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Review

Concentration of rare earth elements during high temperature pyrolysis of waste printed circuit boards

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ABSTRACT

An in-depth investigation was carried out on the recovery of rare earth elements (REEs) from a variety of waste printed circuit boards (PCBs). High temperature pyrolysis was carried out at 850 °C for 15 min using horizontal resistance and thermal plasma furnaces with different levels of turbulence. The concentration of REEs in key pyrolysis residues, namely, copper rich red metallic fraction, lead/tin rich white metallic fraction and slag rich carbonaceous residues, were determined using ICP analysis. Most of the REEs were found concentrated in the carbonaceous residue with negligible levels of REEs recovered in the two metallic fractions. Most of the recovered REEs showed a high affinity towards to refractory oxides silica and alumina, and little affinity towards metals Cu, Pb and Sn. The yield of REEs was significantly higher from the plasma furnace indicating the important role of turbulence in the dissociation & subsequent diffusion of REEs during pyrolysis. While La, Pr, Sm and Y required turbulent conditions for their recovery, Nd, Gd, Ce and Dy were relatively easy to dissociate and extract from the waste. Significant amounts of REEs could thus be recovered from waste PCBs as concentrated recyclates for further processing and extraction of individual rare earths. This study has shown that PCBs could prove to be a valuable urban mining resource of REEs. The recovery of REEs, in addition to precious and other metals, could play an important role towards enhancing the economic and environmental sustainability of e-waste recycling.

1. Introduction

Rare earth elements (REEs) are playing an increasingly crucial and vital role in the electronics industry in applications such as Plasma screens, LEDs, Cathode-ray tubes (CRTs), permanent NdFeB magnets, mobile phones, computers and peripherals, motors, wind turbines, rechargeable batteries etc. (Binnemans et al., 2013). Several REEs, such as Neodymium (Nd), Praseodymium (Pr), Gadolinium (Gd), Dysprosium (Dy), Terbium (Tb), Lanthanum (La), Cerium (Ce), Europium (Eu), Terbium (Tb), Yttrium (Y), are essential to the manufacture of several electronic components. These components include permanent magnets (Nd, Pr, Gd, Dy and Tb); rechargeable batteries (La, Ce, Nd and Pr), phosphors (Eu, Tb, Y, Ce, Gd, La), plasma screens (Eu, Tb, Y, Ce, La), auto catalysts (Dy, Nd, Pr, Tb) and other applications (Curtis, 2010). Due to increasing demand, high prices, restricted supplies and monopoly issues, U.S. Department of Energy (2011) has identified five REEs, i.e., Nd, Eu, Tb, Dy and Y, as most critical resources in terms of medium-term criticality index. Over the next 25 years, the demand for Nd and Dy is expected to rise by 700% and 2600% respectively for applications in green, low-carbon economies and other potential sectors (Alonso et al., 2012).

Rare earth elements are not exactly rare in nature; these can be found in more than 200 minerals (British Geological Survey, 2011). However, key difficulties in their mining are caused by low concentrations in poor grade ores for economic and sustainable mining, the production of radioactive thorium as a biproduct, regulatory pressures etc. (Kara et al., 2010). With China presently supplying over 90% of the market share of REEs, creating a near monopoly situation, the availability of REEs to enterprises outside China can be potentially challenging, limited by export quotas, expensive, crucial and even a political issue (Moss et al., 2013; Hoenderdaal et al., 2013). Other countries that produce REEs include Australia, USA, India, Brazil, Malaysia etc. In view of emerging new technologies based on REEs and the present supply situation, efforts are being made for further exploration, mining, and enhancing process efficiency of various process steps. Recycling

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of REEs (presently < 1%) therefore assumes greater importance as an alternate resource in the current scenario of increasing demand and diminishing supplies especially for those countries without any REE resources of their own.

The recovery of REEs from waste resources has been mainly focussed on recycling production scrap, end-of-life products and left-over residues during the production of REEs or REE based electronics and other products. End-of-life products being recycled for REEs can be organised into several distinct categories depending on the nature of the product, REEs present and the availability of recyclable material (Tunsu et al., 2015). Phosphor based products such as CRT screens, Plasma display panels, LEDs, fluorescent lamps are a good source of Y and Eu, and contain small amounts of La, Ce, Tb, Gd, Nd and Sm etc., and some metals as well (Buchert et al., 2012; Ronda et al., 1998). Another category is based on products containing permanent NdFeB magnets such as hard disc drives (HDDs), electric motors, generators for wind turbines, mobile phones, speakers, head-phones, NMR spectrometers etc. REEs present in these magnets include Nd, Dy, Pr, Gd, Tb and Sm along with metals such as copper, nickel, iron, cobalt etc. (Gutfleich et al., 2011). Another category is rechargeable batteries for domestic applications, portable electronic devices, hybrid electric cars, power tools. NiMH batteries, with significant technological and environmental advantages, have replaced Cd in NiCd batteries with a mixed alloy containing La, Pr, Ce and Nd (up to 7% REEs) (Fernendes et al., 2013). Rare earth catalysts including styrene catalysts, fluid cracking and automobile converter catalysts present yet another category, containing mainly La, Ce, Pr, Sm etc. (Feron and Henry, 2015). Small amounts of REEs may also be present in numerous other components used in a range of applications.

Several of the REE recycling techniques such as physical, hydrometallurgical and pyrometallurgical processing, liquid metal extraction, chemical vapor transport, magnetic separation, hydrogen decrepitation etc. were developed for relatively homogeneous and clean pre-consumer magnetic scrap (Itoh et al., 2009; Zakotnik et al., 2008; Saito et al., 2003, Tunsu et al., 2015). Only a few studies have been reported on the recovery of REEs from heterogenous waste from end-of-life products. Abrahami et al. (2015) have reported on the recycling of hard-disc drives (HDDs) and NdFeB magnets using commercial shredding, thermal demagnetisation, grinding and screening followed by molten slag extraction or by acidic leaching. Recovered products were in the form of high purity rare earth double salt $NaNd(SO_4)_2$ for further processing. Using selective chlorination, Xu and Peng (2009) added aluminium chloride to SmCo manufacturing scrap to recover high purity chlorides of Sm and cobalt. Based on hydrogen decrepitation for breaking RE alloys into powders, Pearson (2013) has developed a recycling technique to extract rare metals from NdFeB and SmCo magnets. Several large manufacturing companies are making serious and concerted efforts towards recycling rechargeable batteries; the Umicore battery recycling division can process up to 7000 tonnes of batteries per annum (Umicore battery recycling, 2015). Some of these technologies for recovering REEs from permanent magnets, phosphors and batteries have reached a level of maturity for commercial utilization.

The volumes of e-waste are continuing to grow rapidly in most countries with no signs of slowing down due to rapid upgrades, technological changes, increasing affordability, product obsolescence and escalating consumption of electronic goods. Approximately 44.7 million tonnes of e-waste were generated globally in 2016, and estimated to increase to 55.2 million tonnes by 2021 (Baldé et al., 2017). In view of volumes generated, composition, costs and environmental impacts associated with mining, e-waste is considered a valuable urban mining resource for materials (Hagelüken, 2010). E-waste constitutes a complex inventory of product categories that are assembled out of a variety of components, multiple sub-assemblies and material combinations.

Most of the material recovery from waste PCBs has been focussed on recovering precious and other metals (Cayumil et al., 2016; Cui and Zhang, 2008). The recovery of REEs from waste electronics has been limited to separating magnetic components, batteries, CRTs, screens etc. from the end-of-life equipment for further processing. However, very little attention has been paid to extracting REEs from waste printed circuit boards (PCBs), the central component of electronic devices. The extraction of relatively small amounts of various REEs present in various electronic components mounted on PCBs was generally considered to be economically unviable.

In this article, we have focussed our attention on extracting REEs from a variety of waste PCBs, in addition to other metals, with an aim to produce a concentrated REE resource in a cost-effective and environmentally sustainable manner. The aim of the present investigation is to recover REEs from waste PCBs as concentrated recyclates for further processing, while enhancing the process efficiency, economic and the environmental sustainability by maximizing overall amounts of materials recovered during the recycling of waste PCBs. The article is organised as follows. Experimental details on processing four different types of PCBs, their initial processing, heat treatments in resistance and plasma furnaces, and the generation of pyrolysis residues are presented in Section 2. Section 3 presents inductively coupled plasma (ICP) results on the concentrations of REEs recovered from various pyrolysis fractions; recovery results on precious and other metals will not be presented. In Section 4, these results are discussed in terms of type of PCB, processing conditions, recovery of light and heavy REEs. Key findings of this study will be presented in concluding remarks.

2. Materials and methods

2.1. Materials

Waste printed circuit boards were collected from a range of sources, waste dismantlers/e-waste recyclers in as received sizes and shapes (see Fig. 1 for representative examples of waste PCBs). These PCBs were labelled as: mobile phones: (MB); mother board: (MTB); power supply: (PS); random access memory: (RAM) in the text as well as in the figures. Electronic components mounted on these boards were left intact and were not removed from the boards for two key reasons. Firstly, REEs have a higher probability of presence within some of the electronic components such as capacitors, integrated circuits, resistors, transistors, LEDs, switches than on the copper laminated substrates. Secondly, the removal of components from PCBs by melting solders with infrared heaters, hot fluids, mechanically breaking solder joints with hammers or grinders, chemical etching etc. is associated with local area contamination, health and environmental risks (Lee et al., 2012). Apart from cutting larger boards into smaller pieces depending on the size and volume of the furnace used for heat treatments, no other mechanical treatment (hammering, crushing, grinding, or powdering) was carried out on these PCBs.

2.2. High temperature pyrolysis

The heat treatment of waste PCBs was carried out in two different types of furnaces: (a) a horizontal resistance furnace, (b) a thermal plasma furnace. The plasma furnace generates a high level of turbulence in the heating zone, whereas only turbulence in the horizontal furnace was caused by the continuous flow of inert gas (1 L/min). Heat treatment temperatures were chosen to be $\sim$850 °C as the generation of harmful dioxins/furans generated