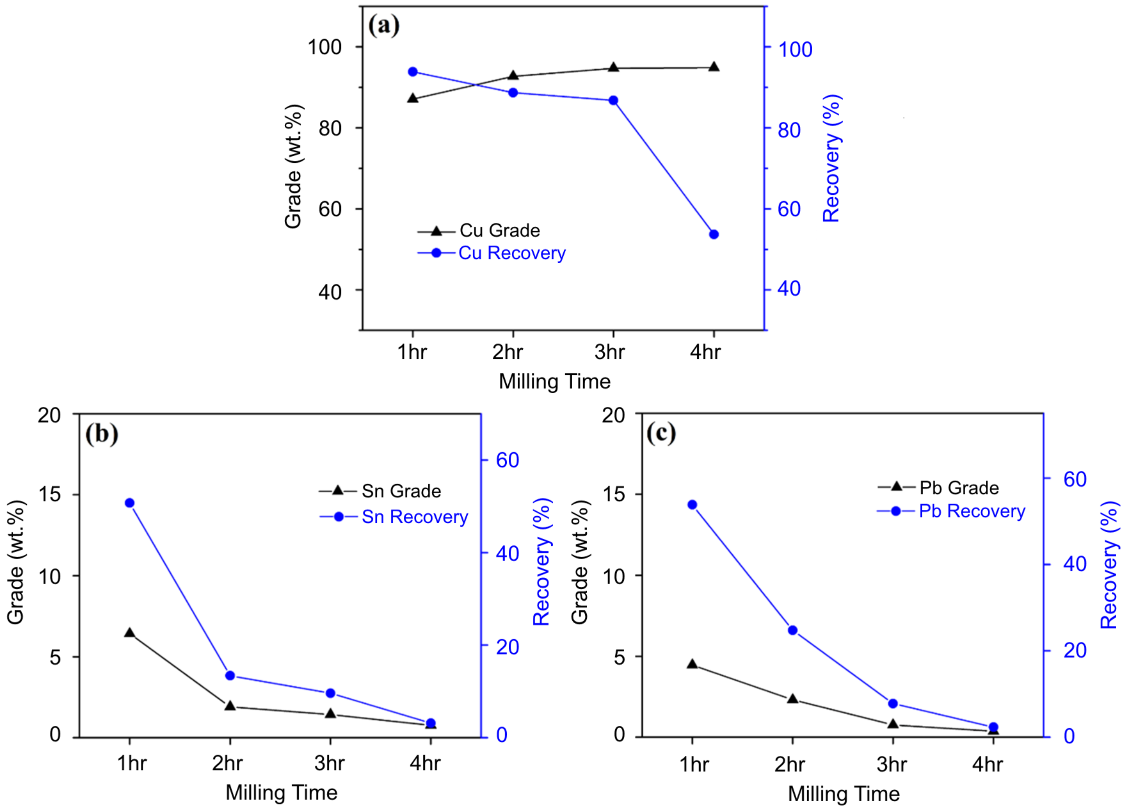


Fig 4. The effect of milling time on metal grade and recovery in the concentrates for (a) copper, (b) tin and (c) lead

concentrate yield. The element grade equals the quality fraction, which was determined by ICP-AES using the previously mentioned methods. The Cu, Sn and Pb grades of the original materials before ball milling were $\alpha_{Cu}$=74.22 wt.%, $\alpha_{Sn}$=10.13 wt.% and $\alpha_{Pb}$=6.63 wt.%, respectively. The copper, tin and lead grades in the concentrates were indicated by $\beta_{Cu}$, $\beta_{Sn}$ and $\beta_{Pb}$, respectively. The copper, tin and lead grades in the tailings were represented by $\upsilon_{Cu}$, $\upsilon_{Sn}$ and $\upsilon_{Pb}$, respectively.

The effect of the milling time on the grade and recovery of Cu, Sn and Pb in the concentrates and tailings were investigated, and the results are shown in Figs. 4 and 5.

Fig. 4 indicates that as the mechanical milling time increased, the copper grade improved significantly, whereas both the tin and lead grades decreased gradually in the concentrate particles. The recovery rates of all three elements decreased as the milling time increased. Fig. 4(a) shows that the copper grade increased from 74.22 wt.% in the original materials to 94.72 wt.% in the concentrate particles, and the recovery rate was 86.78% when the milling time was 3 hr. However, when the milling time was extended to 4 hr, the copper grade in the concentrate was 94.85 wt.%, and the recovery rate was only 53.67%, which was much lower than that after milling for 3 hr. Fig. 4(b) and Fig. 4(c) show that the removal of tin and lead by the mechanical milling process was significant. When the milling time exceeded 3 hr, the extraction effect began to decrease. Fig. 4(b) shows that the tin grade was reduced to 1.43 wt.% in the concentrates compared to the 10.13 wt.% in the original particles, and the removal rate reached 91.4%. Whereas the lead grade was reduced to 0.76 wt.% from 6.63 wt.%, the corresponding removal rate was 92.21% (Fig. 4(c)).

Fig. 5 shows that the recovery rates of copper, tin and lead increased in the tailing particles as the milling time increased. The grade change was different for copper and the other two components. It can be seen in Fig. 5(a) that when the milling time increased to 4 hr, the copper contents increased, which indicates a substantial loss of the concentrates. Moreover, the tin grade and lead grade were reduced in the 4th cycle.

Both the grade and recovery rate are important indicators of the efficiency of the sorting process. The higher the copper grade, the

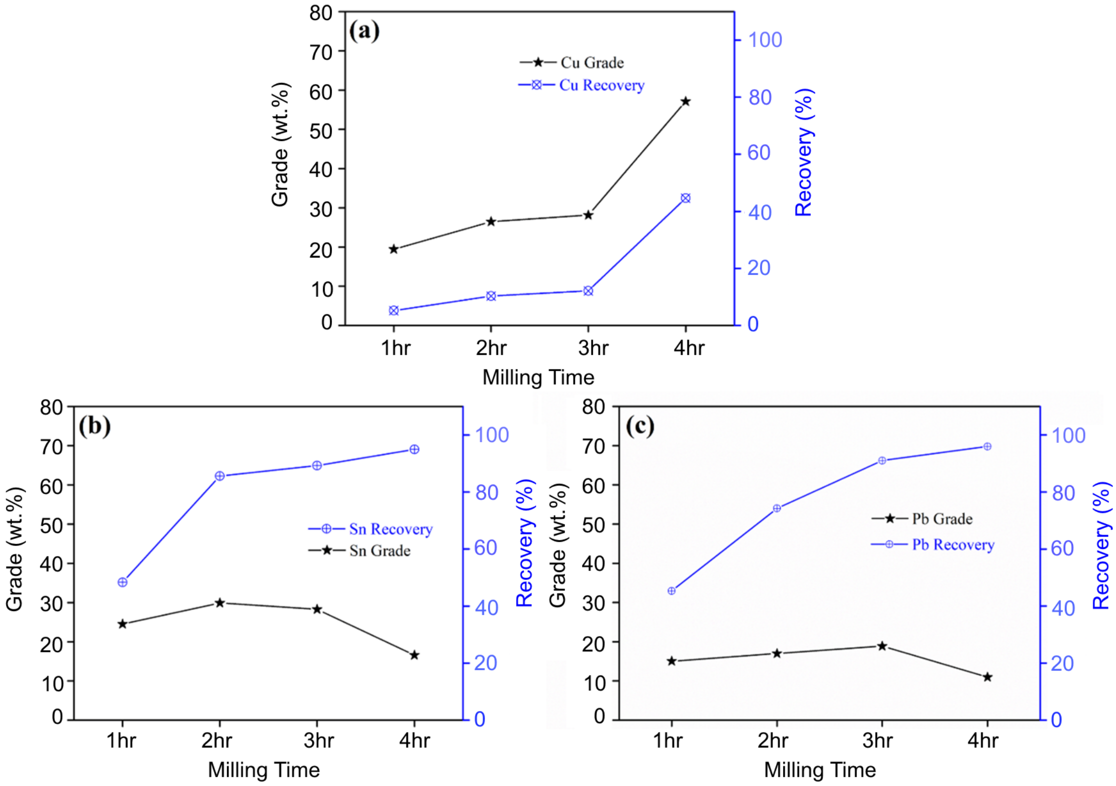


Fig 5. The effect of milling time on metal grade and recovery in the tailings for (a) copper, (b) tin and (c) lead

better is the enrichment of WPCBs. Moreover, the higher the copper recovery rate, the more useful components are recovered in the beneficiation process. Therefore, when processing minerals, it is necessary to increase the degree of extraction of useful components, while ensuring the quality of the concentrate. Based on a comprehensive evaluation, milling for 3 cycles was the preferred ball milling condition in this study.

### *3.4.* Cu, Sn *and* Pb *selective beneficiation evaluation*

The enrichment of the Cu, Sn and Pb under optimized mechanical ball milling conditions is shown in Fig. 6. Fig. 6(a) illustrates the copper selective enrichment in the concentrated particles. Fig. 6(b) indicates the tin and lead enrichment in the tailings powder.

The enrichment ratio δ of Cu is the ratio of the concentrate grade β to the original grade α. It indicates the enrichment efficiency of the useful component (Cu) during the beneficiation process and is calculated based on Eq. (5):

$$\delta_{cu} = \frac{\beta_c}{\alpha} , \qquad (5)$$

where $\beta_c$ is the copper grade in the concentrates, and α is the copper grade in the pretreated upgrade metal-rich WPCB particles.

The enrichment ratios δ for Sn and Pb were calculated based on Eq. (6):

$$\delta_{Sn,Pb} = \frac{\vartheta_t}{\alpha} , \qquad (6)$$

where $\upsilon_t$ is the grade of Sn and Pb in the tailings, and α is the grade of Sn and Pb in the pretreated upgrade metal-rich WPCB particles.

Fig. 6(a) indicates that the grade of copper increased from 74.22 wt.% in the original materials to 94.72 wt.%, with an enrichment ratio of 1.28. In addition, tin and lead were reduced from 10.13 wt.% and 6.63 wt.% to 1.43 wt.% and 0.76 wt.%, respectively. Fig. 6(b) shows that both tin and lead were enriched in the tailings to 28.27 wt.% and 18.86 wt.% from 10.13 wt.% and 6.63 wt.%, respectively. Correspondingly, the enrichment ratios of tin and lead were 2.79 and 2.84 in the tailings, respectively.

Therefore, with an appropriate mechanical ball-milling treatment, not only can copper be upgraded and enriched, but both tin and lead can be enriched at the same time. Since copper was enriched in large particles, tin and lead were enriched in fine powders, similar to direc-

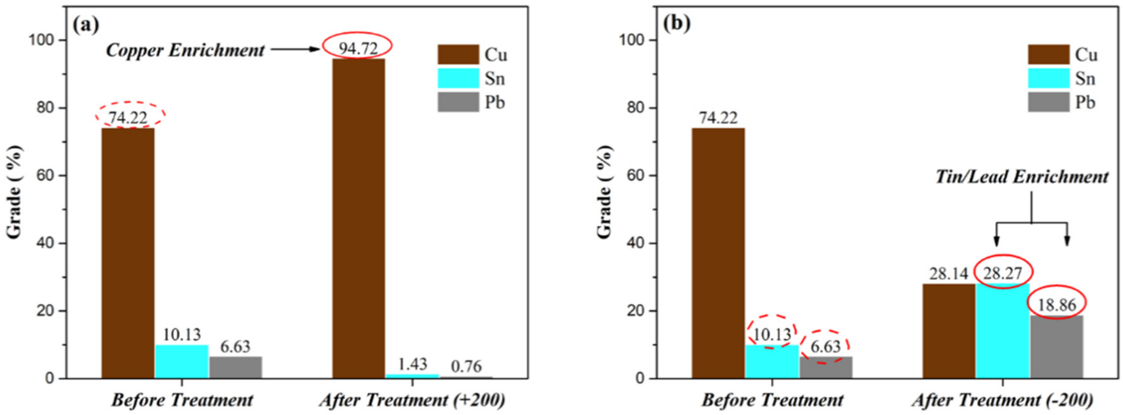


Fig 6. Copper, tin and lead enrichment effect by optimal mechanical ball milling beneficiation: (a) copper enrichment in concentrate particles and (b) tin and lead enrichment in the tailings powder.

tional movement, so this enrichment process was named selective beneficiation. The results showed that the beneficiation effects were obviously good.

### *3.5. Mechanism of the selective beneficiation of copper*

The selective beneficiation mechanism of Cu during ball milling was investigated. Fig. 7 shows the practical particle separation processes under optimal ball milling conditions. The magnetic particles and most of the nonmetallic particles, such as epoxy resin and alumina oxide, were removed by the pretreatment process. During the selective beneficiation process, the copper enrichment effects were significant and could be resolved visually. The copper enrichment particles had a good copper metallic luster and were shaped like a flake or foil after milling for 3 cycles. The tailings were gray-black and powdery, mostly with a polygonal shape of particles.

The directional enrichment was mainly due to the physical properties, such as differences in ductility and strength between particles. All metals and nonmetals in the WPCB particles were deformed because of the collision energy during the milling process. Whether refining or coarsening occurred depended on the original particle size and the stress during the ball milling process. During the milling process of the metal-rich particles from WPCBs, ductile or malleable metals were elongated or extended to form large pieces. However, fracture occurred if the impact force exceeded the strength of the metals; thus, fine particles were obtained.

Ductile metallic particles could withstand an increased plastic deformation before fracture, whereas brittle ceramics and glass fiber-reinforced epoxy resins were milled to a small size preferentially. Similar results can be found in previous studies [19, 28]. Koyannaka et al. [28] investigated the effect of mill operating conditions on the copper shape and size distribution. They revealed that during PCB milling, the shapes of copper particles, glass fibers and epoxy resin were changed to spherical, fibrous and angular, respectively, and the non-copper components were milled to a size smaller than that of copper, and the hammer circumferential speed was a noticeable factor during the milling process. Their results verified that fine glass particles are easily generated by brittle fracture and that metal particles are not as easily ground as resins and glass particles due to their ductility. For the metal particles, since the ductility of tin and lead is weaker than that of copper, the fracture of the tin and lead would occur prior to the fracture of copper.

However, with increasing ball milling time, the plasticity of the copper decreased due to work hardening caused by a continuous stress. Once the accumulated energy from the ball milling exceeded the cohesion of the copper particles, the exfoliation and refining of the copper increased. This is why the copper was substantially lost in the 4th ball milling cycle. The results showed that mechanical ball milling and sieving is an effective method to enrich Cu from metal-rich WPCB particles. Furthermore, appropriate ball grinding conditions are critical for the directional beneficiation process.

In addition, it should be noted that it was almost impossible to extract all the copper from the WPCBs by physical separation. Since the size of copper particles in the original pretreated WPCB particles was not uniform, the degree of plastic deformation during the milling process was not the same. Thus, some of the

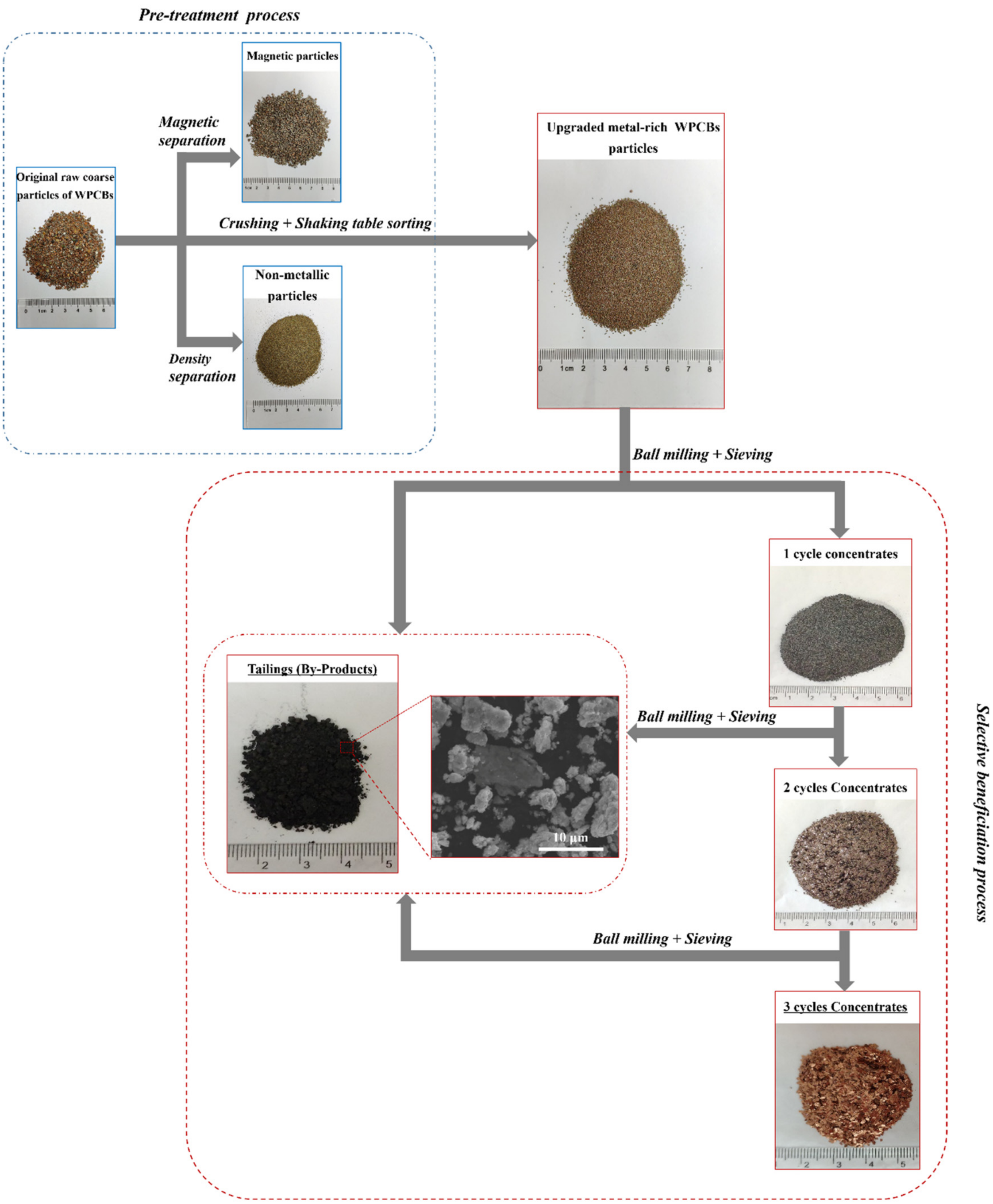


Fig 7. Process of beneficiation of material under optimized conditions of mechanical ball milling

copper (~13.22 wt.%) was inevitably lost in the tailings due to particle refinement during the enrichment process.

XRD measurements were carried out to identify the crystalline phases. The original materials before milling, the concentrates and the tailings were identified using an XRD instrument (PANalytical X'Pert Pro) with Cu Kα radiation, at a scan speed of 0.135°/s, and in the 2θ range from 20°-100°. The results are shown in Fig. 8. The upper line shows the XRD pattern (line a) of the original pretreated metal-rich particles used for mechanical milling treatment. The intense peaks in the XRD pattern indicate that elements, such as Cu, Sn and Pb, were in their pure form. Some low-intensity peaks indicate the presence of a brittle $Al_2O_3$ phase.

The middle line is the XRD pattern (line b) of the concentrates that were milled for 3 cycles. The intense peaks indicate that pure Cu was very abundant; low-intensity peaks indicate the presence of a small amount of Sn and a very small amount of Pb.

In the XRD spectrum of the tailings (line c), there was a variety of diffraction peaks. In addition to peaks corresponding to Cu, Pb and $Al_2O_3$, tin was present both in pure form and as bronze as a result of alloying with Cu. The results also showed that the intensity of the Cu peaks was reduced.

Upon comparing the XRD patterns of the tailings (line c) and the concentrates (line b), three main differences could be seen. First, the Sn and Pb peaks in the tailings were much more intense than those in the concentrates, indicating that both Sn and Pb were enriched in the tailings by the mechanical milling process. Second, the peaks from $Al_2O_3$ in the XRD pattern of the tailings confirmed that the brittle components were directionally enriched to a fine powder by the mechanical milling process. Third, the peaks corresponding to Cu-Sn indicated that an alloy phase was formed during the high-energy milling process, where some of the tin atoms dissolved in the copper lattice, and the Cu-Sn alloy was enriched in the tailings. All of the XRD results agree with the results obtained from the ICP-AES analysis.

Since little metal powder could remain on the mill balls, some metal loss was inevitable. The total metal loss of the whole mechanical milling process was less than 1% based on the metal balance calculation. Overall, the whole selective beneficiation process of copper in this study is environmentally friendly because chemical processes are not involved, which is in accordance with the sustainable policy of the recycling technique. This method provides a good reference for the enrichment and separation of various metal mixtures. However, a certain material loss was inevitable, which calls for further investigation.

### 3.6 Regeneration proposal for the copper concentrates and tailings

The concept of regeneration was recently proposed and practiced for waste PCBs. For instance, regeneration of tin-based solders and copper-based alloys from PCBs could be used as materials for commercial products in the market [29, 30].

In this study, we processed metal-rich particles through ball milling and sieving. Both the concentrates and the tailings obtained could be regenerated by further processing. These obtained concentrates with high-grade copper

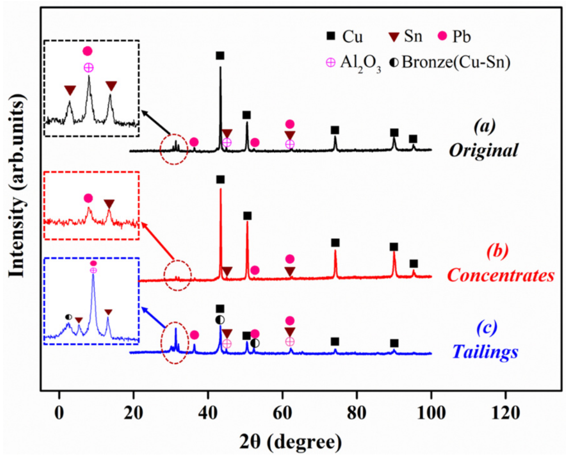


Fig 8. XRD patterns of the WPCB particles: (a) the original pretreated particles before milling, (b) Cu concentrates obtained after 3 cycles, and (c) by-products of the tailings powder

can be refined by ball milling and directly used as copper-based alloy powders for powder metallurgy. We have obtained a recycled copper-based alloy in this way, and the study details will be discussed in future reports. Furthermore, the tailings powder was less than 74 μm in diameter, and it can be feasibly used as an alloy powder after subsequent processing, such as gravity separation, to remove nonmetallic components.

## 4. Conclusions

In this study, a mechanical procedure was proposed herein to beneficiate copper from WPCBs without using any chemical processes. Ball milling and sieving were successfully applied for copper beneficiation. Meanwhile, the tin and lead were enriched in the tailings powder. The following major conclusions can be drawn:

(1) The ball milling time is a crucial factor for the beneficiation process. The grade of copper improved with increasing milling time, but the degree of improvement gradually slowed. A large amount of copper was released into tailings in the 4th hr of milling, and the recovery rate of the copper was only 53.67% after 4 hr of ball milling. However, the improvement in the grade of the copper was not obvious after the 3rd hr of milling (94.85 wt.% for the 4th hr vs 94.72 wt% for the 3rd hr). Considering the high grade and high recovery of the copper, the optimum ball milling condition for copper beneficiation was milling for 3 cycles (3 hr of ball milling).

(2) Under the optimum treatment (3 hr of ball milling), the Cu concentration increased significantly to 94.72 wt.% from 74.22 wt.%

with a high recovery of 86.78%. Moreover, the removal rates of Sn and Pb were 91.4% and 92.21%, respectively.

(3) The selective beneficiation was attributed to the different ductility and work-hardening ability of Cu, Sn, Pb and bronze (Cu-Sn). Selective beneficiation of a specific metal in a multi-component metal mixture could be achieved by suitable mechanical milling and sieving conditions.

### *Acknowledgments*

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