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The geochemically-analogous process of metal recovery from second-hand resources via mechanochemistry: An atom-economic case study and its implications

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ABSTRACT

In the context of recycling metal to embrace the sustainability challenge, this work proposes a geochemically-analogous process of metal recovery through mechanochemistry for the first time, to avoid the limitations of on-going methods and to establish an innovative technology philosophy. This work systematically investigates this geochemically-analogous process, to keep it green and to generalize it further. Copper recovery from waste printed circuit boards (WPCBs), a typical copper-rich waste, is chosen as a case study in this work. Nearly 98% of the copper in the WPCBs can be recycled in the optimized conditions and 82.3% of the sulfur can be reused, by means of the process. Based on the experimental result, this paper purports a closed-loop route of copper recovery which follows the green chemistry principles (high yield, high atom economy and no secondary pollution). This route can be generalized into other second-hand resources that are rich in copper. Some other metals (e.g. lead) that are commonly present as corresponding sulfides in nature can be taken into consideration in this geochemically-analogous process as well.

Contents

1. Introduction

The past decades have witnessed a huge upsurge in mining metal from virgin ores to meet the demand in the burgeoning global market where the consumption of new high-tech products

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containing various kinds of metals (including basic, precious and specialty metals) as essential components, prevails (Kiddee et al., 2003; Ogunseitan et al., 2009). However, metal resources in nature is limited. It is estimated that, based on the comparison of the world mine production and the reserve base, copper in minerals would be drained in 61 years, lead in 43, zinc in 46, tin in 53, mercury in 80, nickel in 100 (Wernick and Themelis, 1998). At the same time, second hand resources, mainly waste electrical and electronic equipments (WEEEs) are rich in different kinds of metals, but metal recycling from them is often inefficient or even essentially non-existent (Chi et al., 2011). End-of-life recycling rates (EOL-RRs) for the commonly used 'base metal' (iron, copper, zinc, etc.) are merely above 50% (these rates are the highest among sixty tested metallic elements) (Ogunseitan et al., 2009). In view of this imbalance, the metal sustainability has been brought to the forefront. There exist many defects in the on-going technologies of recycling metals: secondary pollution (Li et al., 2012), low recycling rate (Kasper et al., 2011), chemicals' overuse, green gas production and energy consumption. To develop new technologies for the recovery of desired metals, green chemistry technologies have been recognized as one of the most significant methods to embrace this challenge (Kiddee et al., 2003). Also, it seems more important to break the preconceived notions of purely focusing on technology itself and to establish an innovative technology philosophy by learning from other related fields.

All chemical elements formed in the furnaces of stars and in powerful supernovae explosions that happened billions of years ago, and continue to this day (Misra, 2012). Then, throughout earth history, the geochemical processes, which are characterized by high temperatures, high pressure and mechanical forces through diastrophism, have selectively concentrated metals into many minable deposits (Pohl, 2011). Metal sulfides are the most common metal-containing compounds existing in the minerals, such as Cu, Pb, Ag, and Zn. Copper in the crust is most commonly present as copper-iron-sulfide and copper-sulfide minerals (more than 80%) (Mark et al., 2011), including chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), villamaninite (CuS_2), covellite (CuS), djurleite ($Cu_{1.95}S$), anilite ($Cu_{1.75}S$), etc. (Mark et al., 2011; Tezuka et al., 2007). The mechanochemical processes are, to some extent, analogous to geochemical ones, in terms of direct mechanical force by collision and high temperature and pressure within the confined colliding point at the moment of collision (Balaz, 2008). It has been reported that copper sulfides and iron sulfides can be synthesized via mechanochemistry (Ou and Li, 2014). So, it can be concluded that mechanochemistry can simulate geochemical processes in metal sulfurization.

Mechanochemistry, which was once application-oriented but is going through its current resurgence in chemistry (James and Friscic, 2013), has been used in the extractive metallurgy for many years (Balaz, 2008). Mechanical activation can influence surface and bulk properties of minerals, create a degree of disordering and break bonds in the crystalline lattice so that both a decrease in activation energy and an increase in the rate of leaching can be obtained (Balaz, 2008). Also, the decrease in activation energy makes thermodynamically difficult or even impossible reactions happen. Extracting metal from second-hand resources is conceptually similar to mining raw ores.

We have published one review paper that summarizes all previous metal recovery works by the aid of mechanochemistry (Ou and Li, 2015). Mechanochemistry has had many successful cases in waste management (Guo et al., 2010). Sasai et al. (2008) utilized the planetary ball mill to extract 99% lead as a lead-EDTA species from cathode ray tube (CRT) powder. Yuan et al. (2012) directly milled the CRT powder and a high yield of 92.5% of lead were leached by dilute nitric acid. In addition, Saeki et al. (2004) and Zhang et al. (2000) applied mechanochemistry to lithium and cobalt recovery from waste lithium-ion batteries. Mio et al. (2001), Zhang et al. (2007), and Zhang and Saito (1998) successfully recovered rare earth from waste fluorescent lamps. Indium recovery from LCD screens was carried out through mechanochemistry by Murakami et al. (2002) and Hasegawa et al. (2013) In these practices, mechanochemistry performs sustainably, enabling metal recycling under environmentally friendly and essentially waste-free conditions (Balaz et al., 2013).

Second-hand resources are synthetic materials, not natural minerals, so that there is a great difference between metal occurrences in second-hand resources and in natural minerals. It is not technically easy to make direct use of traditional metallurgical methods in the mineral extractive processing to deal with second-hand resources. If it is difficult to directly leach the targeted metal from scraps, it is an alternate method, through a geochemically-analogous process, to transform the targeted metal into its corresponding compounds that exist in natural minerals. Afterwards, methods in traditional mineral engineering can be taken into use.

Our preceding work (Ou and Li, 2014) has verified the possibility of mechanochemistry in metal sulfurization and has successfully employed free radical theory and homogenization theory in microstructural assessment on synergism of mechanical activation and sulfurization. Based on our former work, this study, for the first time, proposes the geochemically-analogous process of metal recovery from second–hand resource by means of mechanochemistry. This study mainly gives copper recycling from waste printed circuit boards (WPCBs) as an integrated example. As a result, almost 98% copper was recovered, and left intact was the other main component of WPCBs (resin) which can be further utilized as heavy metal sorbents. Next, green chemistry principles (e.g. atom economy) were utilized to assess this recycling route. We successfully avoid main disadvantages in current technologies (involvement of strong acid and organic chemicals, secondary pollution and low recycling rate) and establish an innovative technology philosophy that directs a green recycling route. In the end, this paper attempts to generalize this geochemically-analogous process to other metal recovery, such as lead.

2. Materials and method

2.1. WPCBs sample

WPCBs are the most common type of wastes that are rich in metals, as PCBs are the essential part of almost all electrical and electronic equipments (EEEs) Duan et al., 2011. WPCBs contain a large amount of metal (~40%) (Duan et al., 2011): copper (the largest ratio), alumina, lead, zinc, nickel, iron, tin, antimony, chromium, molybdenum, aurum, platinum, silver, palladium, etc. The averaged content of copper reaches 17.6% (5.8–26.8% for different sources) (Duan et al., 2011) while typical copper ores contain from 0.5% Cu (open pit mines) to 1 or 2% Cu (underground pit mines) (Mark et al., 2011). About 4 million tons of copper comes from recycled end-of-use objects and manufacturing wastes in about 22 million tons of copper of coming into use per year worldwide (Mark et al., 2011).

The WPCBs used in this work were provided by Dongjiang Environment Co., Ltd in Shenzhen, China. The electronic components were manually dismantled from WPCBs in lab. Then the WPCBs were broken into fragments (referring to Fig. 1A) via an air cooling pulverizer (FL-150, Jiangsu Guibao Co., Ltd, China). The sample was prepared through an 8-mesh screen (particle size <2.5 mm). To ensure the homogenization of sample and reproduction of experimental results, the Carpenter left-right balancing method was

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