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High temperature investigations on optimising the recovery of copper from waste printed circuit boards

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A B S T R A C T

High temperature pyrolysis investigations were carried out on waste printed circuit boards (PCBs) in the temperature range 800–1000 °C under inert conditions, with an aim to determine optimal operating conditions for the recovery of copper. Pyrolysis residues were characterized using ICP-OES analysis, SEM/EDS and XRD investigations. Copper foils were successfully recovered after pyrolysis at 800 °C for 10–20 min; the levels of Pb and Sn present were found to be quite low and these were generally present near the foil edges. The relative proportions of Pb and Sn became progressively higher at longer heating times due to enhanced diffusion of these molten metals in solid copper. While a similar behaviour was observed at 900 °C, the pyrolysis at 1000 °C resulted in copper forming Cu-Sn-Pb alloys; copper foils could no longer be recovered. Optimal conditions were identified for the direct recovery of copper from waste PCBs with minimal processing. This approach is expected to make significant contributions towards enhancing material recovery, process efficiency and the environmental sustainability of recycling e-waste. Pyrolysis at lower temperatures, short heating times, coupled with reductions in process steps are expected to significantly reduce energy consumption and pollution associated with the handling and processing of waste PCBs.

1. Introduction

High consumption of electronic and electrical equipment (EEE), their short life-spans and subsequent obsolescence has resulted in the accumulation of large volumes of electronic waste (e-waste) worldwide. Rapid technological advancements followed by regular upgrades of electronic items such as mobile phones, computers, TVs, laptops, notebooks etc. are playing a significant role in the generation of such waste. With e-waste volumes increasing at the rate of 4–5% per year, it is one of the fastest growing solid waste streams in the world. Nearly 41.8 million tons of e-waste was generated globally in 2014; and the global generation of e-waste in 2018 is expected to be ~49.8 Mt (Baldé et al., 2015). The central components of EEE are printed circuit boards (PCBs), which contain a mixture of polymers, ceramics and metals as part of the boards, circuitry, components, solders, and connectors (Lister et al., 2014). With increasing demands for metals, declining mineral resources, costs and environmental impacts associated with mining and the exploitation of natural resources, there is immense potential in transforming e-waste from a waste product to a materials resource. While the rates for recycling are still quite low, there is an urgent need to take a critical look at the current e-waste recycling techniques and to optimise the recovery of metals and other valuable products.

This article is focussed primarily on optimising the recovery of copper from e-waste, one of the main metallic constituents (up to 20 wt%) of waste PCBs. Along with the key aspects of material recovery, associated waste management perspectives including the volumes of wastes processed, energy consumption, secondary waste generation, and the environmental impact of PCB recycling will be discussed. The recovery of copper from e-waste has been investigated extensively using hydrometallurgical and pyro-metallurgical techniques (Cui and Zhang, 2008; Schluep et al., 2009). We first present a brief overview of the current status of research in the field including techniques/approaches used along with details such as the nature/form of copper recovered, the number of process steps, and process efficiency.

1.1. Commercial approaches

Commercial recycling of e-waste is currently carried out in two industrial operations, namely Noranda and Rönnskar as a part of primary copper processing (Veldhuizen and Sippel, 1994). Up to

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14 wt% crushed e-waste is added as an additive/impurity to the copper ore; the levels of e-waste being recycled are limited by their influence on furnace operations. Copper present in PCBs is heated at 1250 °C in oxygen-rich atmosphere, converted to copper matte; high purity copper is then recovered through electro-refining. Umicore process uses e-waste (up to 10 wt%) as feedstock for recovering copper and precious metals in the metallic phase, followed by subsequent purification in a leach–electrowinning plant (Schluep et al., 2009). While these processes can be used to recycle large volumes of e-waste without producing significant levels of secondary wastes, these multi-stage techniques recover copper in an indirect manner. It is important to note that the copper present initially in waste PCBs generally has quite high purity. These processes however treat e-waste as an impurity/copper ore and carry out high temperature oxidation of pure copper followed by its reduction and purification in order to extract copper. Some of these processes were developed nearly 20 years ago, have low energy efficiency/productivity and do not represent the state-of-the art recycling technology.

1.2. Hydrometallurgical techniques

Hydrometallurgy has been used widely to extract copper from e-waste; these techniques generally include mechanical processing/size reduction followed by extraction through chemical leaching/reactions. Behnamfard et al. (2013) size reduced waste PCBs in a hammer crusher followed by pulverisation to particles sizes ~300 μm. These powders were then leached in a sulphuric acid solution in the presence of hydrogen peroxide for 3 h/200 rpm/room temperature. Up to 85.76 wt% copper was extracted as Cu^{2+} ions in solution; remaining copper could also be recovered through repeated leachings. However, these solutions contained other metallic ions such as Zn^{2+}, Sn^{2+}, Fe^{2+} and Ni^{2+} in addition to copper ions. Silvas et al. (2015) used a number of process steps including size reduction, magnetic separation and two chemical leachings with H_2SO_4 and H_2SO_4/H_2O_2 to recover copper. Recovered copper solution contained Al and Zn as impurities and required further purification/electrowinning steps. Secondary wastes produced included magnetic fractions, chemical effluents and residual solids.

Zhang and Zhang (2014) used an eight-step process for the recovery of copper; waste PCBs were first heat treated at 270 °C to improve their crushing efficiency. The material was then crushed in a hammer mill, followed by air separation. The metallic fraction obtained in the separation step was mechanically processed in a cutting mill to obtain 0.25 mm particle sizes. The material was then leached in a solution of $CuSO_4{\cdot}5H_2O$ and NaCl at 60 °C. After two filtration processes, copper was recovered in the form of cupreous chloride. Although 98.5% copper recovery was achieved, this approach used a number of process steps, producing significant amounts of residual chemicals, spent acids, non-metallic fractions, etc. Ou and Li (2015) used mechano-chemistry to recover copper, an approach involving the grinding and mixing of waste PCB samples with sulphur powder. The mixture was ground in a ball mill for 20 min to form copper sulphide; followed by leaching into a 3 M sulphuric acid solution containing 30 wt% hydrogen peroxide. While up to 95% copper could be recovered in a solution form, other impurities were also present in this solution; additional steps were required to recover metallic copper. Spent acids and resin residues were generated as secondary waste. While successful in recovering copper, these techniques are severely limited by the volumes of waste processed, significant levels of waste handling/initial processing and by the amounts of secondary wastes produced, thereby making large scale e-waste recycling and copper recovery economically and environmentally unviable.

1.3. Pyro-metallurgical techniques

Long et al. (2010) heated waste PCBs to 550 °C at a heating rate of 10 °C/min under vacuum, kept these at 550 °C for 2 h followed by quenching. Solid pyrolysis residues containing glass fibres, copper and carbon were then crushed to fine powders and separated into heavy and light fractions using gravity separation. While up to 99 wt% of copper could be recovered in the heavy fraction, this approach required four process steps, and produced secondary waste in the form of oils and light fractions. Zhou et al. (2007) used a multi-stage pyro-metallurgical approach to recover copper and other metals. Waste PCBs were mixed with 12 wt% NaOH and heat treated at 1200 °C under reducing atmosphere to produce two types of solid fractions: a metallic fraction containing Fe, Cu, Pb and precious metals, and a slag phase containing SiO_2, Al_2O_3 and CaO. The Cu concentrations in the metallic and the slag phase were determined to be ~82 wt% and 0.15 wt% respectively. The metallic fraction was then heat treated at 1200 °C under air; the Cu_2O thus generated was reduced with pyrolysis gas to obtain metallic copper; secondary wastes produced included up to 30% copper as Cu_2O slag.

Zhan and Xu (2011) crushed waste PCBs in a high speed shearing machine, followed by hammer grinding, sieving and the separation of metallic and non-metallic fractions using a corona electrostatic separator, followed by vacuum pyrolysis of these powders at 850 °C. Most of the copper was recovered in the form of (Cu, Pb, Sn) alloys containing up to 92.93 wt% Cu, 2.38 wt% Pb, 3.57 wt% Sn, and small amounts of non-metallic fractions. Cayumil et al. (2014) carried out high temperature pyrolysis of waste PCB chips in the temperature range 1150–1550 °C for times up to 20 min under argon atmosphere; copper was recovered in the form of copper rich and lead rich alloys. While pyrometallurgical approaches do not produce much residual waste such as spent acids etc. and can significantly reduce the volumes of waste after processing, careful attention needs to be paid to the gaseous emissions from PCBs during exposure to high temperatures. The generation of harmful brominated compounds, dioxins, furans from polymer degradation can be a serious issue for processing at low temperatures. However, the generation of dioxins/furans is known to become negligible at temperatures above 800 °C (Mckay, 2002).

1.4. Other approaches

Xiu and Zhang (2009) investigated the recovery of copper from waste PCBs using supercritical water oxidation and an electrokinetic process. PCBs were size reduced in a cutting mill to get particles sizes ~ 0.1 mm. The material was then dissolved in solution of distilled water and hydrogen peroxide; and inserted in a reactor consisting of two electrodes and kept at 713 K and 30 MPa for 60 min. Electrodes were then leached in a 5 M HNO_3 solution for several hours (overnight). The recovery of copper achieved was 84.2%, of which 74% was deposited on the cathode. In this four-step process, other impurities were present in the spent solutions, and solid residues were generated as secondary waste. Fogarasi et al. (2014) investigated the recovery of copper and the concentration of gold from waste PCBs by using electrochemical oxidation without any mechanical processing. The process consisted of leaching the samples into an acidic ferric chloride solution (0.3 M $HCl + FeCl_3$) and electrowinning at 4 mA/cm^2 density. Up to 99% copper was recovered in the form of a deposit, along with a gold rich residue. The process was improved further by adjusting the flow rate in the leaching step and in the deposit of copper in the EW process (Fogarasi et al., 2015). Bioleaching has been also used as an alternative process to recover copper from waste PCBs. However, the process took a very long time to leach the metal (Wang

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