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Effect of Milling Parameters on the Concentration of Copper Content of Hammer-Milled Waste PCBs: A Case Study

Himanshu Ranjan Verma[1] · Kamalesh K. Singh[1] · Shaik Mahaboob Basha[2]

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Abstract

The current study reports optimization of hammer milling parameters to achieve crushed waste printed circuit boards (WPCBs) of − 16 BSS (British Standard Specification) sieve size. The WPCBs, having 22 wt% copper, have been crushed to − 16 BSS sieve size by means of a hammer mill. The result showed that initial milling takes place rapidly and then decreases gradually. Approximately 94% feed material is ground to − 16 BSS sieve size within 7 min, and further increase in the time does not affect the milling rate. It is also revealed that with the increasing feed rate, lower milling rate is experienced due to the distribution of impact energy among more pieces of WPCBs. Study of the size distribution of milled WPCBs (− 16 BSS sieve size) revealed that it follows the similar trend, and the crushed material is mostly concentrated in − 240 BSS and + 72 to − 52 BSS sieve size range. Further, 50–55% crushed fraction attains + 100 BSS sieve size, while the rest is smaller than this sieve size. Chemical analysis of the crushed material of various size fractions elucidated that a fraction above 100 BSS sieve size is copper rich (43 wt%), while − 100 BSS sieve size fraction has lesser copper because the nonmetals which account for majority concentration in WPCBs are milled to a finer size. Microscopic examinations of crushed fraction showed that copper has metallic luster and ruptured foil-type morphology. The fibrous structure of glass fiber and gray/black-colored polygon morphology of nonmetals were also visible.

Keywords Hammer milling · Concentration · Copper · Waste printed circuit board (WPCBs) · Sieve analysis

Introduction

Rapid rejection of electronic items due to technological advancement and shortened lifespan has created serious challenges to electronic waste (e-waste) management globally [1]. E-waste generation is associated with severe environmental problems and health issues due to its toxic contents such as arsenic, bismuth, beryllium, cadmium, chromium, lead, mercury, lithium, polychlorinated biphenyls, polybrominated biphenyls (PBB), tetrabromo bisphenol-A (TBBA), polybromo diethyl ether (PBDE), etc. [2, 3]. However, it contains plenty of valuable metals, and thus, it must be recycled to conserve the natural ore resources [4]. Among different components of e-waste, waste printed circuit boards (WPCBs) are the most complex, and thus, exhibit extreme difficulty during their recycling [5]. PCBs possess heterogeneous composition of various metals (copper, nickel, iron, aluminum, silver, gold, lead, tin, etc.), glass fiber, halogenated epoxy resin (HER), and other ceramics/plastic [6, 7]. The PCBs are manufactured after sticking multiple layers of glass fiber matrix and copper laminates with HER used as a reinforcing substrate.

The recycling of WPCBs may be achieved by mechanical processing followed by hydrometallurgical and thermal techniques. Mechanical processing covers the various aspects like, separation of recyclable, reusable, and magnetic components; size reduction and fine crushing of WPCBs; enrichment of metal content; liberation and separation of metals and nonmetals, etc. [6, 8] It comprises

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✉ Himanshu Ranjan Verma
hrverma.met.iitbhu@gmail.com

1 Department of Metallurgical Engineering, Indian Institute of Technology, Banaras Hindu University, Varanasi 221005, India

2 Research and Development Division, Tata Steel Limited, Jamshedpur, Jharkhand 831007, India

three steps: (i) disassembly, shredding, and sorting; (ii) crushing, grinding, and liberation and separation of metals and nonmetals; and (iii) analysis of concentration of metal contents. The main advantage of mechanical processing is that it neither leads to toxic emission nor requires usage of any corrosive and harmful toxic reagents.

Manual process or automated equipment is employed for WPCBs disassembly, and shredders having high torque have been developed for the demolition of e-waste. Crushing, grinding, and liberation are achieved by methods having the higher impact force due to the rigid and strong structure of WPCBs. Further, a previous study has shown that significant liberation of metals is achievable preferably after crushing WPCBs to size below 3 mm [9], and thus the applications of equipment viz., knife mill, cryogenic mill, ball mill, stamp mill, and hammer mills have been investigated for downsizing of WPCBs. Size reduction of rigid material like WPCBs is difficult by knife mill because milling size is dependent on the inter-blade spacing that is more suitable for elastic materials [5]. Cryogenic milling requires liquid nitrogen to produce cracks, so that achieving fine and uniform size reduction is not possible. Yoo et al. [10] investigated grinding of shredded WPCBs of 10 mm using stamp mill. The study revealed that 80% nonmetallic fraction had concentration of particles of less than 12 BSS sieve size, while 70% metals were condensed as particles with the larger size (more than 5 mm fraction). This is because unlike the nonmetal of brittle nature, the ductile metal elongates during stamping. Lower distribution of metallic phase in wide size range resulted in inefficient metal concentration. On the contrary, due to the transverse elongation of metal, it is not possible to achieve fine size. Koyanaka et al. [11] investigated hammer milling of WPCBs being ground to − 16 BSS sieve size and found that, at higher circumferential speeds, copper is ground to spherical nonhomogenous particles. Further, glass fiber of fibrous shape and resin of angular shape were obtained. Copper is milled to coarser size and non-copper fraction milled to a smaller size due to their inherent brittleness. Koyanaka et al. [12] reported that during hammer milling, WPCBs exert brittle fracture from the edge initially, and later the copper foils are peeled off when reinforced glass fiber structure collapses. Hammer mills have been extensively used for grinding of WPCBs as it results in excellent liberation of various constituents. Cui and Forssberg [13] reported 96% liberation for WPCBs crushed achieving particle size of less than 5 mm, while 99% liberation is achieved with particle size of less than 2 mm [14]. After successful liberation of metals, the metallic fraction of crushed WPCBs is concentrated by means of different techniques [15]. Those techniques comprise multi-step operations, such as corona discharge, magnetic eddy current separation [16–19], vibrating screen [20, 21], air classification [22], flotation [23], gravity- and density-based separation [24], etc. A good liberation and separation of metal–nonmetal is achievable once liberation and concentration techniques are implemented in tandem [25]. In spite of years of practical attempts, the maximum recovery of metal achieved so far is limited to 75–80% [4] due to inefficient liberation, over pulverization, the presence of a high fraction of nonmetallic materials, etc.

Keeping all the above facts in mind, our investigations focused on the optimization of hammer milling operation and upgradation of the grade of hammer-milled WPCB products, which ensures less nonmetallic material fraction. In the present study, the effects of different parameters on the hammer-assisted milling of WPCBs to yield crushed WPCBs of − 16 BSS sieve size, followed by metal enrichment by means of the simple sieve separation technique have been studied.

Materials and Method

WPCBs of computers were collected from local e-waste scrap collectors. All the WPCBs were cleaned, and the mounted electronic components were detached from them. The bare WPCBs obtained were downsized to 15 × 15 mm by using an abrasive wheel cutter. The chemical composition of WPCBs was determined using atomic absorption spectrophotometer (AAS) supplied by *Elico SL 168, India.* For analysis, 10 g of WPCBs was digested in freshly prepared aqua regia ($HCl:HNO_3$ = 3:1) at 80 °C for 1 h. The samples were digested by placing the WPCBs into a beaker after pouring a requisite quantity of aqua regia and heated by a digital hot plate with a temperature controller. A quartet of digestion experiments were performed with random sampling to estimate the average composition of WPCBs. The hydrochloric acid and nitric acid of analytical grade were supplied by *Sisco Research Lab (SRL) India Pvt. Ltd.*

The downsized WPCBs (15 × 15 mm) were crushed to − 16 BSS sieve size by means of a hammer mill supplied by *Ikon Instruments, India*. Experiments under varying milling times (30 s, 1, 1.5, 3, 5, 7, and 10 min) and feed rates (3, 8, and 12 $kg \cdot h^{-1}$) were performed to obtain optimal milling parameters. To study the particle size distribution of downsized WPCBs, the sieve analysis was carried out. For sieve analysis, a series of nine test sieves of BSS 16, 25, 30, 52, 72, 100, 120, 150, and 240 sizes were mounted in descending order of mesh size on a vertical test sieve shaker. The sieve aperture of respective sieves is shown in supplementary data (Refer supplementary data: Table 1). After 15 min shaking, particles retained in various sieves were collected and their weight was recorded. To estimate the amount of copper in different size fractions, 0.5 g of the respective sample was digested in aqua

Table 1 Average composition of WPCBs

S. no.	Element	Concentration (wt%)
1	Cu	22.3
2	Zn	0.606
3	Ag	0.001
4	Au	0.0002
5	Fe	0.35

regia as mentioned above. After digestion, excess acid was evaporated and the digested liquor was diluted to 50 mL by adding distilled water. The diluted samples were analyzed by Atomic Absorption Spectroscopy (AAS) by using a hollow cathode lamp of copper operating at 324.8 nm. Microscopic examinations of milled WPCBs were carried out by using an optical microscope at ×10 magnification. The scanning electron microscopy (SEM) analysis of the samples was performed on instrument make—'*Zeiss Evo-18 Research 2045*' with Energy Dispersive X-ray Spectroscopy (EDS) attachment make—'*Oxford X-act INCAx-act*'.

Results and Discussion

Chemical Analysis of WPCBs

The analysis of WPCBs by the AAS technique showed the presence of ~ 22 wt% copper in the WPCBs along with zinc, silver, gold, and iron. The average chemical composition of WPCBs is represented in Table 1.

Hammer Milling of WPCBs

Effect of Time on Milling of WPCBs

To study the effect of time on the milling of WPCBs to − 16 BSS sieve size, the preliminary experiments were carried out on WPCBs at the feed rate of 3 kg·h^{-1}. Figure 1 shows the variation of crushed (− 16 BSS) and uncrushed (+ 16 BSS) fractions of WPCBs at different times. It is evident that the undersize fraction increases with the increasing milling time. Figure 1 also elucidates that 37% of fed WPCBs is milled to − 16 BSS sieve size in 30 s. The nature of the curve shows higher slope values (47.9% WPCBs·min^{-1}) up to 1.5 min indicating relatively faster milling rates. This is because the impact forces transferred to pieces of WPCBs by the swing hammers result in the fracture of the rigid nonmetallic content of WPCBs. The nonmetallic fraction of WPCBs is brittle in nature, and thus undergoes brittle fracture rapidly. It is notable that after 1.5 min, 72% of fed WPCBs are crushed to − 16 BSS sieve size. Further, after 1.5 min, the slope of the curve is decreased (4.03% WPCBs·min^{-1}) because the ductile metal fraction of WPCBs starts getting elongated initially and then is sliced into pieces of small sizes leading to appreciable size reduction. After 7 min, 94% of fed WPCBs were crushed to − 16 BSS sieve size and later, the curve tends to be flattened with a slope of 0.123% WPCBs·min^{-1} as shown in Fig. 1.

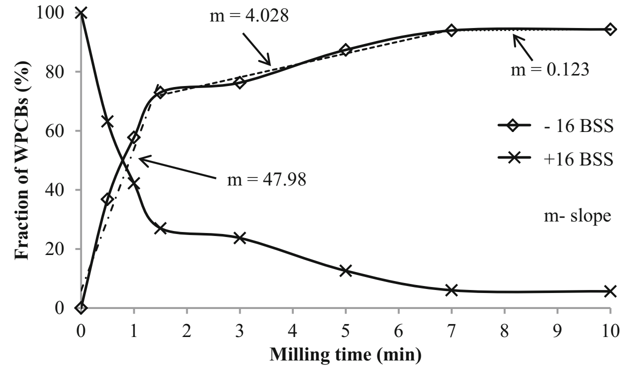

Fig. 1 Fraction of WPCBs in − 16 BSS and + 16 BSS sieve size after different milling time

Effect of Feed Rate on the Milling of WPCBs

Increased feed rate of WPCBs from 3 to 12 kg·h^{-1} led to 30% reduction in the milling rates of WPCBs crushed to − 16 BSS sieve size (Fig. 2). This is because the increase in the feed rate results in more resistance to the movement of hammers and subsequently reduces the hammer's impact velocity. Further, higher feed rates also result in the distribution of exerted impact energy among more pieces of WPCBs, relatively. These forces may not be enough to induce the brittle fracture, and thus the impact energy is absorbed by the pieces of WPCBs. The absorbance of

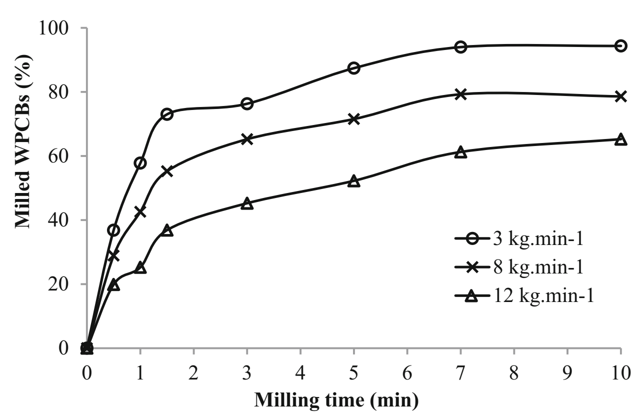

Fig. 2 Fractions of WPCBs milled to − 16 BSS sieve size at different feed rates

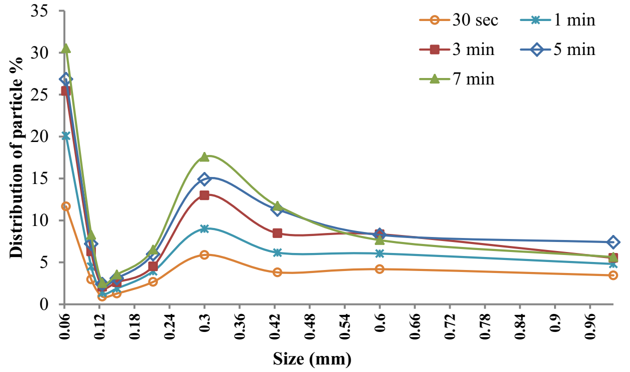

Fig. 3 Particle size distribution of WPCB powders (− 16 BSS sieve size)

impact energy not only deteriorates the milling rate, but it may result in the overheating of WPCBs. Excessive heat may lead to softening and the sticking of WPCBs together, and which, in turn, may lead to the breakdown of moving parts of the hammer mill.

Sieve Analysis of Milled WPCBs

Sieve analysis of WPCBs crushed to less than 16 BSS sieve size has been carried out. The fractions of particles retained in each sieve after different milling times are shown in Fig. 3. It is evident that the cumulative amount of retained particles increased by 2–3 times after 7-min milling compared to that after 30 s. It is found that 50–55% of the milled WPCBs possess + 100 BSS sieve size, while the rest 45–50% particles have attained − 100 BSS sieve size. Distribution of undersize in different size fractions is presented in Fig. 3, and it elucidates that distribution of particles follows a similar trend but the mass of retained WPCBs keeps increasing in each sieve. This may be because the metal and nonmetal fractions obey a specific behavior during milling, which remains unchanged regardless of time. Sieve analyses also showed that crushed WPCBs had particles mostly concentrated in the − 240 BSS and + 72 to − 52 BSS sieve sizes (Fig. 4). After 7-min milling, 30% of the particles were retained in − 240 BSS sieve size and 17% were collected in + 72 to − 52 BSS sieve size range.

Distribution of Copper in the Different Size Fractions

Copper contents estimated by chemical analysis of retained WPCB particles in each sieve after different milling times are shown in Fig. 5. It reveals that coarser size fractions

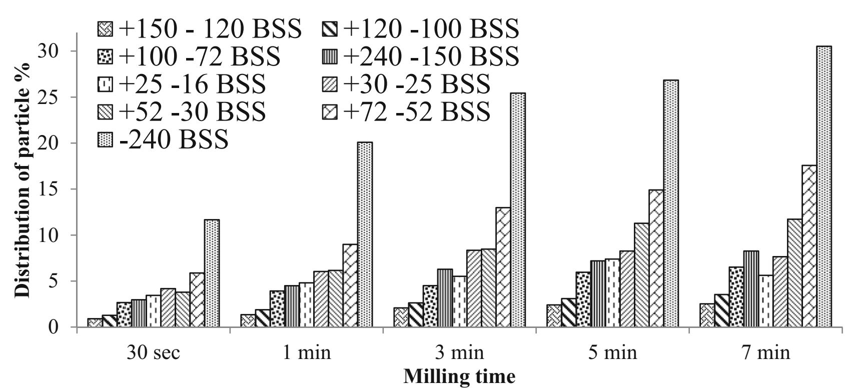

Fig. 4 Distribution of crushed WPCB powders in different size fractions

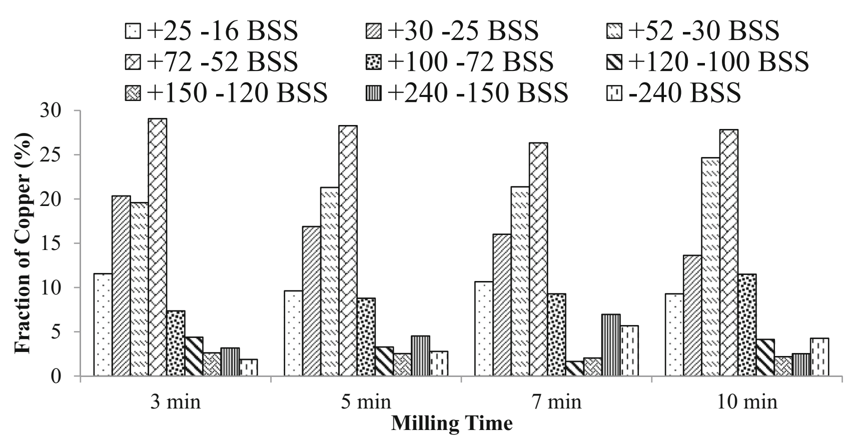

Fig. 5 Distribution of copper in different sizes of milled WPCBs

Table 2 Grade–recovery data for copper metal present in WPCBs of different size fractions

Size range	Grade (wt% Cu)	Recovery (%)
+ 25 to − 16 BSS	39.62	10.65
+ 30 to − 25 BSS	43.83	16.01
+ 52 to − 30 BSS	38.16	21.38
+ 72 to − 52 BSS	31.39	26.34
+ 100 to − 72 BSS	29.84	9.29
+ 120 to − 100 BSS	9.77	1.65
+ 150 to − 120 BSS	16.91	2.04
+ 240 to − 150 BSS	17.63	6.96
− 240 BSS	3.90	5.68

(+ 100 BSS sieve size) are rich in copper, while the fine fraction has a copper content of even less than 8%. It is because copper elongates during milling and hence could not be crushed to a very fine size. The typical grade–recovery data for WPCBs of different size fractions are shown in Table 2. Chemical analysis of sieved WPCBs also showed that nearly 75–80% of copper contents are concentrated in + 52 BSS sieve size. Further, 83–87% original copper content has been retained, and concentrated in the + 100 BSS sieve size. Since the fraction of + 100 BSS sieve size comprises 50–55 wt% of milled WPCBs, it may be interpreted that WPCBs of + 100 BSS sieve size contain nearly 43 wt% copper. Further, crushed WPCBs to less than 100 BSS sieve size contain around 8 wt% copper only.

Microscopic Examination of Milled WPCBs

Optical microscopic examination results of milled WPCBs of − 16 BSS sieve size at ×10 magnification are shown in Fig. 6. The result shows that particles of copper, glass fiber, and nonmetallic resin possess different surface

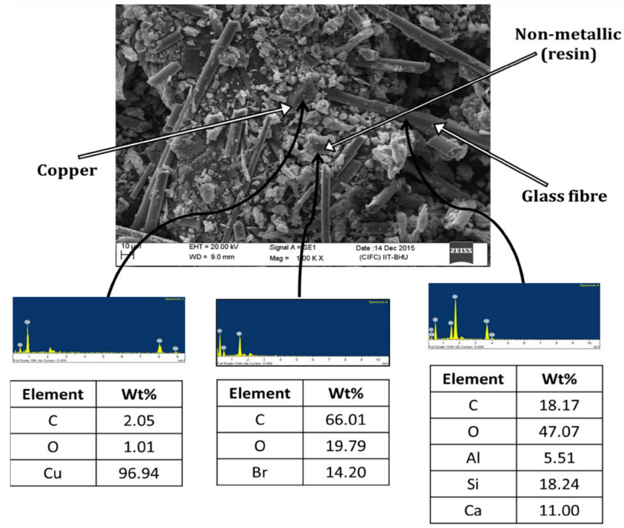

Fig. 7 SEM image of ground WPCBs of − 16 BSS sieve size after 7–min milling

morphologies and thus they can be easily distinguished. During the milling, copper particles attain a flaky structure having reddish-brown luster which is in resemblance to a thin foil of sliced copper. Glass fiber particles possess bamboo-like shape having fibrous morphology. On the other hand, the nonmetallic resin showed irregular polygon morphology with grayish luster.

The SEM analysis of milled WPCBs (milling time—7 min) was carried out, and similar morphology is observed as seen in the optical microscopy (Fig. 7). The EDS analysis of various particles showed varying compositions. The glass fiber particle exhibits bamboo-like fibrous structure and contains calcium, aluminum, and silicon which are the major constituents of glass-based material. On the other hand, a nonmetallic particle having a polygon shape showed the presence of a majority of carbon, oxygen and bromine. The nonmetallic fraction apart from glass fiber is composed of the HER, and thus its EDS

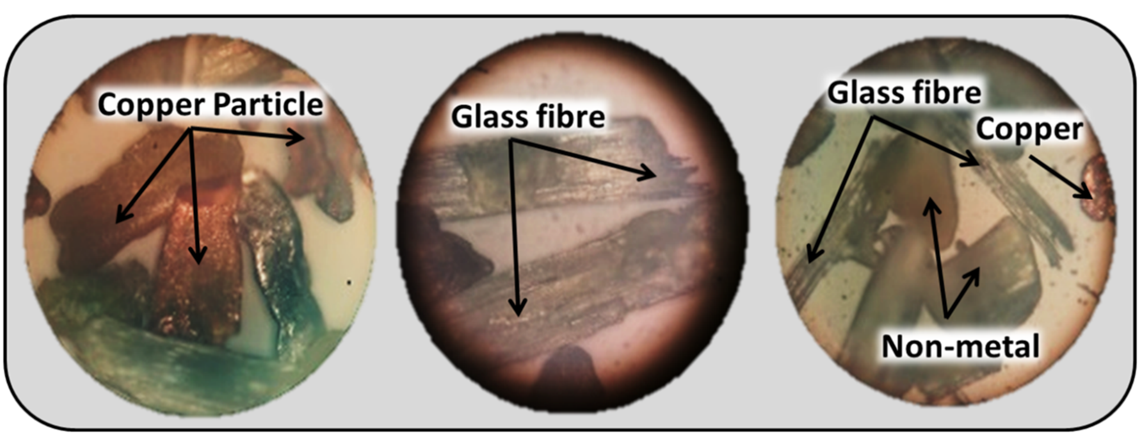

Fig. 6 Copper, glass fiber, and nonmetallic particles of crushed WPCBs (−16 BSS sieve size)

showed the presence of bromine and carbon. The copper particles are easily distinguishable in SEM due to their smooth surface morphology. The EDS at a particular point showed a majority of copper confirming that the particle is copper. These results indicate that a good liberation of metal and nonmetal has been achieved after the milling and it would be beneficial during the subsequent processing for separation of metal–nonmetal.

From the above study, it is clear that milling by hammer mill at the feed rate of 3 $kg \cdot h^{-1}$ and for 7 min is an optimal method to achieve a satisfactory downsizing of WPCBs to less than 16 BSS. Further, the separation of particles of + 100 BSS sieve size results in doubling the yield of copper content. Thus, it may be inferred that simple technique of sieve separation may be used for primary beneficiation of WPCBs.

Conclusions

The present study showed that under optimized parameters of hammer milling, viz., the feed rate of 3 $kg \cdot h^{-1}$ and time of 7 min, ∼ 94% of the fed WPCBs may be crushed to − 16 BSS sieve size. The study also showed that the milling rate decreases with the increasing feed rates and increases with the increasing time. The sieve analysis showed that the distribution of crushed particles follows the specific trend, and the particles accumulated in sieve size ranges of − 52 to + 72 BSS and − 240 BSS are the highest among all size fractions. Chemical analysis of crushed WPCBs of different size fractions showed that 83–87% initial copper concentrations are of the + 100 BSS sieve size. Quantitative analysis of crushed WPCBs of + 100 BSS sieve size showed the presence of ∼ 43 wt% copper and remaining nonmetal. Thus, the current study revealed that the sum of material content obtained after optimized hammer milling and sieving using the sieve of aperture 0.15 mm (BSS 100 sieve size) amounts to ∼ 87% of the original copper amounting 43 wt% of sum.

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