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Metals recovering from waste printed circuit boards (WPCBs) using molten salts

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ABSTRACT

Recycling of waste electrical and electronic equipments (WEEE) has been taken into consideration in the literature due to the large quantity of concerned wastes and their hazardous contents. The situation is so critical that EU published European Directives imposing collection and recycling with a minimum of material recovery [1]. Moreover, WEEEs contain precious metals, making the recycling of these wastes economically interesting, but also some critical metals and their recycling leads to resource conservation. This paper reports on a new approach for recycling waste printed circuit boards (WPCBs). Molten salts and specifically molten KOH–NaOH eutectic is used to dissolve glasses, oxides and to destruct plastics present in wastes without oxidizing the most valuable metals. This method is efficient for recovering a copper-rich metallic fraction, which is, moreover, cleared of plastics and glasses. In addition, analyses of gaseous emission show that this method is environmentally friendly since most of the process gases, such as carbon monoxide and dioxide and halogens, are trapped in the highly basic molten salt. In other respects, under operation without oxygen, a large quantity of hydrogen is produced and might be used as fuel gas or as synthesis gas, leading to a favourable energy balance for this new process.

1. Introduction

Waste electric and electronic equipment (WEEE) is diverse and complex, in terms of materials and components, and is increasing dramatically. Electronic waste is made of a mixture of various metals, particularly copper, aluminium and steel, mixed with various types of plastics, glass fibre-reinforced epoxy resin and ceramics [1]. Electronic equipment has a relatively short average lifetime, i.e., 2–3 years; consequently, large quantities of electronic waste need to be discarded [2–4]. Many countries and organizations have drafted national legislation to promote re-use, remanufacturing, and recovery of materials by recycling techniques to reduce the quantity of waste. As an example, in Europe, according to the directive 2002/96/EC, since January 2007, the rate of recovery will be increased up to at least 75 wt.% and components, materials and substances re-use and recycling will be increased to at least 65 wt.% per Information Technologies and Telecommunications equipment appliance [5]. Incineration of electronic waste by traditional incinerator is also dangerous. For example, copper is a catalyst for dioxin formation when flame-retardants are incinerated. Recycling is important, not only from the point of view of waste treatment, but also from the aspect of recovering valuable materials.

The proportion of waste printed circuit boards (WPCBs) is about 3% of electronic waste [2,6]. Unlike other solid waste, WPCBs contain a variety of heavy metals and hazardous substances (i.e., lead, cadmium, mercury, PVC, halogenated flame retardants, etc.) that may seriously pollute the environment. The typical composition of PCBs is non-metal (i.e., plastic, resins, glass fibres, etc.) >70%, copper ∼16%, solder ∼4%, iron, ferrite ∼3%, nickel ∼2%, silver ∼0.05%, gold ∼0.03%, palladium ∼0.01%, and so on [6]. It can be clearly seen that except for the hazardous substances, a lot of valuable materials contained in WPCBs make them worth being recycled: the precious metals make up more than 70% of the value and copper ca. 20%. Therefore, developing a non-polluting, efficient, and low-cost processing technology for recycling of WPCBs cannot only avoid environmental pollution, but also help recycle valuable resources. However, PCB waste is a heterogeneous mix of polymer, metal and fibreglasses, which makes its recycling difficult. For example, over the years, PCBs have evolved from uncomplicated single and double-sided plated-through-hole (PTH) to multi-layered PCBs.

The recovery of precious metals from electronic waste is now carried out by physical separation processes [7–9], pyrometallurgical processing, hydrometallurgical processing, and biometallurgical processing [10–15]. High temperature Pyrometallurgy, i.e., 1200 °C, as usual technology requires high investments. NaOH can be used as slag formation material to separate metal from slag and decrease the melting temperature [16]. Low temperature Pyrolysis can be considered as an alternative method of recycling WPCBs, because in the pyrolysis process (heating without oxygen),

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the organic material is decomposed into low molecular products (liquids or gases), which can be used as fuel or chemical feedstock [17–20]. Vacuum pyrolysis has several advantages over other pyrolysis methods because of the short organic vapour residence time in the reactor and low decomposition temperature, which reduces the occurrence and intensity of secondary reactions [21].

Hydrometallurgical processes require various steps, including a series of acid or caustic as leaching media for solid material, followed by various separation and purification procedures [22–25]. However, if hydrometallurgy is now demonstrated as sustainable route for waste processing, unfortunately, extraction of precious metals and mainly gold is only possible in cyanide media.

Therefore, the traditional technologies cannot meet the future requirements of industry because of environmental contamination, high cost and low efficiency. Two recycling processes at industrial scale, i.e., Pyrocom and Haloclean, are used presently [14,26–30]. Developing new clean technologies for recycling valuable resources from WPCBs is of great significance, with two main objectives: saving in energy (using recycled materials in place of virgin materials results in significant energy savings) and reduction in pollutions.

The challenge remains the access to encapsulated metals as we are in front of complex matrix containing non-ferrous metals, precious metals, ceramics, thermo-polymers and resins. Molten salts offer the best available technology to catch metals encapsulated in other matrices. The main objectives of this method are:

- recovering the precious metal fractions, without any dissolution or melting,
- increasing halides retention
- restricting CO_2 emission, and
- developing an economically viable process.

Molten salt oxidation (MSO) has been proposed for coal gasification and destruction of hazardous organic mixed oils, chlorinated organic solvents, chemical weapons, energetic materials, etc. [31–33]. In these processes, wastes are introduced in molten carbonate salts under oxidation condition using air injection. The salt, at temperatures in the range 900–1000 °C, catalyzes waste oxidation. Carbon dioxide and acid gases such as HCl and HF are trapped in the bed. The inorganic compounds contained in the wastes lead to final residues, which are retained in the molten salt bed. MSO has several advantages over incineration:

- Low cost environmentally acceptable process (no formation of dioxin or furan).
- Flameless oxidation process.
- Owing to high solubility of waste in molten carbonates, reduced volumes are necessary, with no effluents.
- Oxidation of most organic waste is exothermic; therefore the heat of oxidation can be used to keep the salt molten.
- Scale-up is adapted to small and medium size of installation while classical incineration is not economically feasible below a capacity of 100 000 tons/year.

The process can also be operated under reducing conditions, so that carbon monoxide and hydrogen gases are produced and can be used as fuel gas or as a synthesis gas.

The molten salt selected in the present work was a mixture of hydroxides, specifically NaOH–KOH, with eutectic composition ($T_{melting}$ = 170 °C). The main attractive features of molten hydroxides are:

- The low melting temperature allowing working at about 250 °C, which reduces the energy cost and limits the corrosion of the installation.
- A wide electrochemical window.
- The high solubility of gases such as halogens and CO_2, which limits toxic emissions.
- A high solubility of oxides, glasses and plastics.
- The behaviour of metals in the salt mixture is described in the literature [14] and it is shown that metals like, copper, gold, nickel and silver are not oxidized in the absence of oxygen.
- Valuable metals can be recovered in the solid state.

The objective of this paper is to describe the WPCBs recycling method using molten KOH–NaOH eutectic, to evaluate the efficiency of this method, and to discuss its impact on the environment.

2. Materials and methods

2.1. PCBs characterization

PCB waste used in this study was obtained from IT equipment.[1] The samples were broken into pieces (20 mm × 10 mm) before experiments.

2.1.1. General structure of PCBs

PCBs are insulating substrates on which the connections between electronic components are made by copper tracks. There are several kinds of electronic waste: single and double-sided plated-through-hole (PTH) or multilayered printed circuits. Before experiments, the structure of PCB was analyzed by SEM, coupled with energy dispersive spectrometry (EDS).

2.1.2. Metal contents

The valuable metal contents are obtained by using inductively coupled plasma/atomic emission spectroscopy (ICP AES Perkin Elmer – Optima 3000XL). Before analysis, an acid leaching of the sample with aqua regia (3:1(V:V), 35% HCl:60% HNO_3) was carried out during 24 h. Then, part of the digestion solution was diluted with ultrapure water (Milli Q). For each analyzed metal (Fe, Ni, Au, Cu, and Ag), the mean concentration was averaged from five measurements.

2.2. Treatment of PCBs in molten KOH–NaOH eutectic

2.2.1. Experimental reagents

Treatments were carried out with pure sodium hydroxide and potassium hydroxide (NaOH purity > 98% and KOH purity > 85%). The experimental salt had the eutectic composition, i.e., 41 wt.% NaOH–59 wt.% KOH. 30 g of hydroxide mixture was used for each run.

2.2.2. Experimental setup

The experimental setup, as shown in Fig. 1, consists of a stainless steel sealed cell, flown through by pure argon, and allowing the recovery of the output gases. Crushed PCBs samples were placed in an iron melting pot containing the salt. The waste was mixed with solid granules of hydroxides so that $wt_{PCBs}/wt_{salt} = 0.3$ (for a total of ca. 40 g). The cell was heated in a tubular electric furnace. After melting of the salt, the temperature was kept at 300 °C during about 1 h. Pure Argon, with a flow rate of 2 L h^{-1}, was used as flowing gas.

2.3. Analyses of reaction products

After cooling, the solid mixture was lixiviated in ultrapure water and the solid residues were separated from the solution by

[1] *PCB waste provided by Company VMA, Pontcharra, France.