Sustainable recovery of precious metals from end-of-life vehicles shredder residue by a novel hybrid ball-milling and nanoparticles enabled froth flotation process

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ABSTRACT

It is hereby reported a simple, effective and sustainable method for the recovery of precious metals from end-of-life vehicle shredder residue and/or automobile shredder residue based on a hybrid ball-milling and microbubble froth flotation process. A ball-milling treatment of automobile shredder residue along a mixture of Fe/Ca/CaO nanoparticles had as main result the entrapment of precious metals and in subsidiary an improvement of the floatability of the various size fraction particles (1.0, 0.425, and 0.25 mm, respectively). Therefore, a separation of the settled fraction (poor in precious metals) and the floating fraction yielded a recovery of approximately 83–89% precious metals in the latter. Scanning electron microscopy-energy dispersive X-ray spectroscopy maps of gold (Au), silver (Ag), platinum (Pt), palladium (Pd), Iridium (Ir), and copper (Cu) confirmed that result.

1. Introduction

Precious metals (PM) are found in modern end-of-life vehicles (ELV), including printed circuit boards in audio systems, electronic displays and navigation systems, onboard computer monitors, powertrain control modules, engine control units, emission controls, oxygen sensors, and other engine functions (Simic, 2013; Ahmed et al., 2014; Cossu and Lai, 2015). In general, printed circuit boards contain approximately 28–40% metals (including PM), 23–30% plastics, with the remainder being ceramics and glass materials (Sakai et al., 2014; Widmer et al., 2015; Restrepo et al., 2017). Selecting and removing some of these specific components, which contain valuable quantities of PM (i.e., gold (Au), palladium (Pd), platinum (Pt), silver (Ag), rhodium (Rh), and copper (Cu)), is difficult from ELV during the dismantling and shredding process (Binnemans et al., 2013; Andersson et al., 2016). Therefore, the presence of PM in end-of-life vehicle shredder residue (ELV-SR)/automobile shredder residue (ASR) is inevitable. As a consequence, the amount of PM in ASR residues can be remarkably high. Recently, Cucchiella et al. (2016) and Rosa and Terzi (2016) reported the management of electronic systems embedded into ELV and introduced an innovative economic model to identify profitability within the recovery process of automotive waste printed circuit boards.

Automobile recycling generates approximately five million tons of ASR annually worldwide (about 5% of the world's industrial waste); most of this residue ends up in landfill or is converted thermally (Simic, 2013; Cossu and Lai, 2015; Nicolli et al., 2012). ASR consists of a wide variety of materials, including precious metals, plastics, glass, rubber, wood, foam, tramp metal, wire, fibers, sand, and dirt (Simic, 2013; Cossu and Lai, 2015; Widmer et al., 2015). A recent study reported that there are significant amounts of Pt, Pd, Au, Ag, and Cu in ASR residues (Mallampati et al., 2015a). Considering their relevant concentrations, these metals should be recovered properly for recycling purposes before the ASR residues are disposed of. Recovering PM from ASR will help increase the recycling rate and provide additional income within the disposal process of ELV along with better environmental protection.

The potential routes for the recovery of PM from printed circuit boards and other e-wastes have been reviewed extensively in recent years (Li et al., 2007; Sun et al., 2015). According to these reviews, the main routes for the recycling of PM from e-waste are hydrometallurgical, pyrometallurgical, electrometallurgical, and biometallurgical processes, as well as their combinations; each method has its own advantages and disadvantages. For example, Diaz et al. (2016) and Ghosh et al. (2015) reported that hydrometallurgical treatments are more efficient and environmentally friendly than other recovery processes, such as physical separation and pyrometallurgical processes. For example, Cui and Zhang (2008) considered hydrometallurgical processes to be more exact, predictable, and easily controllable. On the other hand, conventional hydrometallurgical procedures for gold extraction involve the use of high concentrations of the hazardous cyanide ion, whereas bacteria, such as *Bacillus megaterium*, *Chromobacterium violaceum*, *Pseudomonas aeruginosa*, *Pseudomonas fluroscens*, and *Pseudomonas plecoglossicida*, and fungi, such as *Clitocybe* sp., *Polysporus* sp., and *Marasmius oreades*, can produce cyanide, which makes the biorecovery of PM more environmentally friendly for gold leaching (Natarajan et al., 2015). More recently, a combined redox − fuel cell method for the recovery if Au from e-wastes was reported (Zhang et al., 2017). However, these methods are still at the laboratory-scale level. Thermal processes, such as pyrolysis, which is a common technique used for the degradation of plastics to oils, gases, and tar, can be applied to enrich the treated material in PM and ease the separation of metallic materials and glass fibers (Guo et al., 2010). Experimentally, the pyrolysis of e-waste generates about 25% oils, 5% gases, and metal-rich residue (Bidini et al., 2015). The pyrolysis of e-waste yields a wide range of aromatic compounds and non-aromatic compounds (Evangelopoulos et al., 2015).

While the field of PM recovery from "usual" WEEE/e-waste (Waste Electric and Electronic Equipment) is a well-documented and dynamic field of study (Li et al., 2007; Sun et al., 2015), the same cannot be said for e-wastes from automobiles. This is despite the fact that the use printed circuit boards for the management of almost all the functionalities of a vehicle has increased drastically over the past few decades (Kim et al., 2014). Selecting and removing some of the specific components that contain valuable quantities of PM from ELV during the dismantling and shredding process is difficult (Mallampati et al., 2015a). Although ELV are one of the most important sources of waste and the basic guidelines for the reuse, recovery, and recycling of ELV have been established, the recycling of scrap automobile electronics has only been studied superficially (Wang and Chen, 2012; Cucchiella et al., 2016). Some authors identified the limited technological development of scrap automobile electronics processes as one of the reasons for the lack of research interest in this area (Zeng et al., 2016). Owing to the chemical and structural complexity of electric/electronic and automotive equipment as well as the presence of hazardous contents, the selective fractioning of different materials, and the separation of various valuable and hazardous substances into easily recyclable fractions is a very difficult and highly expensive task. The amount of ASR, i.e., the fine fraction that remains after the recovery of valuable materials, which are mainly metals, vary but can be 20% or more of the total.

Therefore, although ASR contains a certain amount of PM, it is still simply disposed of in landfill. Granata et al. (2011) used nitric acid (alone, or in combination with HCl) to determine the metal concentration in ASR, however, to the best of the author's knowledge, there are no reports in this field. In addition, the chemical and structural complexity of e-waste and ASR make it difficult to transfer the results from one material to another.

One of the starting points of this study was observation of the influence of cementation processes of recent PM recovery from e-waste (Birloaga and Veglio, 2016; Agarwal et al., 2016). The presents study applied the cementation-like immobilization of heavy metals in ASR with the help of a nano-size mixture of Fe, Ca, and CaO (Lee et al., 2015). On the other hand, recent studies demonstrated that the new nano-particle froth flotation technology for the more efficient separation of gold, silver, copper, and other valuable materials from rocks and ores (Yang et al., 2012, 2013a, 2013b). The present authors successfully used froth flotation and Fe/Ca/CaO treatment for the separation of chlorinated plastics from e-waste, along with the immobilization of heavy metals (Mallampati et al., 2016). The intent was to combine, in a single process, the capacity of a Fe/Ca/CaO mixture to trap PM, and as nano-size particles of bound PM, to separate them from the rest of the ASR with the help of a microbubble integrated froth a flotation procedure. Therefore, Fe/Ca/CaO nanoparticles will act both as a trapping agent for PM and as a "collector", increasing the hydrophobicity of the collected PM particles, allowing smooth separation by froth flotation. This study evaluated the capability of a Fe/Ca/CaO nanoparticle coating and microbubble-integrated froth flotation separation on the recovery of PM from ASR.

2. Materials and methods

2.1. ASR samples collection

All laboratory procedures met the QA/QC requirements (SINAL 0286), including the application of triplicate experiments. ASR, often referred to as "light" ASR (or "fluff"), contains an extremely inhomogeneous mixture of plastics but larger fractions of non-ferrous metals, glass and lot of sand and dirt. In the present study, samples of heavy ASR (size about 5 mm) were collected at three different times during the day from an ELV treatment plant in Pohang City, South Korea. The metallic and non-metallic contents were assessed rapidly and proven to be in the normal range for modern ASR (Passarini et al., 2012; Miller et al., 2014). The collected ASR samples were mixed thoroughly, affording a homogenized composition, which was then sieved into three different fractions (1.0, 0.425, and 0.250 mm corresponding to 20, 45, and 35 wt %, respectively (see Fig. S1, Supplementary material). Coarser fragments (sand, soil gravel, and other plastic waste crusts) were observed in the 1.0 mm-sized ASR fraction. The 0.425 and 0.250 mm fractions contained finer sand and soil gravel structures. High accuracy quantitative analyses of the main inorganic components in the samples of the three ASR fractions were performed by X-ray fluorescence spectroscopy (XRF, EDX-720; Shimadzu Corp.); please see Table S1 in Supplementary material. All values presented in the table are the averages of three replicate analyses. The major inorganic components of the three ASR fractions were SiO_2, Fe_2O_3, CaO, and Al_2O_3. The contents of halogenated organic compounds (values as gross chlorine [Cl] and bromine [Br]) were also considerably high.

2.2. Fe/Ca/CaO nanoparticles synthesis

A dispersed mixture of Fe/Ca/CaO nanoparticles was prepared using a solvent-free planetary ball-milling procedure. Granular particles of metallic Ca (99%, 2–2.5 mm particle size distribution, 0.43–0.48 m^2 g^{-1} surface area), iron (0.15 mm diameter), and fine grade CaO were purchased from Kishida Chemical Co. Ltd. Dry CaO (pre-heated at 825 °C for 2 h) and dry Fe and Ca (Fe/Ca/CaO = 2/2/5 ratio) were introduced to a planetary ball-mill (20 pieces SUS, 32 g/ ball). Milling was conducted at room temperature under Ar for 1 h at 600 rpm and a rotation-to-revolution ratio of 1 to −2. The particle size distribution was determined using a ZETA-SIZER,