



## Innovative Method to Extract Indium from LCD Panels

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Liquid crystal displays (LCDs) are becoming of common use as a replacement for the old cathode ray tube monitors. The new technologies largely rely on the use of critical raw materials, such as indium. This element makes up the transparent conductive coatings in the thin film displays. Considering the high demand of indium for electric and electronic equipment and the limited size of the reserves, the importance of indium recycling is increasing. Waste electric and electronic equipment (WEEE) represents a valuable source for secondary production of indium, as its concentration in WEEE is often higher than in the ores where it is present in association with zinc and extracted as a by-product. In the last years the focus of the research has been pointed out to find technologies addressed to the extraction and recovery of indium from WEEE. In the present paper we describe the results of indium recovery from waste LCD panels using sulphuric acid leaching followed by zinc cementation. The problem of the low concentration of indium in the leach solution has been overcome by applying an innovative technology: cross-current leaching. This methodology is based on two leaching steps using the same leach solution to solubilise indium from different stocks of LCDs. Overall, we found that indium was recovered from waste LCDs with an efficiency of about 90 %, with important consequences from an economic and environmental perspective.

### 1. Introduction

The replacement of old cathode ray tube (CRT) technology with higher performance systems has caused a huge increase of LCD market. Indeed, these devices guarantee lower energy consumption combined with smaller weight and volume compared to CRTs (Menozzi et al., 1999). The widespread use of this equipment caused a strong interest for raw materials requested for their manufacture. In particular, indium was classified in 2010 as a critical raw material for Europe by the European Commission for the high risk of supply interruption (European Commission, 2010). This metal is the main component of indium tin oxide (ITO), a film composed by indium (90 %) and tin (10 %) oxides (Leung et al., 2013), used for its high optical transparency and electrical conductivity (Tseng et al., 2010). Currently, indium is mined as a by-product of zinc production (Fthenakis et al., 2009) and China is the largest producer (USGS, 2014). Typically indium is present in sphalerite (Alfantazi and Moskalyk, 2003), a zinc mineral, with a concentration between 1 and 100 ppm (Dodbiba et al., 2012). Considering the current global consumption of the metal and its concentration in end-of-life LCD, generally higher than 100 ppm (Wang et al., 2013), this waste represents an important secondary source of indium. Literature data about this topic is still scarce but many technologies are being developed for the recovery of valuable elements from WEEE (He et al., 2006) with the final target to undertake "urban mining" policies (Beolchini et al., 2013). The reduction of the dependency from other countries for the supply of raw materials (Ardente and Mathieux, 2014) represents a priority, as confirmed by the several studies recently published (Granata et al., 2011; Patel et al., 2014). The present paper describes an innovative hydrometallurgical process for indium recovery from LCD scraps. After a first washing phase, a multistage extraction (cross-leaching) was

carried out with the purpose to maximize indium extraction and minimize the concentration of co-extracted metals. Finally, a recovery step was carried out by zinc cementation.

## 2. Material and methods

### 2.1 Characterisation of LCD scraps

The waste LCDs used for the development of a process for indium recovery were provided by different companies that deal with collection of waste electric and electronic equipment (WEEE). An X-ray fluorescence (XRF) analysis was carried out to identify the qualitative composition of LCDs. With the aim to define the average indium concentration, three stocks were characterised by an inductively coupled plasma (ICP) technique, after acid digestion of the samples. Before the treatment, the scraps were crushed in order to obtain dimensions of about 10 mm, as showed in Figure 1. Glass and plastic fragments bigger than 10 mm, about 10 % of the total waste, were removed for their low indium content.

### 2.2 Process description

The process for indium recovery consists of three main steps, as showed in Figure 2. A first washing phase with deionised water was carried out at room temperature to remove the organic component of LCDs. The phase of metals extraction was performed using sulphuric acid, at 80 °C for 10 min. This kind of acid was selected because it allowed a lower dissolution of  $\text{As}_2\text{O}_3$ , a highly toxic compound, compared to nitric and hydrochloric acids (Ruan et al., 2012). With the purpose to set up a cross-leaching configuration with two steps, the leach liquor produced in the first step was filtered, restored with a small amount of fresh sulphuric acid and used to treat a second waste amount. The final step of indium recovery consisted of cementation by zinc powder addition. Zinc was chosen because its reduction potential (-0.76 V), lower than that of indium (-0.34 V; Habashi, 1999), allows to reduce  $\text{In}^{3+}$  to metallic In form. Cementation was carried out for 1 h at a pH value between 2 and 3, obtained by sodium hydroxide addition. These operating conditions were selected on the basis of previous tests that showed that a low pH value promotes hydronium ion reduction instead of In (III). Liquid samples were collected at the end of each leaching step, after sodium hydroxide addition and every 10 minutes during the cementation phase.



Figure 1: LCD scraps crushed with dimensions of about 10 mm

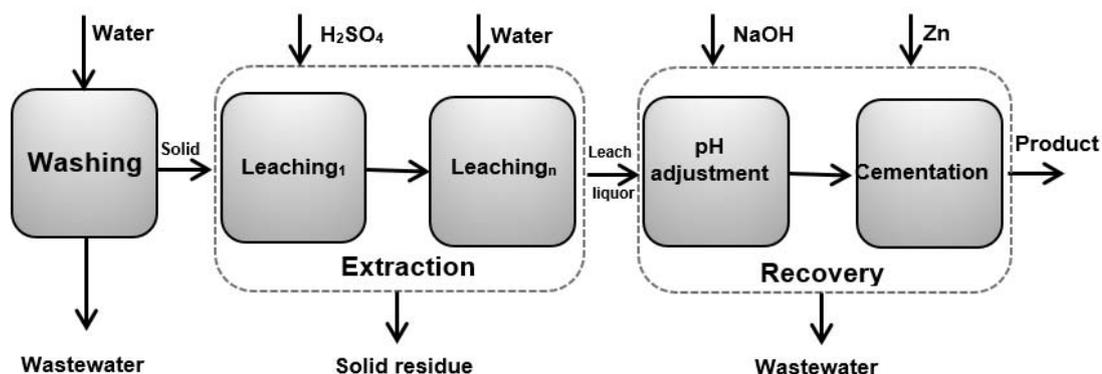


Figure 2: Flow chart of indium recovery process

### 2.3 Liquid samples analysis

The concentrations of metals in the liquid samples collected during the process were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

## 3. Results and discussion

### 3.1 Characterisation of LCD scraps

Figure 3 summarizes the results of qualitative analysis and shows all elements present in the LCD scraps. Indium is not visible in the spectrum for peaks overlap, but significant information relative to the impurities present in the sample were obtained. Table 1 reports the experimental data of indium concentration in the three stocks analysed, in comparison with literature data of LCD scraps. The composition of the stocks was not homogenous: stock 1 had a concentration of indium that was about a half of the concentration present in stock 2 and 3. The variability in indium content is also confirmed by literature data that reports values higher than that determined in the present study but still comparable. Overall, data about LCD characterisation obtained in the present study and in other scientific publications confirm that indium concentration in LCD scraps is similar to that observed for the mineral ores. Dodbiba (2012) reports values between 1 and 100 ppm of indium in zinc ores, in accordance with the concentrations showed in Table 1 for LCD waste.

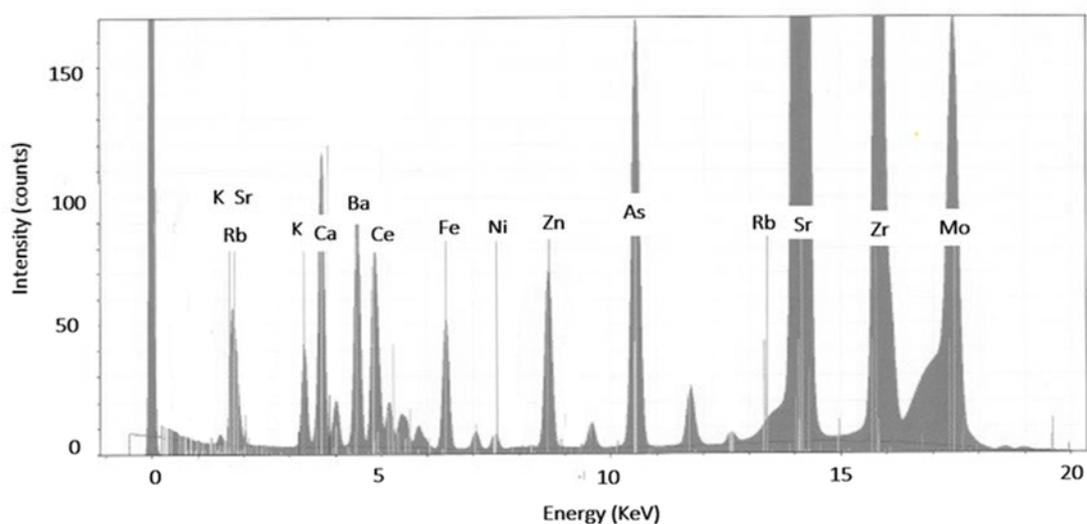


Figure 3: Results of XRF analysis of LCD scrap (indium is not visible for peak overlaps)

### 3.2 Indium recovery

The cross-leaching configuration with two steps allowed to obtain an indium extraction efficiency of about 100 %. This innovative method permitted to concentrate indium into the leach liquor overcoming the issue of low content of the metal in the LCD scraps, one of the principal weak points of traditional recovery processes. In addition, a high efficiency of indium extraction was associated to a lower reagent consumption and a reduced volume to treat in the following step compared to conventional leaching. Ten minutes of leaching, carried out at 80 °C, were sufficient to obtain the maximum yield, as showed in Figure 4. Furthermore, preliminary tests showed that a long leaching time causes a significant increase of dissolution of other metals. The cementation process allowed to obtain an efficiency of indium recovery of about 90 % after 10 min. The solid product obtained included both the indium precipitated during pH adjustment as hydroxide and the amount reduced after zinc addition. Ten minutes of time was selected also to obtain a product as pure as possible. Indeed, a long cementation time and changes of pH value in the solution caused the precipitation of other metals, as iron and calcium, with a decrease of indium purity in the final product (Figure 5).

Table 1: LCD characterisation

	Experimental data (ppm)		Literature data (ppm)
Stock 1	53 ± 6	(Wang, 2009)	102
Stock 2	130 ± 60	(Hasegawa et al., 2013)	380 - 410
Stock 2	110 ± 20	(Ma and Xu, 2013)	219

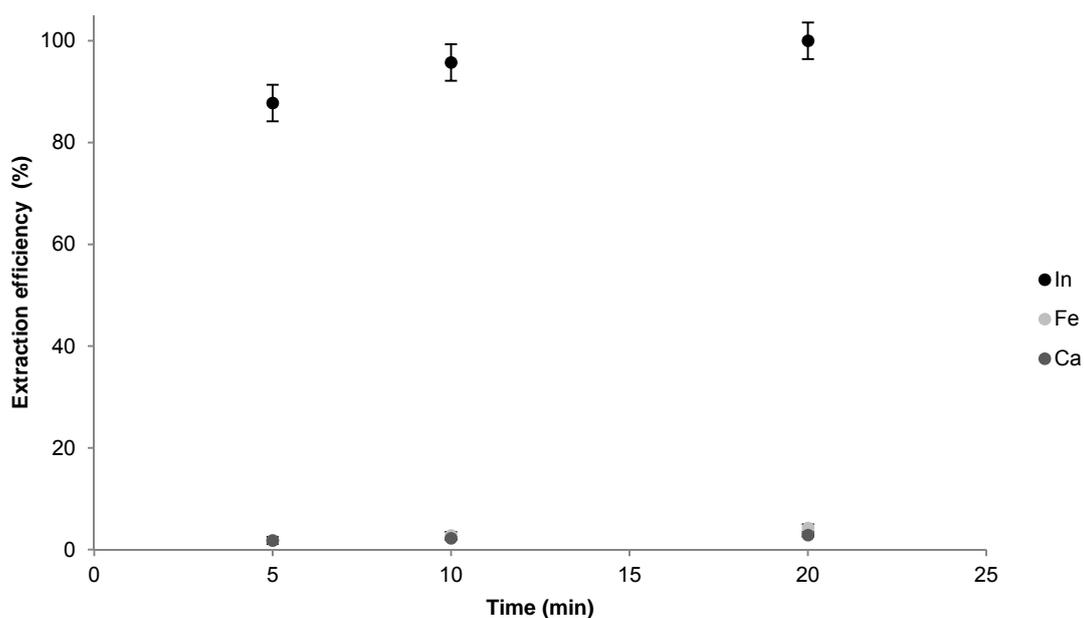


Figure 4: Temporal changes of metals extraction efficiency in preliminary leaching step

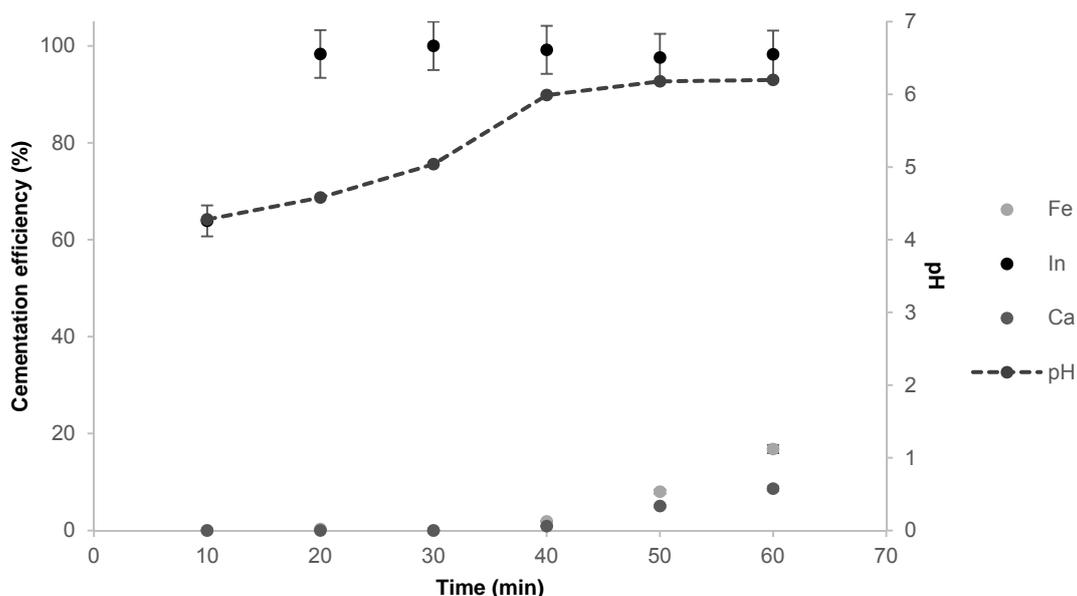


Figure 5: Temporal changes of metals recovery efficiency in the cementation process

#### 4. Conclusion

Considering that the medium lifetime of LCD devices is about 3 - 8 y (Ma and Xu, 2013), the problem of the management of the resulting huge amount of waste electric and electronic equipment is a hot topic. This issue, combined with the present risk of indium supply and literature data still scant, makes the development of metal recovery strategies a priority. This paper describes a process for indium recovery from LCD scraps. The characterisation of the three stocks of LCDs used in the present paper revealed a non-homogeneous composition. Nevertheless, these concentrations are comparable with those found in other scientific publications about LCDs and in minerals. This fact makes the recovery process very promising. The leaching phase allowed to obtain a total efficiency of about 100 % using sulphuric acid at 80 °C for 10 min. Furthermore, the cross-leaching configuration determined economic and environmental advantages. Indeed, the use of the same leach liquor to treat a second amount of LCD scraps, allowed to obtain from the one hand the complete indium dissolution with a sulphuric acid saving, and on the other hand, an increase of indium concentration into the solution. In the cementation step, the efficiency of indium recovery reached values up to 100 % after 10 min of treatment. The results described in the present paper are promising since this simple and efficient process could be extended to recover other high valuable metals from different kinds of waste.

#### Acknowledgements

The authors thank the European Commission for having funded the research project HydroWEEE-DEMO 308549.

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