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Recovery of indium from liquid crystal displays

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A B S T R A C T

Indium is a critical raw material with economic importance and high supply risk. In the present study, we recovered indium by means of cementation from a leaching solution of waste liquid crystal display panels. Cementation with zinc powder was optimized through the investigation of the effects of different variables (zinc concentration, pH, cementation time) on cementation efficiency and purity of the solid product. Almost all the indium present in the leaching solution passed to the solid phase when cementation was performed with a low (2–5 g/L), a medium (15–20 g/L) and a high (100 g/L) concentration of zinc, at pH 3. At pH 2, a complete cementation was obtained only with the highest concentration of zinc. Moreover, the highest purity of the indium product (62% indium percentage in the solid product, calculated in the 4-metal system indium-aluminum-calcium-iron) was achieved after a cementation of 10 min, whereas the presence of impurities increased with time. An empirical model successfully fitted the experimental data and suggested that the highest purity of the cemented product was expected at pH 2. A quantification of the environmental impact of the process for indium recovery from end-of-life liquid crystal display panels was also carried out through a life cycle analysis approach, and it outlined that relevant benefits to the environment were obtained thanks to the recovery of indium from waste electric and electronic equipment. The results obtained in the present study are promising since this is the first time that cementation was applied to a leaching solution of waste liquid crystal display panels. In this paper we found that indium cementation took place also with low concentrations of zinc at pH 3, allowing important reagent saving. Investigations in progress are aimed at increasing the purity of indium and at improving the environmental sustainability of the process. The approach presented here is considered extremely useful in the frame of urban mining strategies. It can help ensure progress towards sustainable societies, encourage industrial innovation of the recycling companies and the implementation of cleaner processes.

1. Introduction

The European Union has identified 20 critical raw materials for economic importance and high supply risk, including indium (European Commission, 2014). Indium is mainly used for the production of liquid crystal display (LCD) screens, and it comes mainly from Chinese mines (Lin, 2007; Lin et al., 2009; Yuan and Shi, 2009). Recently, recycling routes have been developed throughout the world, in order to solve the critical situation of indium supply. One common way for indium secondary production is indium tin oxide (ITO) recycling after the sputtering phase, that is the deposition of a transparent thin layer of ITO on a surface. Another option for indium secondary production is its recycling from waste electric and electronic equipment (WEEE; Menikpura et al., 2014). This approach, also recognized as an innovative mining strategy (i.e. urban mining), is becoming a common practice, as WEEE displays a high content of valuable elements compared to ores, and allows to save resources reducing the primary production (Beolchini et al., 2013; Rocchetti et al., 2013). An important source of indium is represented by LCD flat screens, where indium is present as ITO on the surface of the two glass substrates which contain liquid crystals. Critical points for indium recovery are its extraction from ITO, maximizing the yield, and the achievement of a product with high purity (Nelen et al., 2014). Furthermore, also the management of waste LCD is considered as critical, affecting the subsequent indium recovery steps: for example, the presence of mercury in the backlight fluorescent lamps requires procedures for lamp removal through manual disassembly, in order to avoid complex procedures

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regarding the mercury elimination from the liquid solution, during indium recovery. The state of the art about the leaching technologies applied to LCD panels to extract indium is described elsewhere, along with an innovative promising approach based on cross-current leaching (Rocchetti et al., 2015). For the purification and recovery of secondary indium from the leaching solution, many approaches can be used, such as ion exchange resins, ionic liquids, solid separation, extractants (Hasegawa et al., 2013; Kubota et al., 2009; Liu et al., 2012). Some metals, such as iron and aluminum, show precipitation properties similar to indium, making it difficult to separate and to obtain a high purity indium product. Cementation is a potentially effective way to recover indium from solutions, based on the different oxidation potential of indium when compared to other elements. For this purpose, aluminum, zinc and magnesium are used to deposit indium on their surfaces (Hsieh et al., 2009; Jiang et al., 2011). Although indium cementation is a quite consolidated method, further investigation is necessary to identify the best operating conditions, that allow a selective recovery of indium from a leaching solution that contains other metals. Only a few studies in the scientific literature address the cementation to recover indium from ITO and/or LCDs. Li et al. (2011, 2014) recovered indium from waste ITO using zinc plates. Moreover, cementation with aluminum plate (pH 2, 60 °C) was reported to be effective to obtain indium sponge from ITO scrap (Park, 2011). Some patents have also been granted, but either the methodological approach is not detailed and clear, or they are not written in the international language. Indium cementation with zinc seems a feasible way for the recovery of indium from waste LCD panels. On the basis of the reduction potential, the reaction of indium reduction is favored in presence of zinc as cementation agent (Table 1). Indeed, zinc has a lower reduction potential than indium, therefore In^{3+} is reduced to metallic In. Cementation time, pH of the reaction and the choice of the amount of zinc, when zinc powder is used, is controversial. Especially for the quantity of zinc powder used, most of the available information can be found for other systems. Koleini et al. (2010) carried out indium cementation from a stripping solution of zinc sulfide concentrate at pH 3 for 6 h at 25 °C. The amount of zinc powder consumed was 1.5 times the stoichiometric quantity of indium, and its recovery ratio and purity of the precipitate were more than 95%. Other authors, using a higher amount of zinc powder (1.8 times the stoichiometric quantity of indium) in similar cementation conditions (pH 3 for 7 h at 25 °C), obtained a recovery ratio of indium and purity of the product above 97% (Jiang et al., 2011). Barakat (1998) used zinc powder to recover indium from alloy wire scrap through the cementation in a stoichiometric ratio of 1.2 at pH 1.4 at 30 °C, and obtained an indium recovery of 98.8%. According to this researcher, although increasing the ratio of zinc could slightly enhance the indium recovery, this is detrimental to the indium purity, as the excess of zinc contaminates the indium sponge. In all the papers found in the scientific literature about indium cementation, the amount of indium and the stoichiometry of the reduction reactions are used to determine zinc dosage. Conversely, pH is a key variable in order to achieve the right zinc dosage: indeed, also zinc consumption for hydrogen formation has to be taken into account.

Table 1
Standard reduction potential of aluminum, calcium, iron, indium and zinc (25 °C, 101 kPa, 1 M; Habashi, 1999). In the left the half-reactions are presented, including hydrogen used as reference, and in the right the values of reduction potentials.

Half-reaction	Reduction potential (V)
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$2H^+ + 2\ e^- \rightarrow H_2$	0
$In^{3+} + 3\ e^- \rightarrow In$	−0.34
$Fe^{2+} + 2\ e^- \rightarrow Fe$	−0.44
$Zn^{2+} + 2\ e^- \rightarrow Zn$	−0.76
$Al^{3+} + 3\ e^- \rightarrow Al$	−1.66
$Ca^{2+} + 2\ e^- \rightarrow Ca$	−2.87

Consequently, the aim of this study was to identify the best process conditions for the downstream section of the process to recover indium from LCD displays, considering both the cementation efficiency of indium and the purity of the indium product as targets.

2. Materials and methods

2.1. Cementation with zinc powder

Cementation tests were carried out with solutions that resulted from cross-current leaching with sulfuric acid of end-of-life LCD panels (Rocchetti et al., 2015). Different experimental conditions were investigated, for a total of 16 treatments. The experimental factors considered were the concentration of zinc powder, pH and cementation time. The concentration of zinc was chosen on the basis of 2 main aspects: the concentration of indium in the leach liquor and the consumption of zinc due to the hydronium ion reduction. Three intervals of zinc concentration were evaluated: low zinc (2–5 g/L), medium zinc (15–20 g/L) and high zinc (100 g/L). Table 2 summarizes the experimental conditions of each cementation treatment. In each test, a volume of leach liquor was treated at a temperature of 55–60 °C on a magnetic stirrer. When the temperature was reached, pH was adjusted with sodium hydroxide and then pure zinc powder was added to the solution. Samples were collected at different time intervals to monitor the time course of the cementation.

2.2. Chemical analyses

The concentration of metals in the liquid phase was determined by means of inductively coupled plasma-atomic emission spectrometry in accordance with Maxfield and Mindak (1985). The metals analyzed during the cementation treatments were indium, aluminum, calcium and iron. These elements were considered the most significant for their average concentration in the waste LCDs on the basis of a previous chemical characterization and on the literature information as well (Rocchetti et al., 2015).

2.3. Statistical analysis

Analysis of variance and regression analysis were carried out with the software UNISTAT 6.5 to evaluate the effects of zinc concentration, pH and cementation time on cementation efficiency and on the composition of the solid product.

2.4. Environmental impact evaluation

We evaluated the effects of the recovery process described in the present paper by means of the life cycle assessment (LCA). The goal of LCA was to identify the environmental benefits and impacts of leaching and indium cementation, and to compare this management option for waste LCD panels with incineration and landfilling. For the analysis, we simulated a process to recover indium carried out in the industrial plant built within the HydroWEEE FP7 231962 project, with a capacity of 5 m^3, an energy consumption of 0.13 kWh/kg LCD panel treated and solid concentration 0.2 kg/L. Considering previous (Rocchetti et al., 2015) and present results, the process consisted of a 2-step cross-current leaching with 2 M sulfuric acid, followed by pH adjustment to 3 with sodium