Cross-current leaching of indium from end-of-life LCD panels

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A B S T R A C T

Indium is a critical element mainly produced as a by-product of zinc mining, and it is largely used in the production process of liquid crystal display (LCD) panels. End-of-life LCDs represent a possible source of indium in the field of urban mining. In the present paper, we apply, for the first time, cross-current leaching to mobilize indium from end-of-life LCD panels. We carried out a series of treatments to leach indium. The best leaching conditions for indium were 2 M sulfuric acid at 80 °C for 10 min, which allowed us to completely mobilize indium. Taking into account the low content of indium in end-of-life LCDs, of about 100 ppm, a single step of leaching is not cost-effective. We tested 6 steps of cross-current leaching: in the first step indium leaching was complete, whereas in the second step it was in the range of 85–90%, and with 6 steps it was about 50–55%. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Then, we hypothesized to scale up the process of cross-current leaching up to 10 steps, followed by cementation with zinc to recover indium. In this simulation, the process of indium recovery was advantageous from an economic and environmental point of view. Indeed, cross-current leaching allowed to concentrate indium, save reagents, and reduce the emission of CO_2 (with 10 steps we assessed that the emission of about 90 kg CO_2-Eq. could be avoided) thanks to the recovery of indium. This new strategy represents a useful approach for secondary production of indium from waste LCD panels.

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1. Introduction

Currently liquid crystal displays (LCDs) are largely used because they have replaced the old technology of cathode ray tube (CRT) in different applications as PC monitors, laptops, tablet PCs, mobile phones, televisions. Compared to CRT monitors, the small weight and volume, and the cost that is becoming cheaper, favor the wide diffusion of LCDs. In addition, the lower power consumption and heat emissions make LCDs more convenient also from an ecological point of view (Lee and Lee, 2006).

As a result, the broad spread of LCD technology requires much more raw materials for their production. This is particularly true for indium, that in LCDs is present in an optoelectronic material called ITO (indium tin oxide), it features transparency to visible light, electric conduction and thermal reflection (Li et al., 2011). ITO is a mixture of indium (III) and tin (IV) oxides, with a typical composition of 90% In_2O_3 and 10% SnO_2 by weight (Leung et al.,

2013). According to the European Commission, almost 90% of indium is used in electronics, a sector with a quick development (European Commission, 2014a). Currently, indium is extracted from ores where it is present in concentrations of about 1–100 ppm (Alfantazi and Moskalyk, 2003). China is the largest producer of indium, followed by Korea, Japan and Canada, with an estimated world refinery production in 2013 of 770 metric tons (USGS, 2014). The European Commission has classified indium as a critical raw material for Europe for its high supply risk and high economic importance (European Commission, 2014b). Approximately 84% of the worldwide indium consumption is used for the production of LCDs, where it is present in concentration from 100 to 400 ppm (Gotze and Rotter, 2012; Hasegawa et al., 2013; Lee et al., 2013; Ma and Xu, 2013; Wang, 2009). Considering that the lifetime of these electronic devices is generally 3–8 years (Ma and Xu, 2013), obsolete displays are a valuable alternative resource for indium secondary production (Ma and Xu, 2013; Park et al., 2009). As a matter of facts, LCD recycling creates benefits in several compartments: it may avoid both waste of valuable resources and also the high environmental impact usually generated by conventional management

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options of incineration and/or disposal in landfill sites (Li et al., 2009; Ryan et al., 2011).

For these reasons, among waste electrical and electronic equipment (WEEE), LCD recycling is becoming an important research focus in the field of urban mining (Beolchini et al., 2013; Rocchetti et al., 2013). Indeed, some display components, as the top cover and the printed circuit board mounting frame can be directly recovered and reused, whereas other parts need specific treatments for their complex structure and hazardous characteristics (Wang et al., 2013). In the recent years, several physical and chemical treatments have been tested to recover indium from LCD panels, as reported in Table 1. The process of indium mobilization is generally carried out by means of strong acids under different reaction conditions. Table 1 also reports details regarding possible treatments to recover indium after its mobilization (e.g., precipitation, cementation, extraction with solvents or surfactants).

The aim of the present paper is to apply a process for indium leaching from end-of-life LCD panels. We investigated different operative conditions to identify the best conditions for indium mobilization. The approach consists of maximizing indium leaching efficiency and minimizing the concentration of co-mobilized metals in the leach liquor. Furthermore, a single step of leaching is not feasible considering the low concentration of indium in waste LCD. Therefore, we investigated a cross-current configuration for leaching. According to this approach, a multistage mobilization is carried out: in the first step a quantity of waste LCD is leached, and in the next steps the same leach liquor is used to treat other LCDs. To the best of our knowledge, for the first time this approach is applied to end-of-life LCD panels to mobilize indium. A large scale simulation for indium recovery is also presented, along with an evaluation of process costs and CO_2 saving thanks to the new proposed approach of cross-current leaching applied to LCDs.

2. Materials and methods

2.1. Characterization of LCD fragments

End-of-life LCD panels ground by a 4-shaft shredder were provided by companies that collect and treat WEEE (Fig. 1a). In order to identify metal distribution in fragments of different size, we carried out further grinding and sieving. The ground panels contained pieces of several centimeters in length, and a blade grinding operation carried out by means of a Retsch knife mill, allowed us to obtain particles that could pass through a sieve of 10 mm (Fig. 1b). Before blade grinding we removed big plastic and glass fragments, representing about 10% of the total amount of shredded LCDs. Their characterization revealed no significant indium content. Then we obtained 2 fractions: the coarse fraction, containing fragments between 1.25 mm and 10 mm in size (Fig. 1c), and the fine fraction, smaller than 1.25 mm (Fig. 1d). Once removed gross fragments of plastic and glass, the fine material was 40% and the coarse fraction was 60%. In the present study, we carried out leaching on the whole stocks, to obtain a high concentration of indium in the leachate solution.

2.2. Leaching treatments

Before each leaching treatment, we washed a quantity of ground LCD panels using deionized water (pulp density, 0.2 kg/L) for 30 min on a magnetic stirrer at room temperature. This pretreatment was necessary to physically remove the organic compounds of the LCDs (rod-shaped molecules containing benzene ring; Ma and Xu, 2013), as checked in preliminary tests. In the present study we investigated different leaching conditions for a total of 10 replicated treatments. Table 2 shows the experimental

Table 1
State of the art of processes for the recovery of indium from waste LCD panels. For the studies with many experimental conditions investigated, the table reports only the best operative conditions.

LCD panel pre-treatment	Organics removal	Leaching conditions Acid	Time (h)	T (°C)	Pulp density (kg/L)	Acid consumption[a] (kg acid/kg LCD)	Post-treatment for indium recovery	Reference
Shredding/milling, washing with deionized water	No	2 M H_2SO_4 3-step cross-current	0.17	80	0.1	0.7	n.i.[b]	This work
Thermal shock at 220 °C, shredding and ultrasonic cleaning	No	5.4 M HCl and 0.8 M HNO_3	0.5	60	2	0.27 (HCl) and 0.04 (HNO_3)	n.i.[b]	Li et al. (2009)
Hot isostatic pressing (HIP) treatment, manual breaking and pulverization	Yes	1 M H_2SO_4	2	90	0.1	1	Cementation	Li et al. (2011)
Grinding and incineration at 500 °C	Yes	6 M HCl	2	n.a.[c]	0.036	17	n.i.[b]	Dodbiba et al. (2012)
Electrical disintegration	No	6 M HCl	2	n.a.[c]	0.5	1.2	n.i.[b]	Dodbiba et al. (2012)
Freezing with liquid N_2, stripping of the polarizing film, grinding <1 mm	No	9 M H_2SO_4	1	160	1	0.9	Extraction with D2EHPA, stripping with HCl	Ruan et al. (2012)
Crushing and thermal shock. Ultrasonic cleaning and milling	Yes	6 M HCl	0.5	r.t.[d]	0.04	15	n.i.[b]	Lee et al. (2013)
Shredding	No	<1 M H_2SO_4 or >1 M HCl	8	n.a.[c]	0.1	<1 (H_2SO_4) or >1 (HCl)	Solvent extraction and stripping	Yang et al. (2013)
Pyrolysis at 450 °C	Yes	0.6 M H_2SO_4	0.7	65.6	0.5	0.1	Purification	Wang et al. (2013)

a 98% H_2SO_4, 37% HCl, 70% HNO_3.
b Not investigated.
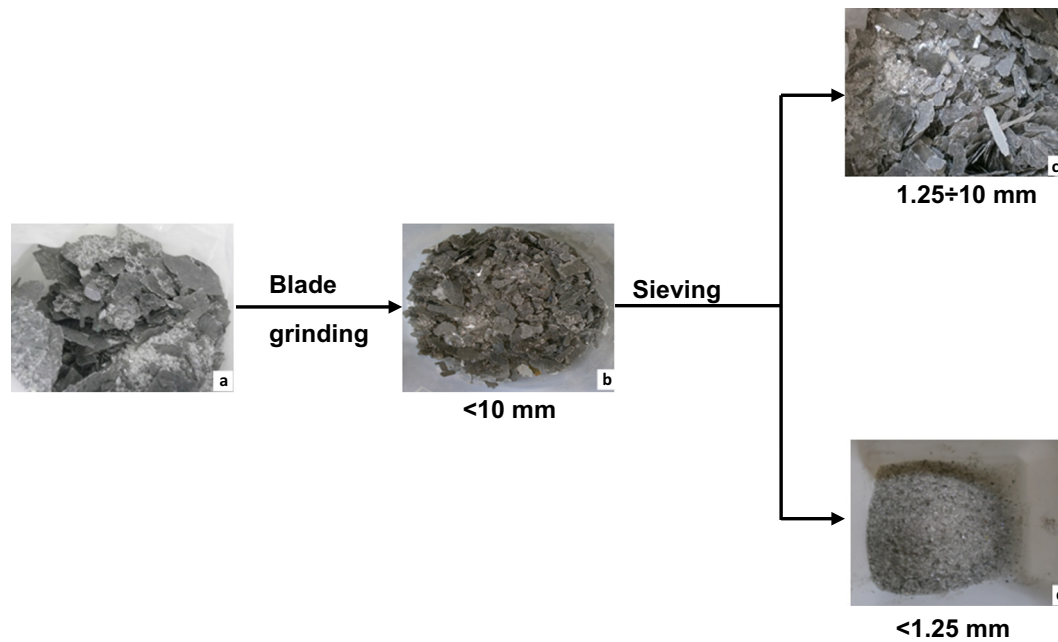c Not available.
d Room temperature.

Fig. 1. Different size of ground LCDs. (a) as provided by a company, after shredding, (b) after blade grinding and sieving at 10 mm (c) sieved fragments between 1.25 mm and 10 mm in size (d) sieved fragments smaller than 1.25 mm.

conditions for each leaching treatment. We considered the following variables: acid concentration, leaching temperature and time and number of steps in the cross-current leaching. All leaching treatments were performed treating the ground LCDs, washed and filtered, in a solution of H_2SO_4 on an agitation system. We collected a sample every 10 min. Data in literature reports process time between 30 min and 8 h (Table 1), therefore in the present study times smaller than 10 min are not taken into account. At the end of leaching, we filtered the solid and collected the remaining leach liquor for chemical analyses.

The treatment of cross-current leaching (number 10 in Table 2) needs further explanation. We filtered the leach liquor produced in a first leaching step and we used it to treat a second amount of LCD fragments, adding a small amount of fresh H_2SO_4 to restore the volume lost for the high temperature (Fig. 2). We carried out 6 leaching steps.

2.3. Chemical analyses

We determined metal content in the ground LCD panels after microwave-assisted acid digestion of the solid samples by means of inductively coupled plasma (ICP) analysis (using Agilent ICP-MS 7500, Agilent technologies; EPA, 1996, 2007). Before the chemical digestion, we finely ground each sample to avoid any error in chemical determinations. Chemical analyses determined the content of indium, aluminum, calcium, cerium, gallium, iron,

manganese, molybdenum and tin. As a whole, the chemical characterization was performed on three different stocks supplied by different companies in different periods of time. We carried out further analyses to determine the concentration of indium and tin in the following 5 size intervals: 0–0.125–0.25–0.50–1.25 and >1.25.

The concentration of metals in the aqueous phase was determined by inductively coupled plasma-atomic emission spectrometry in accordance with EPA (2001). Before the analysis, liquid samples were centrifuged and diluted by 2-fold with a solution of H_2SO_4 (pH 2) to avoid precipitation of metals.

Leaching efficiency (M) was calculated according to Eq. (1):

$$M = M_L/M_s * 100 \tag{1}$$

where M_L is the amount of metal in the leach liquor and M_s is the amount of metal in the solid sample.

We analyzed a sample resulting from leaching with 2 M H_2SO_4 for 20 min at 80 °C with 10% LCD by X-ray fluorescence (XRF; Spectro Xepos) for a qualitative analysis of the composition of the solution.

2.4. Evaluation of costs and CO_2 emissions

We calculated the possible economic income determined by the sale of indium produced in a simulated process at industrial scale, and the CO_2 emissions as well. In the simulation for the large scale

Table 2
Leaching conditions in the treatments of indium leaching.

| Treatment	H_2SO_4 (M)	Temperature (°C)	Volume (mL)	Pulp density (kg/L)	Mixing system	Leaching steps	Leaching time (min)
1	2	80	100	0.10	Magnetic stirrer	1	180
2	2	80	100	0.10	Dubnoff bath	1	180
3	2	25	400	0.15	Magnetic stirrer	1	20
4	2	80	400	0.15	Magnetic stirrer	1	20
5	1	80	100	0.10	Dubnoff bath	1	180
6	2	80	100	0.10	Dubnoff bath	1	180
7	2	80	500	0.20	Magnetic stirrer	1	10
8	2	80	500	0.20	Magnetic stirrer	1	30
9	2	80	500	0.20	Magnetic stirrer	1	60
10	2	80	100	0.20	Magnetic stirrer	6	10 (each step)
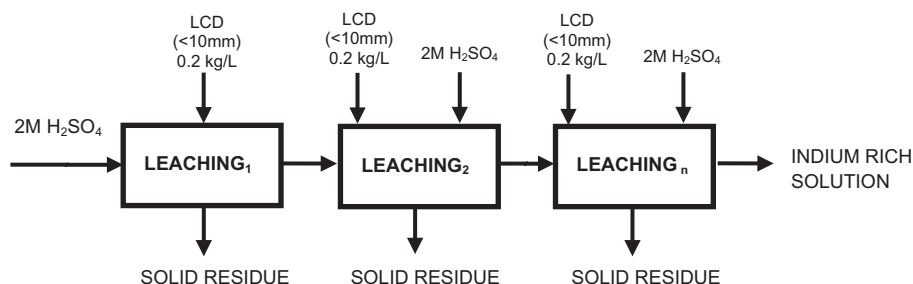
Fig. 2. Scheme of the cross-current leaching proposed for indium mobilization from end-of-life LCD panels. The sulfuric acid addition following the first step aims to refresh the solution volume.

process, the plant is of 5 m³ in volume and works with a pulp density of 0.2 kg/L. The hypothetical extensive process includes cross-current leaching (based on the results achieved in the present study), pH adjustment with sodium hydroxide and cementation with zinc powder to recover indium (not investigated in the present study, based on literature data and on the research group expertise as well). The process costs were estimated for 1 kg LCD treated. They included raw materials, waste disposal, energy and man power, estimated for a wide range of leaching steps of the cross-current leaching, from 1 to 10, as predicted by Eq. (2), followed by cementation.

We fit an empirical model (Eq. (2)) to the experimental data of indium leaching:

$$M_{CC} = M_{max}/(a + b * N) \qquad (2)$$

where M_{CC} is the mobilization efficiency at different number of steps in the cross-current leaching, M_{max} is the maximum mobilization efficiency of indium, a and b are adjustable parameters and N is the number of steps in the cross-current leaching.

The costs of the reagents were set as follows: an average cost of 0.2 $/kg for sulfuric acid, 0.19 $/kg for sodium hydroxide and 0.37 $/kg for zinc (www.alibaba.com).

We estimated indium income based both on the amount of indium recovered in the hypothesized 10-step leaching treatment, and indium price. We considered indium maximum (about 800 $/kg) and minimum (about 500 $/kg) quotations in the last 3 years (www.metalprices.com).

We used the same hypothesized process for indium recovery also for the evaluation of the environmental impact of the process in the category of global warming (expressed as CO₂-Eq.). We used the software GaBi 5 (PE International) to quantify the CO₂ emissions according to the CML2001 – Nov. 09 problem-oriented method of the Institute of Environmental Sciences, Leiden University, Leiden, The Netherlands (previously the Centrum voor Milieukunde Leiden; hence CML). The production processes of

the chemicals and energy used for the evaluation were taken from the GaBi database, integrated with EcoInvent 2.2.

3. Results and discussion

3.1. Characterization of ground end-of-life LCD panels

Experimental data concerning panel characterization are extremely relevant for the evaluation of the sustainability of indium mobilization from waste LCD panels. Indeed the composition of such waste is not homogeneous due to different production processes and data are poorly available in the scientific literature. Table 3 reports the metal content in the 3 stocks analyzed in this work (particle size up to 10 mm), along with the few data present in the literature. The different stock compositions of ground LCD panels showed a variability in an acceptable range of about 20%, in accordance with literature data. Such observed variability in the composition was probably due to the origin of ground LCD panels (e.g. different brand on the panels).

We also evaluated the content of other elements of commercial interest through a qualitative X-ray fluorescence analysis. We observed that arsenic, strontium, zirconium were also present with remarkable peaks in the emission spectrum (Fig. S1). The presence of arsenic, found at a concentration of 2 mg/L in the leach liquor, requires the application of an appropriate wastewater treatment (Beolchini et al., 2006, 2007).

3.2. Distribution of indium in LCD fragments with different size

In order to understand whether indium was mainly present in a specific fraction of ground LCDs or equally distributed, we analyzed the content of indium and tin in several size intervals in the fraction smaller than 10 mm. The study of the distribution of indium was worthy of investigation, also considering the high variability in the choice of the fraction used in the literature. Indeed, it is reported that the range of size of LCD treated is wide, from scrap

Table 3
Metal content in LCD panels (ppm, unless specified otherwise), as outcome of own determinations and comparison with literature data.

Metal	This work stock 1	This work stock 2	This work stock 3	Wang (2009)	FEM and IUTA (2011)	Götze and Rotter (2012)	Hasegawa et al. (2013)	Lee et al. (2013)	Ma and Xu (2013)
In	53 ± 6	130 ± 30	110 ± 20	102	174	195	380–410	260.7	219
Al (%)	3.3 ± 0.7	5 ± 2	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ca	n.a.[a]	29,000 ± 6000	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ce	n.a.[a]	n.a.[a]	18 ± 1	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Fe	3100 ± 600	600 ± 400	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ga	n.a.[a]	<10	<10	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Mn	53 ± 7	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Mo	14 ± 3	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Sn	260 ± 30	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	33

[a] Not available.

size of around 5 mm and 2–3 mm, to dimension smaller than 1 mm and 0.16 mm (Kato et al., 2013; Lee et al., 2013; Ma and Xu, 2013; Ruan et al., 2012). Fig. 3 reports the granulometric distribution of the <10 mm sample, along with indium and tin concentration in the different fractions. Indium concentration decreased as the size of the fragment increased. In the smallest fraction (<0.125 mm), that was only 10% of the total mass, we observed the highest concentration of indium (about 400 ppm). It is known that leaching efficiency increases with the reduction of particle size (Olanipekun, 1999; Shin et al., 2005). However, in the present study, we used both the fine and the coarse fractions resulting from blade grinding operations, to leach the highest amount of indium. In the perspective of a possible industrial application, the choice to treat end-of-life LCD panels with particle size up to 10 mm allows a considerable energy saving avoiding the mechanical pretreatment finalized to particle size reduction.

3.3. Indium leaching from end-of-life LCD panels

Indium was mobilized from LCD panels using sulfuric acid in all the leaching treatments described in the present study. Differently from other acids currently used for this purpose (e.g. HCl and HNO_3), H_2SO_4 has many advantages (Dodbiba et al., 2012; Wang et al., 2013). One of these is that arsenic, in the form of highly toxic As_2O_3 in the LCDs, has a low dissolution concentration when H_2SO_4 is present (Ruan et al., 2012). However, we found that the concentration of arsenic remaining in the solid residue was below the Italian regulatory limits for disposal. In addition, sulfuric is less expensive than the others, has a higher leaching efficiency and a limited environmental impact (Wang et al., 2013). The following part describes the results of the treatments.

3.4. Effect of temperature

Room temperature, which is about 25 °C, compared to 80 °C has the advantage that does not require any energy for its achievement. We observed that the extent of indium mobilization was significantly higher at 80 °C. Indeed, at 25 °C the efficiency of indium leaching was lower by 20% after 20 min, whereas at 80 °C it was almost complete after 10 min. At 80 °C leaching of metals requires a shorter time and therefore treatment scale-up to larger plants may lead to an increase of leaching cycles.

3.5. Effect of acid concentration

The results of the treatments aimed to identify the best concentration of H_2SO_4 showed that indium was almost completely mobilized both at 1 M and at 2 M. In the perspective of reagent saving, 1 M H_2SO_4 should be preferred. Some authors,
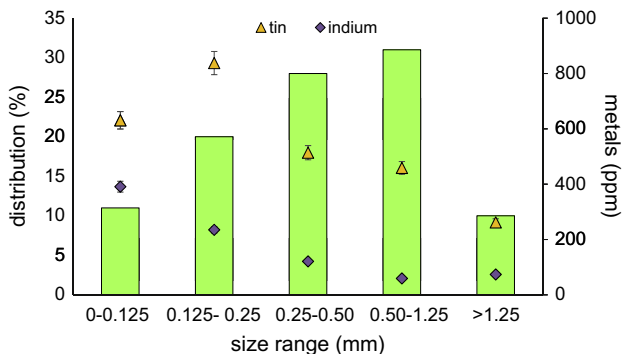
using systems with ITO powder rather than LCD fragments, found that the selectivity of the acid was higher when H_2SO_4 had the lowest concentration (Virolainen et al., 2011). For example, they observed that with 0.1 M H_2SO_4 all the indium was leached, and tin was not leached, whereas with 1 M H_2SO_4 both indium and tin where completely mobilized. Nevertheless, in our systems with ground LCD panels containing indium, a higher concentration of H_2SO_4 (2 M) should be used in the perspective of a multistage cross-current leaching. Moreover, 2 M H_2SO_4 can guarantee the presence of more acidic conditions than 1 M acid, and as observed by other authors the rate of leaching increases with the increase of the acidity of the solution (Li et al., 2011).

3.6. Effect of leaching time

Some considerations about the time required for leaching were done based on the state of the art and by evaluating different mixing systems. On the one hand, literature data reports a wide range of leaching time at operative conditions different from those reported in the present study, from 30 min to 8 h (Lee et al., 2013; Li et al., 2009; Yang et al., 2013). On the other hand, with an equal efficiency of indium mobilization, we observed that with the Dubnoff bath, which determines a mild mixing, a longer time of leaching is required compared to magnetic stirrer, which produces a vigorous agitation. In the final perspective of scaling up the leaching process, the magnetic stirrer better simulates the mixing system used at industrial scale. Therefore, we carried out most of the treatments with the magnetic stirrer.

The treatments addressed to indium leaching showed different mobilization efficiencies and selectivity. The leaching time was a key variable to improve the selectivity of indium mobilization
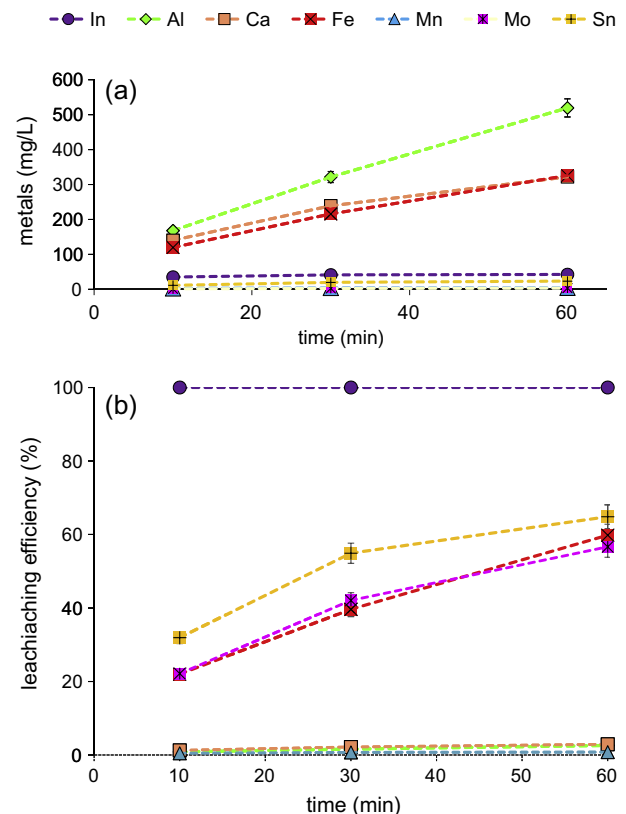
Fig. 4. (a) Concentration of the considered elements in the leach liquor after 10, 30 and 60 min of contact of ground LCD panels with sulfuric acid (treatments 7-8-9 in Table 1). (b) Leaching efficiencies of the considered elements after 10, 30 and 60 min of contact time.

Fig. 3. Granulometric distribution of ground LCD panels (columns), indium and tin concentration (symbols).

(Fig. 4a). Indeed, by increasing the time of leaching, we observed a significant increase of the concentration of iron, aluminum and calcium in the leach liquor. Conversely, a longer contact time of the LCD fragments with sulfuric acid did not determine important variations in indium, tin, manganese and molybdenum concentrations, which reached the maximum value within the first 10 min of treatment.

Fig. 4b confirms the complete mobilization of indium and shows the correlation between mobilization efficiencies of molybdenum, iron and tin and time. Indeed, these impurities doubled their leaching efficiencies up to 55% after 60 min. The structure of LCD could explain this different behavior of the considered elements. Under the glass substrate, there is a layer of ITO, and underneath a layer containing manganese (Rack and Holloway, 1998). Therefore, the elements indium, tin and manganese are more accessible to acid attack. To obtain a leach liquor containing indium in presence of other co-mobilized metals in traces, we observed that 10 min of leaching is the best option. In this way metals associated to the inner parts are leached to a minor extent.

For a better comprehension of the effect of time on the quality of the leached indium, Fig. 5 shows the percentage of each metal calculated in the 7-element system Al–Ca–Fe–In–Mn–Mo–Sn at time 10, 30 and 60 min. We observed the highest percentage of indium, 7.3%, after 10 min from the start of the leaching operation (Fig. 5a). As the leaching time increased, indium percentage in the metals system decreased (Fig. 5b and c). Therefore, for the purpose of the present study, the shortest leaching time (10 min) was favorable for the highest percentage of indium mobilized. The percentage of the co-mobilized metals was minor, especially aluminum.

3.7. Effect of the number of steps in the cross-current leaching

The main aim of cross-current leaching was to concentrate indium to obtain a cost-effective process, given the low content of indium in LCDs. Once the best conditions had been determined (2 M H_2SO_4, 10 min leaching at 80 °C), we investigated how many steps of leaching were necessary to mobilize as much indium as possible, with a satisfactory efficiency. Fig. 6 shows that as the number of leaching steps increased, the concentration of indium in the solution also increased, as expected. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Conversely, the mobilization efficiency significantly decreased from a step to the next one. For example, in the first step indium leaching was complete, whereas in the second step it was in the range 85–90%, and with 6 steps it was about 50–55%. Also for the other metals analyzed and co-mobilized with indium (iron, aluminum and calcium; data not shown), we
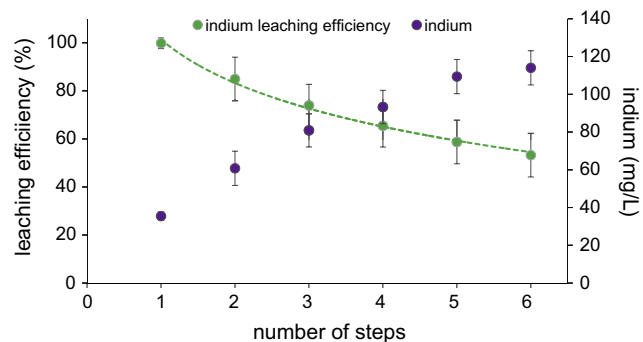

Fig. 6. Theoretical trend of indium mobilization efficiency (line) compared with real data (symbols) in the treatment of cross-current leaching (based on treatment 10 in Table 1). Data of indium concentration are also reported.

observed a lower efficiency when the number of leaching steps increased.

The decreased mobilization efficiency is the reverse of saving the acid solution. Indeed, as the same acid solution is used to sequentially leach metals from LCD panels, eventually adding a small amount of new acid lost from a leaching step to the next, as a result the mobilization capacity decreases. Nevertheless, indium is more concentrated and the amount of leaching solution to treat in the following steps to recover indium is significantly minor. This observation is true for 6 steps (investigated in the present study), but the same trend should be observed also for a higher number of steps. The model described in Eq. (2) well fits experimental data of indium leaching efficiency in the treatment of 6-step cross-current leaching (dotted lines in Fig. 6).

3.8. Advantages of cross-current configuration

In this last part of the paper, we have made a draft estimation of the possible economic income determined by indium sale in a simulated scaled-up process. We estimated the process costs, for cross-current leaching with 10 steps, as predicted by Eq. (2) (Fig. 7a), followed by indium cementation. Therefore, 2 curves were drawn, which represent the maximum (about 500 $/kg) and the minimum (about 100 $/kg) income. Fig. 7a shows that the possible income from indium sale increases almost by 4-fold when 10 steps of leaching, rather than only 1, are carried out (predicted by Eq. (2)). Conversely, the costs of the process per kg of LCD treated drastically reduce by increasing the number of steps of leaching. One of the main advantages of cross-current leaching is reagent saving (0.7 kg acid/kg LCD treated; Table 1). In the phase of
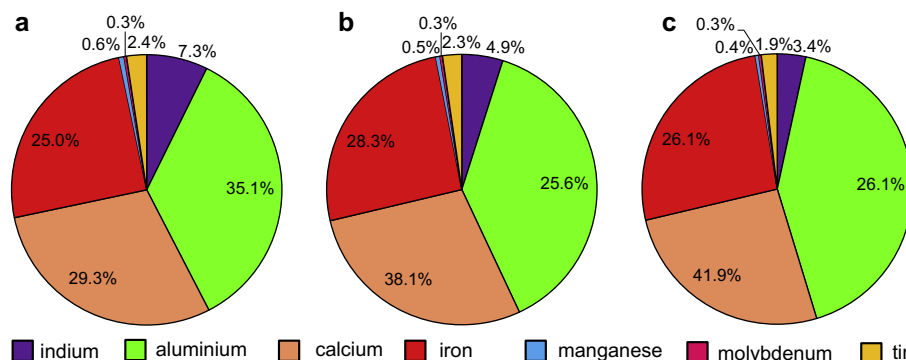

Fig. 5. Percentage of metals in the leach liquor collected after: (a) 10, (b) 30 and (c) 60 min (treatments 7-8-9 in Table 1).
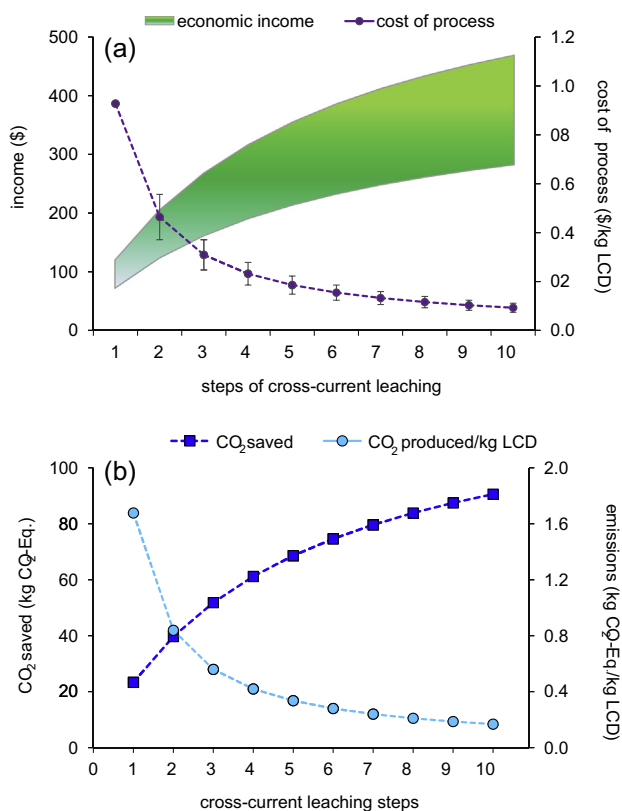
Fig. 7. (a) Cost of process for indium recovery from LCD panels and income from its sale. (b) Emissions of CO_2 produced in the treatment of cross-current leaching and avoided emissions of CO_2 as a result of secondary production of indium. In both the cases, we considered a hypothetical scaled-up process based on cross-current leaching, based on treatment 10 in Table 1, followed by cementation.

leaching, the amount of sulfuric acid is lower than conventional leaching, as the leaching solution used to mobilize metals from a LCD amount is then used in the following steps, eventually adding a small amount of new acid. Therefore, the cost of reagents considerably decreases with the number of leaching steps, and benefits to the environment are achieved.

Analogously, we evaluated both the CO_2 emissions produced by the simulated 10-step cross-current leaching process and the CO_2 saved thanks to the hypothesized recovery of secondary indium. Fig. 7b shows that CO_2 emissions are remarkably reduced when the number of leaching steps increases, starting from an average value of 1.7 kg CO_2-Eq./kg LCD treated in the first step, they are about a half in the second step. Environmental benefits were assessed in terms of CO_2 saved, calculated as avoided primary production of indium. In this case we observed that since at the first step about 20 kg CO_2-Eq. are saved, with 10 steps the emission of about 90 kg CO_2-Eq. could be avoided, considering to recover about 150 g of indium treating 1 ton of LCDs in a plant with a volume of 5 m³.

4. Conclusions

The concentration of indium in end-of-life LCDs was about 100 ppm. The heterogeneity within each sample is acceptable, with maximum variations of 20%. Indium concentration in LCDs is comparable or even higher than that in minerals making LCD scrap an interesting source of metals. In the present paper, for the first time, we applied cross-current leaching to LCD scrap. The results showed that the best leaching conditions for a complete indium leaching were 2 M sulfuric acid at 80 °C for 10 min. With longer leaching

time, indium leaching was always complete, but this increased the co-extracted element concentrations. The use of the cross-current design with a multiple step configuration represents an essential factor since it may overcome the challenge of economic and environmental sustainability, due to lower content of indium. Indeed, thanks to the application of several steps of leaching (we have tested 6 steps), the content of indium in the leach liquor is enhanced, and the expense of reagents is reduced. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Moreover, hypothesizing a cross-current leaching scale-up process followed by cementation, the process for indium recovery would determine a reduction of CO_2 emissions, with important benefits to the environment. The results show that cross-current leaching is a promising process for the effective mobilization of indium from LCDs. Considering the risk of supply of critical raw materials such as indium, new effective methods to leach them from urban mines should be optimized and used at industrial scale. The process of cross-current leaching may represent a solution to concentrate critical elements and a step forward economical sustainability of processes for the recovery of elements with concentrations on the order of hundreds of ppm in WEEE.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2015.04.035.

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