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Recovery of base metals, silicon and fluoride ions from mobile phone printed circuit boards after leaching with hydrogen fluoride and hydrogen peroxide mixtures

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ABSTRACT

The recovery of copper, nickel, zinc, silicon, iron, aluminum, tin and fluoride ions from fluoride leach liquors of non-ground printed circuit boards (PCBs) from mobile phones is described in detail. These PCBs were leached with HF + H_2O_2 mixtures after previous treatment with 6 mol L^{-1} NaOH (removal of the solder mask). A combination of solvent extraction (SX) and precipitation techniques was used. 99.5 wt% zinc, copper and nickel, in this order, were extracted in one stage (Zn, Ni) or two stages (Cu) with di-2-ethylhexylphosphoric acid (D2EHPA) diluted in kerosene (25 °C, A/O = 1 v/v) after adjusting the pH of the leachate. They were easily stripped by aqueous H_2SO_4. Iron, aluminum and tin did not interfere because they were masked by fluoride ions. Iron and aluminum were precipitated together as $Na_3FeF_6 + Na_3AlF_6$ by careful addition of aqueous NaOH. Silicon, tin and fluoride ions were recovered together ($Na_2SiF_6 + Na_2SnF_6 + NaF$) by careful evaporation of the aqueous solution after SX of nickel. The tin salt was leached from this solid by absolute ethanol. High HF concentration (10 mol L^{-1}) in the leachant affected SX of Cu(II) and precipitation of iron/aluminum flurocomplexes since some NaF partially precipitated at acidic pH.

1. Introduction

In the last decades, enormous amounts of Waste Electrical and Electronic Equipment (WEEE or "e-waste") have been generated with the fast upgrading of electronic products such as personal computers, mobile phones and other consumer electronics on a day-to-day basis. WEEE is one of the fastest growing hazardous waste streams (Xiu et al., 2017; Torres and Lapudus, 2017). The average lifetime of electronic products has also been drastically reduced due to the rapid increase in demand of advanced products (Huang et al., 2014; Hadi et al., 2015; Sarvar et al., 2015).

E-waste is a rising global concern due to its alarmingly increasing volume and toxicity. It has detrimental effects on the environment and public health (Torres and Lapudus, 2017). It contains more than a thousand different substances, many of which are high-valued or highly toxic (Ikhlayel, 2017). Printed circuit boards (PCBs) are the most economically attractive portion of WEEE (Ghosh et al., 2015; Xiu et al., 2017; Huang et al., 2014; Kavousi et al., 2017; Ikhlayel, 2017).

Modern electronic devices contain up to 60 different elements. These elements can be classified into precious metals (Ag, Au, Pd, Pt, Rh, Ir, Os, Ru), base metals (Cu, Ni, Zn, Cr, Al, Sn, Fe), hazardous elements (Hg, Cd, Be, Pb) and scarce or trace metals (In, Te, Ga, Se, Ta and Ge) (Vats and Singh, 2015; Kasper et al., 2011; Ikhlayel, 2017). Copper is by far the most abundant metal followed by zinc, iron, nickel, aluminum, lead and tin (Gold Denad Trends, 2013; Camelino et al., 2015).

PCBs from mobile phones usually contain higher amounts of valuable metals compared to other small-sized e-wastes (Torihara et al., 2015). These PCBs contain up to 40 times the concentration of copper, silver, gold and palladium in their ores/concentrates (Cui and Zhang, 2008; Hadi et al., 2015; Riedewald and Gallagher, 2015; Sarvar et al., 2015; Huang et al., 2014; Wang et al., 2015). The Electrical and Electronic Equipment (EEE) industry is among the largest consumers of these metals, especially silver and copper (Vats and Singh, 2015; Charles et al., 2017). The high content of base metals and precious ones in PCBs makes

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them a potential secondary resource for metal recovery (Rubin et al., 2014; Wang et al., 2015). Precious metals are the most economically attractive portion of PCBs, followed by copper, tin, aluminum, lead, zinc and nickel (Gold Denad Trends, 2013; Cui and Anderson, 2016; Sheng and Etsell, 2007). However, the heterogeneous mix of organics, metals, fiber glass and plastics makes PCB processing a challenging task (Hadi et al., 2015), and is the main barrier in the recovery of metals from them (Petter et al., 2014; Rubin et al., 2014; Torres and Lapudus, 2017). Only about 15% of the scrap PCBs are subjected to some kind of recycling (Riedewald and Gallagher, 2015).

The increasing attention on the recovery of metals such as gold, silver and copper from waste PCBs has boosted the development of new processes including physical (Kaya, 2016; Jiang et al., 2009; He and Duan, 2017) and thermochemical techniques (Bidini et al., 2015). Hydrometallurgical methods are one of the key technologies in metal recycling because they enable a fine separation between chemically-similar metals in small-scale operation (Xiu et al., 2017; Yang et al., 2017; Tuncuk et al., 2012). They consist of leaching and recovering of metal values from the leached liquor. Acidic leaching (HCl, H_2SO_4, HNO_3) in the presence of an oxidant is often exploited as the first stage for the extraction of base metals, particularly copper (Tuncuk et al., 2012; Ghosh et al., 2015, Cui and Anderson, 2016). Metal leachability depends upon its affinity with the acid leachant (Buaztu et al., 2013). Previous leaching of base metals ensures the enrichment of precious metals in the solid residue, making it easier to subsequently leach out them (Ghosh et al., 2015).

Recovery of metal values is another essential step in hydrometallurgical operations. For the purification of pregnant leach solutions and recovery of base/precious metals from these solutions, a variety of methods including solvent extraction, ion exchange, precipitation, cementation and electrowinning can be readily exploited. The selection and development of downstream purification and metal recovery processes are essentially based on the leaching reagent system, metal concentration and the impurities/interferents present (Tuncuk et al., 2012; Flandinet et al., 2012). The most simple, cheap and current metal separation method in hydrometallurgical routes is chemical precipitation (Buaztu et al., 2013; Ferella et al., 2008; Sayilgan et al., 2009; Ma et al., 2013). However, metals present in small amounts may influence the purity of the final products.

Solvent extraction (SX) has received much attention due to its advantages such as high selectivity and convenient scale up (Lacerda et al., 2009; Sadegh et al., 2007; Sayar et al., 2009; Kasper et al., 2011). Due to the presence of additional metal cations, especially iron(III), SX is an effective tool for the separation of copper from leachates (Willner et al., 2015; Kavousi et al., 2017). The reagents of the hydroxy oxime group have exceptional selectivity for copper extraction from acidic (pH 1–2) sulfate/chloride solutions in the presence of iron(III) (Gotfryd and Pietek, 2013; Qiu et al., 2017; Willner et al., 2015; Sole et al., 2005; Lu and Dreisinger, 2013).

Hydrometallurgical processes are easy to generate large amounts of aqueous wastes and sludge that cause secondary pollution (Zhu et al., 2012) Metal recycling from waste PCBs may be long and complicated due to the poor selectivity of inorganic acids as leaching agents (Ghosh et al., 2015), leading to high recovery cost (Zhou and Qiu, 2010; Huang et al., 2014). But their management is essential to minimize environmental impacts (Silvas et al., 2015).

The aim of this paper is to describe a detailed processing of the acidic solutions after leaching PCBs from mobile phones by a novel leachant consisting of $HF + H_2O_2$ mixtures. Precious metals remained in the insoluble matter, whereas base metals and silicon were leached with high yields (90–100 wt%). Some elements were complexed by fluoride ions (Al, Fe, Sn, Si), whereas others were not (Cu, Ni, Zn). Based on these distinct chemical behaviors, SX and precipitation techniques were combined in an innovative way to recover copper and other leached elements. Recovery of fluoride ions from the final products was another target because of economic and environmental reasons.

2. Experimental

2.1. Reagents and leachates

Di-2-ethylhexylphosphoric acid (D2EHPA, 98 wt%) was supplied by British Drug Houses Limited (BDH). Deodorized kerosene (Exxon) was used as diluent. Sodium hydroxide, sulfuric acid, hydrofluoric acid, aqueous hexafluorosilicic acid and absolute ethanol were of analytical grade. The solutions were prepared with distilled water.

The leachates were obtained from the leaching of non-ground PCBs of mobile phones with $HF + H_2O_2$ mixtures (Silva et al., 2018). The polymeric transparent thin film (solder mask) was previously removed by immersion of the PCBs in 6 mol L^{-1} NaOH at 50 °C for 1 h. The treated samples were leached by HF (2.5–10 mol L^{-1}) + H_2O_2 (2.5–5 mol L^{-1}) mixtures (10 mL g^{-1} PCB) at 200 rotations per minute. After adding the treated PCB to the leachant (25 °C), temperature increased by 15 °C. Temperature decreased to ~30 °C at the end of the experiment (~1 h). The rise of temperature is explained by the decomposition of the oxidant, which is catalyzed by various transition metals (such as silver, gold and platinum), their oxides and aqueous ions (such as Cu^{2+}, Ni^{2+}, Co^{2+} etc.) (Greenwood and Earnshaw, 2010). The PCB laminate (epoxy resin) was removed using plastic tweezers. The insoluble matter consisted of the components released from the PCBs (chips, connectors, relays etc.) and a fine solid containing metal fluorides (Mg, Ca, Sr, Ba, Pb) and noble metals (Ag, Au, Pd). The leachate was passed through a plastic sieve (0.5 mm) in order to retain the PCB components. They were washed with water (6 mL g^{-1} processed PCB). The washings and the filtrate were combined and filtered (under vacuum) through an ordinary quantitative filter paper. The fine solid was washed with water (4 mL g^{-1} processed PCB), dried at 110 °C for 2 h and weighed. The leachates typically contained 13 g L^{-1} Cu(II), 1.8 g L^{-1} Zn(II), 1.7 g L^{-1} Ni(II), 1.6 g L^{-1} Si(IV), 0.8 g L^{-1} Sn(IV), 0.4 g L^{-1} Al(III), 0.4 g L^{-1} Fe(III) and 0.05 g L^{-1} Cr(III). Their blue color was due to Cu(II) ions. Free fluoride was in the range 0.3–3.9 mol L^{-1}, according to the HF concentration in the leachant. pH was in the range 1.2–1.4. The leachates were left to stand overnight to finish the release of dioxygen (O_2) bubbles due to H_2O_2 decomposition. The separation procedure employed (Fig. 1) was based on precipitation and solvent extraction techniques conducted under increasing pH and evaporation of the final solution to recover fluoride compounds. Handling of these leachants was performed using appropriate personal protective equipment in a fume hood.

2.2. Leachate processing – SX of Zn(II), Cu(II) and Ni(II) and stripping procedures

Extraction experiments were performed in plastic separatory funnels at 25 °C. D2EHPA, a cation exchanger, was used as it is frequently used as extractant in both, research and industrial applications (Virolainen et al., 2011). Many elements can be extracted and selectivity can be controlled by pH adjustment (Ritcey and Ashbrook, 1984). Its concentration varied from 1 to 20 vol%. The aqueous/organic (A/O) phase ratio was fixed at 1 vol/vol. pH of the leachate was adjusted by adding the appropriate amount of 6 mol L^{-1} NaOH. The system was shaken for 10 min. Phase separation was achieved in ~10 min. The experiments were carried out in