Novel mechanical pre-treatment methods for effective indium recovery from end-of-life liquid-crystal display panels

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Declarations of interest: none

Abstract:

This study investigated the suitability of mechanical pre-treatment methods (mechanical abrasion and treatments of heat, laser, and plasma) together with a hydrometallurgical process comprising leaching and cementation for recovering indium from used LCD screens. With mechanical abrasion pre-treatment, 96.2% of indium was recovered and black mass with an indium content of 15.6 weight percent was obtained. Following the mechanical recovery, sulfuric acid leaching was used to produce leachates with an indium purity ranging from 86.3 to 98.0% with an 88.7 to 100% yield for indium. Indium was recovered from the leachate by cementation with zinc powder, but also the impurity metals were cemented. The suggested mechanical pre-treatment involving the indium recovery process was seen as a viable option since it dramatically reduces the mass fed to the hydrometallurgical purification process (by roughly a factor of 1000), and up to 97.1% pure indium product can be obtained with a simplified process. The purity of the indium product can be further increased by additional purification steps.

1. Introduction

Waste electrical and electronic equipment (WEEE) is seen as valuable raw material in the circular economy. Closing the materials loop reduces the exploitation of primary resources, waste disposal and energy consumption while creating economic growth. The global generation of WEEE in 2016 was 44.7 million metric tons (Mt) but only 20% was recycled. The total value of raw materials in WEEE is estimated to be about 55 billion euros. The growth rate of WEEE generation is expected to be between three and four per cent annually (Baldé et al. 2017), which is approximately three times faster than that of other forms of municipal solid waste (Burke 2007, Ohajinwa et al. 2017). For example, the amount of devices with a life cycle of under than five years has increased by 4.8 percentage points during less than ten years (UBA 2016).

A good example of a mass-produced item with a short lifespan (three to five years on an average) is the liquid crystal display (LCD) (Zhang et al. 2015). LCDs contain several components which have recoverable materials. The panel of an LCD consists of a sandwich structure with two plates of glass with polarizer films on the outer sides and a liquid crystal mixture between the glass plates. The inner surfaces of the glasses are coated with a functional indium tin oxide (ITO) film (Zhuang et al. 2012). Considering the price of indium, used LCDs are an interesting raw material for its recovery.

Indium is mainly a by-product of zinc mining (Alfantazi and Moskalyk 2003). The largest production of indium occurs in China and in the Republic of Korea (approximately 75% of global production) (USGS

2018). Several remarkable organizations around the world, such as the United Nations Environment Programme (UNEP), the US Department of Energy (DOE), the European Commission (EC), the US National Academy of Sciences (NAS), and the American physical society and materials research society, have expressed their concern about the criticality of indium (Swain et al. 2016). For example, the European Commission has a created a list of critical raw materials (CRMs) which involve the risk of supply shortages and high economic impacts, and the list also includes indium (EC 2017).

Indium is used in certain high-tech applications due to its favorable characteristics, such as transparency, electric conduction and thermal reflection (Wang et al. 2015), but more than 70% of the global indium production has been consumed in LCD panels (Amato et al. 2017, Zhang et al. 2015). Although the use of LCD panels is declining due to other technological innovations, all flat panel displays still contain ITO films (Ardente et al. 2014). Other applications for ITO include flexible displays, solar cells, and touch screens.

The demand for indium has increased ten-fold between 1985 and 2015 (Boundy et al. 2017) and a significant further increase has been forecast (Pavel et al. 2016, Choi et al. 2018). For example, it has been predicted that China will need 350 t of indium annually by 2035 (Wang et al. 2015), which is more than the country's whole estimated indium production in 2018 (USGS 2019). In addition to electronic equipment, the photovoltaic industry is another market increasing the need for indium in the future (Zuser and Rechberger 2011). Despite the indium is widely labeled as critical raw material, the primary reserves (356 000 t) are abundant compared to the demand (800 t/y) (Werner et al. 2017; Werner et al. 2018).

In spite of remarkable growth in consumption and future expectations, the recycling rate of indium has been less than 1% (Graedel et al. 2011). In the EU, the end-of-life recycling rate of indium is zero (EC 2017). A large amount of indium may currently be in the possession of consumers because the sales of LCD TVs (excluding monitors) have increased over sevenfold between 2003 and 2015 (Babbitt et al. 2017). The EU directive on waste electrical and electronic equipment (WEEE) states that 80% of WEEE should be recovered and 70% should be prepared for re-use and recycled (EU 2012). Currently, recycling is expensive and inefficient, but at the same time, it means that there will be a stockpile of low-grade materials. (Ayres and Talens Peiró 2013). According to estimates, the growing amount of LCD waste is a potentially relevant supply source for indium, and a sufficiently high content of indium in the panels can make its recovering economically and qualitatively viable (Ardente et al. 2014, Dang et al. 2017). It has been estimated that in Europe the amount in anthropogenic wastes would be 500 t (Ciacci et al. 2018), which is not huge compared to the above mentioned primary resources, but it may have spatial and short-term significance especially if an economically feasible recycling method would be developed. For example in Europe, the primary resources are quite scarce, especially excluding Russia (Werner et al. 2017). As the logistic distances for transportation of the waste are short, the recycling seems more attractive than in global level.

The indium content in LCD glass is typically 220–260 mg/kg (Ma and Xu 2013, Lee at al., 2013) but also remarkably lower and higher indium contents have been reported (Rocchetti et al. 2015). Ueberchaar et al. (2017) have demonstrated that the indium mass fraction varies between 10–550 mg/kg in a similar range in various LCD devices and the variations do not correlate with the screen size. The typical thickness of the ITO layer is 125 nm, which corresponds to 235 mg/m^2 of indium content (Böni and Widmer 2011). The indium content varies also in the layers of the sandwich structure (color filter (CF), thin-film transistor

(TFT)). The front part of the glasses (CF) usually has a higher ITO content than the rear part (Yoshida et al. 2015, Wang et al. 2017).

Previous research on recovering indium from secondary sources has focused on hydrometallurgy. Rocchetti et al. (2015; 2016) leached metals from shredded glass with sulfuric acid (H_2SO_4), followed by direct cementation with zinc powder. However, the purity of the precipitated indium was only 62% and the process needs a further purification step to 4N (i.e. 99.99%), purity which is a market standard (Lokanc et al. 2015). Other recent research in this field includes for example leaching with aqua regia followed by recovery with chelating ion exchange resins (Assefi et al. 2018), leaching with H_2SO_4 followed by recovery with iminodiacetic acid resin (Ferella et al. 2017), and leaching with organic acids at supercritical CO_2 conditions (Argenta et al. 2017). Solution purification prior to cementation to recover indium metal is possible with liquid-liquid extraction. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) is the most commonly used liquid-liquid extraction reagent, but the selectivity for indium over iron, aluminum and tin is not high in sulfate media (Yang et al. 2014). These studies have shown that the recovery of indium can be technically feasible but the cost-efficiency is questionable. This study includes also preliminary techno-economic analysis of the suggested process.

The proposed hydrometallurgical processes start from the leaching of indium from the glass. A major problem here is the low indium content, as it is present only in the thin ITO layer. Pre-treatment methods could be an interesting way to improve the collection of the ITO layer from the LCD glass surface before the hydrometallurgical process. Brushing is a traditional method for mechanical separation. Mechanical exfoliation with a negative-pressure dry polisher and mechanical stripping has given promising results (Wang et al. 2017, Zhang et al. 2017). Zhang et al. (2017) used vacuum pyrolysis after the mechanical stripping of ITO film from the glass, but the purity was only 78% with a 98% yield. It is generally known that heat will change the properties of glass, and the application of heat in indium recovery from LCD screens has been tested (He et al. 2014). The surface properties of materials can be modified also with plasma (Chen et al. 2017). Laser treatment is used as a cutting method in industrial applications but has not been studied extensively in connection with material recovery.

The purpose of the present study is to improve the efficiency of previously suggested processes for indium recovery from LCD screens. This is done by combining novel pre-treatment methods to extract the ITO layer from the panels with leaching and cementation of the indium from the ITO rich “black mass” thus obtained.

2. Materials and methods

2.1. Sampling and preparation

Different types of LCD panels were obtained from Kuusakoski Recycling where the panels (the substrates of two glasses with functionality components) were removed manually from different LCD devices, such as computers and laptop screens, and televisions. The panels (sizes varied between 15 ” and 50 ”) were mainly in good condition without major cracks and were sorted according to their size. The LCD panels were split into glass substrates using a thin knife. The liquid crystals were removed from the glass substrates by wiping them with acetone. The description of the proposed and studied process is presented in the following Fig. 1.

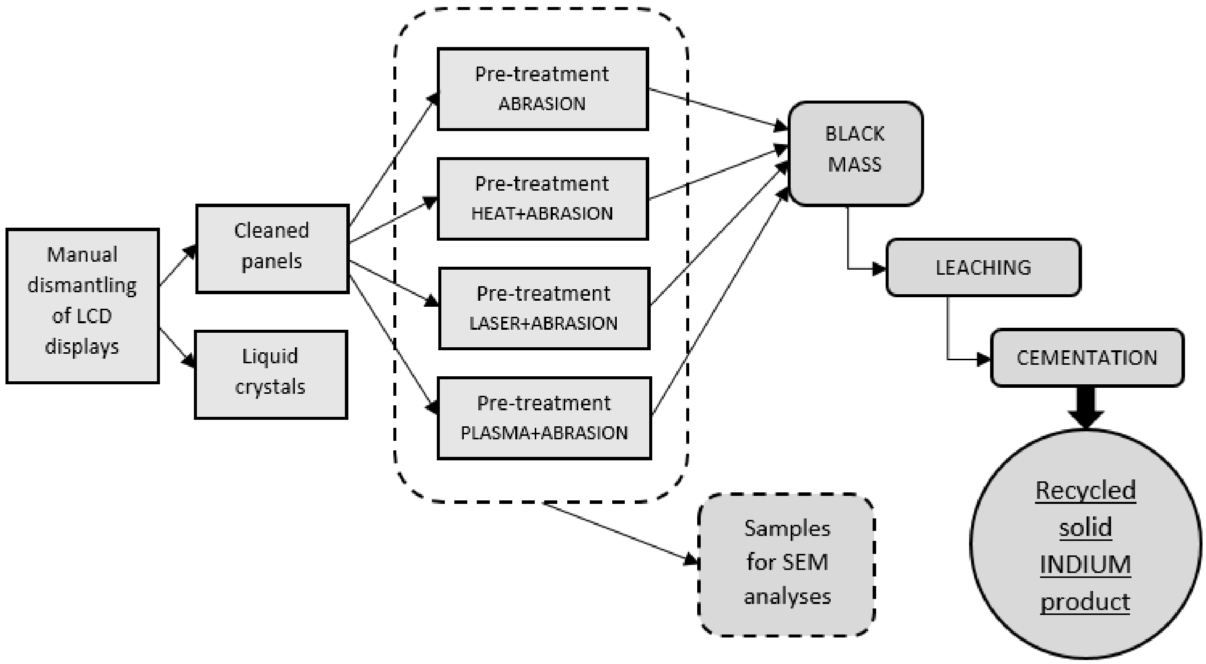

Fig. 1. A process diagram of this study.

2.2. Physical treatment methods

Indium recovery from the cleaned glass substrates was studied with various treatment methods: brushing, plasma, heat, and laser. The outcomes of the methods were determined by elemental analyses and a scanning electron microscope (SEM). Brushing, *i.e.* mechanical abrasion, tests were conducted with two tools (an abrasive roller brush and a hand sanding tool), producing black mass material for later analyses. The details of the abrasive roller brush equipment were as follows: power 860 W, load speed 367 rad/s, and brushing with a 100×200 mm aluminum oxide based sanding lamella roller K240. The other tool was a 270 W hand sanding tool, and oscillations and orbits without a load varied between 1047 and 2723 rad/s and 524 and 1361 rad/s, respectively. The sanding base surface of the tool was 90×187 mm and an aluminum oxide based abrasive paper was used with four grit sizes: 60, 80, 100, and 150. Black mass material was recovered with both mechanical abrasion tools by using a 500 W dust recovery vacuum which was integrated with the tools. The described mechanical abrasion process was integrated with the plasma and heat treatments. The heat-treated samples were post-treated by sanding, while the plasma-treated samples were post-treated with an abrasive roller. The atmospheric plasma treatment was performed with a 1000 W cold plasma device, including a plasma generator (FG 5001/Plasmatreat Ltd.) and plasma head (RD 1004/Plasmatreat Ltd.). The spin speed of the plasma device was over 209 rad/s and the air pressure 4–8 bar. The processing width was over 50 mm and the sample distance from the plasma head was at most 15 mm. The LCD panels were heat-treated in an oven at temperatures of 300 and 600 °C with an effective heating time of 30 min. Laser treatment was performed with 2500 W CO_2 laser equipment using 200 W power and +30 focal length. The laser equipment treated 29×36 mm areas from 43 cm diagonal screens with three different speeds: 300, 400, and 500 mm/s.

2.3. Hydrometallurgical methods

The material collected from the physical treatments (black mass) was treated with hydrometallurgical indium recovery and a purification process consisting of H_2SO_4 leaching and cementation with zinc powder. Six leaching experiments were conducted in a 50 mL thermostated glass reactor at 40–60 °C and with 0.5–2.5 mol/L H_2SO_4 concentration. A 105 rad/s mixing speed with a single-bladed glass impeller was used. The liquid to solid ratio (L/S) was 25.1–27.8 mL/g. Cementation was studied by using two of the six leachates in the same experimental set-up at 25 °C with a mixing speed of 58 rad/s. The amount of added zinc powder was 3.66 g/L.

2.4. Analyses

Metals from all solid samples were analyzed as pretreatment digesting the samples by wet combustion and then analyzing the metals from the aqueous phase with inductively coupled plasma – mass spectrometry (ICP-MS, Agilent 7900). Wet combustion was done with the Milestone UltraWAVE MA149 device at 250 °C and 40 bar for 10 min with the aid of ultrasound and microwaves using a 4:1 mixture of concentrated HNO_3 and HCl as the digesting reagent. Three parallel analyses were done on every glass sample. A scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS, Hitachi SU3500) was used to inspect the LCD sample surfaces qualitatively and to high detection limit quantitative metals analysis. Acceleration voltage in SEM-EDS analyses was 7–15 kV.

2.5. Economic feasibility analysis of the suggested recovery processes

The economic feasibilities of the physical recovery methods were also analyzed. The analysis was done by the assessment of energy consumption (*ec*) and cost (*c*) for treatment of 1 m^2 sized substrate with industrial scale equipment. The calculations of energy costs for the sanding route were done for industrial wide belt sander and industrial dust blotter. In the cases of plasma and heat treatment, the calculations were based on the used equipment in the experiments. For laser treatment the economic feasibility was not calculated as the important recovery of the created gaseous indium compounds was not studied in this research. The calculations were based on machine power rating, the time required for the recovery, and a constant price of electricity (0.12 €/kWh) that corresponds to the average price for non-household consumers in the euro area (Eurostat 2018).

$$ec\ (kWh) = Power\ (kW) \times Time\ (h) \qquad (1)$$

$$c\ (€) = ec\ (kWh) \times Price\ (\frac{€}{kWh}) \qquad (2)$$

The combination of needed equipment in the tested physical recovery methods are described in Table 1. The investment costs of the apparatus and labor costs were not taken into account in this study.

Table 1. Description of the physical treatment methods

	Treatment			
Apparatus	Mechanical abrasion	Heat treatment at 300 °C	Heat treatment at 600 °C	Plasma Treatment
Sanding machine	X	X	X	X
Blotter	X	X	X	X
Oven	-	X	X	-
Plasma devices	-	-	-	X

Hydrometallurgical part of the process (leaching + cementation) was evaluated by calculating the costs for chemicals and energy consumption. Capital and labor costs, and the costs related to waste treatment and recycling of the chemicals were not taken into account.

3. Results and discussion

3.1. Raw material characterization of LCD panel

The LCD panels were classified into three (a, b, c) categories based on their quality. The average content of indium and five other metals were measured for each panel quality category with wet combustion and the ICP-MS method, and Table 2 presents these values. The results show significant variations in metal contents between the panel qualities. The split and cleaned glass substrates were separated into their own groups according to their structure. The glass substrates are known as thin film transistors (TFT) and color filter (CF). The CF is a darker substrate of glass due to a black matrix, and it generally has a higher content of ITO (Wang et al. 2017). The outside layer of both substrates is coated with polarizing film which does not need to be removed, as only the inner surface is treated for ITO recovery. Previously, the recovery of liquid crystals had been improved by using acetone due to the greater polarity (Zhao et al. 2013). Therefore, acetone was chosen as a solvent for cleaning. However, some SEM images showed residues of liquid crystals on the surface, which indicates that the cleaning process requires more diligence.

Table 2. Metal content of raw material LCD panels.

Panel quality	Content in substrates (mg/kg)					
	Indium	**Tin**	**Aluminum**	**Iron**	**Copper**	**Zinc**
a	370	49.3	379	3.13	11.7	3.15
b	274	39.0	587	2.56	5.76	25.0
c	423	52.6	231	1.58	16.1	3.93

3.2. Physical separation of indium

Table 3 presents the metal contents of raw material LCD panels and the results of six treatment methods. The purities P_{In}, were calculated as shares of indium in all analyzed metals per treatment phase. The yields, Y_{In}, were calculated from the glass panel analysis before and after treatment. The following subsections 3.2.1–3.2.4 discuss the results in details.

Table 3. Metal contents of raw material LCD panels and results of mechanical treatment.

Panel quality	Treatment	Metal content of glass panels (mg/kg)						Black mass (%)		
		In	**Sn**	**Al**	**Fe**	**Cu**	**Zn**	c_{In} **wt.%**	P_{In}	Y_{In}
a	Sanding abrasion	156	15.6	2.66	1.20	5.41	1.64	15.6	85.5	96.2
b	Roller abrasion	71.5	8.96	7.46	5.29	3.15	1.56	7.14	73.0	91.3
c	Roller abrasion	125	16.1	6.67	1.11	5.92	0.61	12.5	80.5	95.8

a	Heat 300 °C +sanding	147	18.3	3.66	0.79	5.13	0.87	14.7	83.6	4.96 ht / 92.0 ht&s
a	Heat 600 °C +sanding	142	17.9	4.13	1.10	5.24	0.65	14.2	83.0	74.6 ht / 84.8 ht&s
b	Plasma +roller	88.6	11.1	5.48	0.85	3.99	0.42	8.86	80.2	96.2

ht yield from only heat treatment, without sanding recovery
ht&s yield from combination of heat treatment and sanding recovery

3.2.1. Mechanical abrasion

The indium results in Table 3 demonstrate that sanding abrasion induces slightly higher purity and yield values compared to the two roller abrasion methods. A significant difference between the abrasion methods was obtained for the indium contents in the collected black mass product, where the best result was achieved with sanding abrasion.

The results were analyzed also with SEM images, including content map analyses illustrated in Fig. 2, where Fig. 2c presents a CF substrate with a partly brushed region. Estimated penetration depths (based on material densities) with the used voltages (7–15 kV) are 300–800 nm for the ITO and 795–2490 nm for the glass, respectively. The thickness of the ITO layer is typically 125 nm meaning that the SEM beam penetrates significantly more to the glass after penetrating through the entire ITO layer. However, purpose of these SEM analyses was mainly to visualize the effect of the brushing. The EDS results of the material content are qualitative in nature. The underlying glass substrate (4) can be identified as an area where the organic material and ITO layer are completely scraped. The image depicts the (1) ITO layer atop the (2) organic and (3) passivation layers. Fig. 2d demonstrates the previously mentioned structures with a content map analysis.

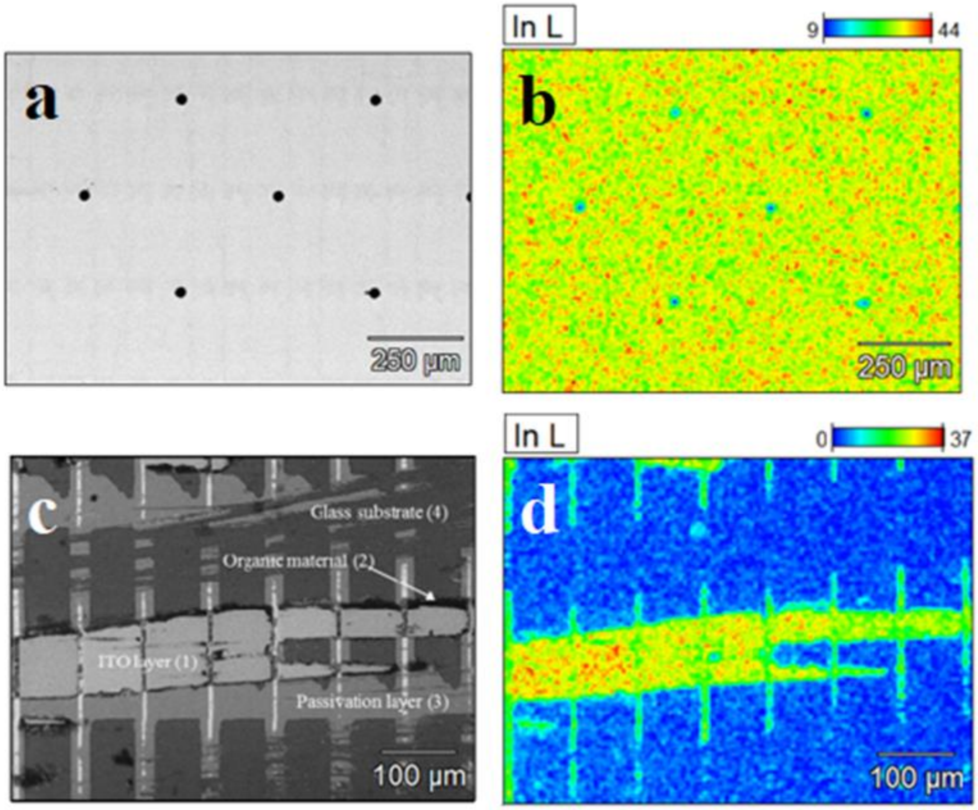

Fig. 2. SEM images of untreated and brushing studied samples presented as BSE images (a, c) and explained by content map images for indium (b, d). The untreated substrate sample is presented at the top (a, b) and the brushed substrate sample at the bottom (c, d) (Please, refer to online version for more illustrative color version of the figure).

As Fig 2c and Fig 2d show, mechanical abrasion has an effect on the indium and ITO layer of the glass substrate. The known fact that CF substrate contains more indium than TFT substrate is proven also in this study as results showed over double the content for indium in CF substrate compared to TFT.

Content analysis showed that mechanical abrasion can remove indium from the substrate as the amount of indium in the abraded area is zero, whereas in the un-abraded region the amount was at most 37 wt.%. The correct type of abrasive base is needed in mechanical abrasion. An aluminum oxide based abrasive was sufficient for untreated and plasma-treated samples of CF substrate, while silicon carbide based abrasive performed better on the heat-treated samples. The silicon abrasive base resulted in gouging the substrate and removing the glass, which is an undesired result. The potential unstacked ingredients from the aluminum oxide based abrasive may have an influence on the purity of results because aluminum already has a large share of the total content, as is shown in Table 2.

3.2.2. Heat treatment

Fig. 3 illustrates the effect of heat treatment on the CF substrate of the LCD panel. The studied samples were at room temperature (20–22 °C) before heating, and after a fixed time, the material was cooled again to room temperature. As a result of the heat treatment, there are areas of indium (ITO) co-vaporization and patches of decomposed material. The content map shows a zero indium content in the vaporized area of the heat-treated sample while the patches of the non-vaporized region have an indium content of up to 43 wt.%.

The effect of the treatment temperature is significant to the vaporization and material decomposition of ITO (Table 3). In treatment at 300 °C, 4.96% of indium was lost, while at 600 °C the corresponding value was 74.6%, indicating that it was not a pre-treatment method but an actual recovery method. However, in the experimental equipment in this work, gas washers were not included, and therefore, the vaporized indium was not collected. The purities of the collected black mass products and yields in the overall mechanical recovery process were not affected by the heat treatment. The treatment temperature affects properties of ITO and it has been reported to volatilize completely at 850 °C (Yoshida et al. 2014).

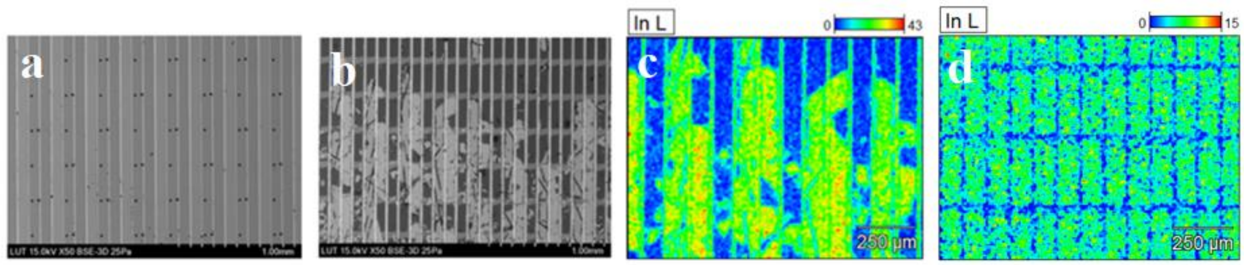

Fig. 3. SEM image of untreated (a) and heat-treated (b) LCD panel samples at a 600 °C temperature with an indium content map of CF substrate (c) and of TFT substrate (d) (Please, refer to online version for more illustrative color version of the figure).

The results of heat-treated and brushed samples confirmed the previous observation about the grit size of 60 abrasive not having a significant effect on the substrate, but the efficiency increased with the increasing grit size. Heat treatment had less impact on the ITO layer in the case of the TFT substrate, where the ITO layer was mainly intact after the heat treatment (Fig. 3d). TFT and CF substrates have a slightly different hardness (Won et al. 2014), which might explain the mentioned mutual differences between the substrates. The hardness of indium increases as the temperature decreases (Iliev et al. 2018).

An additional remarkable observation after the heat treatment was the fragility of the glass material, which should be taken into account in further processing. Especially immediately after heating, the material might be challenging to handle. The fragile glass makes physical brushing much more difficult. However, the altered structure of heat-treated glass caused less friction between the material and working platform, which led to faster mechanical abrasion.

3.2.3. Plasma treatment

The effect of cold atmospheric plasma treatment on the structure of ITO film prior to brushing was studied, and Fig. 4 shows the effect with varied influence time. The ITO layer of the CF substrate has degraded after the treatment, and the duration of the treatment has caused deterioration.

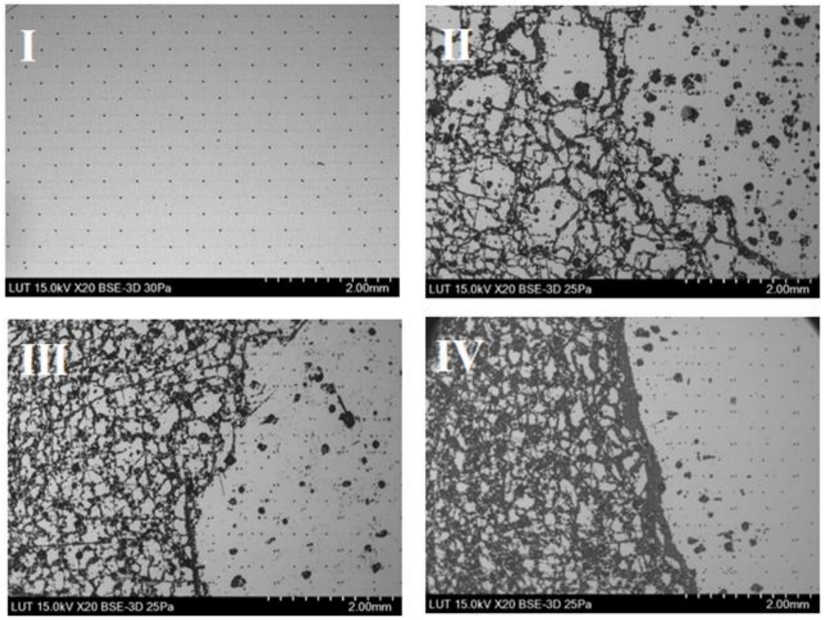

Fig. 4. CF substrate of the untreated sample (I) and plasma treated sample durations after 1 (II), 2 (III), and 5 (IV) seconds.

The plasma treatment of surfaces is known as a method for removing unwanted contaminants and enhancing the adhesion of coatings on materials. Here, the samples were plasma-treated manually with the processing distance of the plasma beam being approximately one-fourth of the nozzle diameter. The treated substrates showed color changes in the areas of exposure, and the level of discoloration was also influenced by the exposure time. The ITO layer might remain almost unmodified after the treatment, but the transistor circuits of the substrate were broken. This could be due to the shorting of the transistor circuit by electric arcs of plasma. The study showed that the recovery of the ITO layer was easy for the plasma treated CF substrate, but the TFT substrate was a more challenging structure for plasma treatment. Compared to heat treatment, plasma treatment is easy to perform without any cracks in the glass matrix, as plasma affects only the surface. The plasma modification may be unfavorable because the conductive ITO film became nearly non-conductive due to the increased oxygen concentration (Chen et al. 2017). The plasma treatment method also includes blowing air to the surface of the glass, which can remove affected ITO and organic material during the process.

No observations indicate that only plasma treatment without roller abrasion could have an effect on the indium content in the panel substrate. The yield and purity values of the plasma-treated and roller-abraded LCD panels for indium were 96.2 and 80.2%, respectively. The values were similar with only roller-abraded panels (95.8 and 80.5%); therefore, the plasma treatment did not improve the indium recovery.

3.2.4. Laser treatment

The laser treatment trial included a preliminary experiment to determine the effect of the laser beam on the ITO layer. Fig. 5 presents the effect of laser with various treatment speeds. Due to the high reflectivity of the laser on the TFT substrate, only the CF substrate was laser treated.

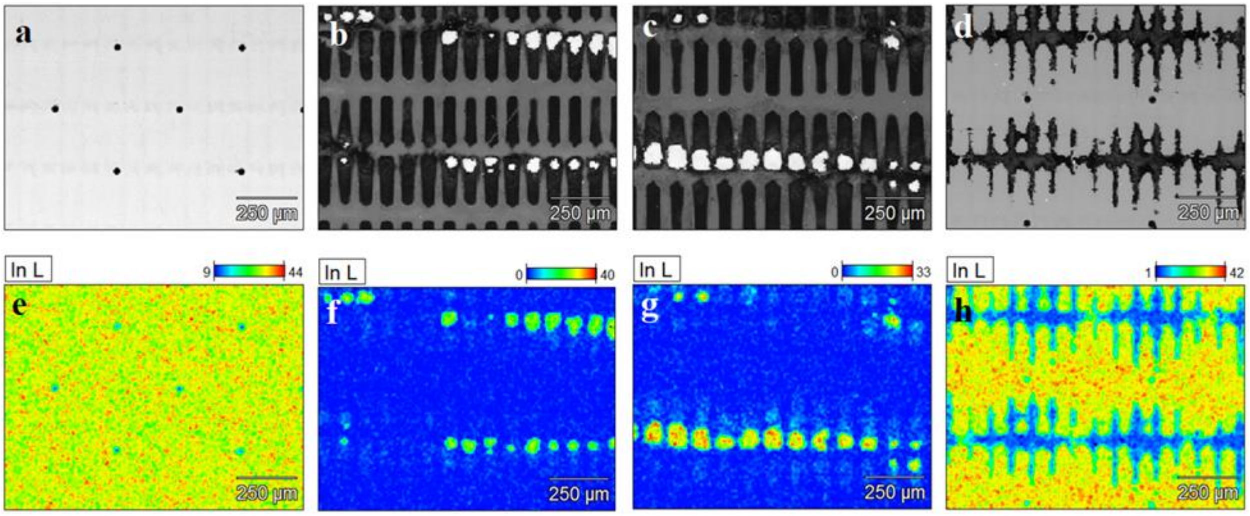

Fig. 5. Untreated (a) samples compared with 200 W powerful laser treatment with 300 mm/s (b), 400 mm/s (c), and 500 mm/s (d) speed of scanning. The content maps (a=e, b=f, c=g, d=h) indicate the indium share after the laser treatment (Please, refer to online version for more illustrative color version of the figure).

Laser treatment is capable of removing the indium from the CF substrates efficiently. However, the removal efficiency decreased when the speed was increased from 300 mm/s to 400 mm/s, and further increase to 500 mm/s caused already inefficient removal (Fig. 5, Table 4). This highlights the fact that the scanning speed needs to be chosen carefully for the best possible performance. Another thing to be highlighted is that the mechanism of recovery is evaporation, and therefore wet scrubbers would be needed to recover the removed indium.

Table 4. Metal content of the untreated and laser treated panel samples.

Treatment speed mm/s	**Content in substrates (mg/kg)**					
	Indium (In)	**Tin (Sn)**	**Aluminum (Al)**	**Iron (Fe)**	**Copper (Cu)**	**Zinc (Zn)**
untreated	423	52.6	231	1.58	16.1	3.93
300	7.98	2.30	288	1.90	5.22	0.80
400	23.4	6.24	670	5.73	4.96	1.47
500	259	33.3	376	3.62	11.6	1.64

However, as the indium vaporized in the laser treatment, it could not be recovered with the experimental set-up in this work. Wet scrubbing – a well-known industrial technique used especially for cleaning gaseous effluents – would be required to capture the indium. However, based on these preliminary laser treatment experiments, the method seems as an interesting option for further study.

3.3. Hydrometallurgical downstream processing

Increasing the temperature from 40 to 60 °C and the H_2SO_4 concentration from 0.5 to 2.5 mol/L improved the kinetics of the indium leaching from the plasma + roller brushing collected dust (Fig. 6). However, these conditions did not have an effect on the final yields after 1440 min (Table 5), which were satisfactory: at least 88.7%. While the decreased acid concentration decreased the indium yield, it increased the purity of the resulting solution. The results suggest that leaching take place at a low temperature and with low acidity to minimize costs and increase purity. A shorter leaching time would decrease the yield by several percentage points, but on the other hand increasing the leaching time tenfold would increase the energy consumption significantly due to mixing and heating. A remarkable results was that better quality raw material, *i.e.* higher indium and lower aluminum content, significantly improves the yield (to 100%) and purity (to 96.4%) (Table 5). Therefore, direct sanding abrasion is the preferred pretreatment technique from the downstream processing point of view.

Table 5. Details of the dust leaching experiments. The yields, Y_{In}, have been calculated based on the aqueous phase and solid starting materials analysis, and the purities, P_{In}, were calculated as the share of indium from all analyzed metals (In, Sn, Al, Fe, Cu, Zn).

Experiment	***T*, °C**	***c*(H_2SO_4), mol/L**	**Dust (see Table 2)**	**Y_{In} (120 min), %**	**Y_{In} (1440 min), %**	**P_{In} (1440 min), %**
L1	50	1.5	Panel a, Sanding abrasion	90.8	100	96.4
L2	50	2.5	Panel b, Plasma + roller	87.8	92.1	86.3
L3	50	0.5	Panel b, Plasma + roller	80.3	88.7	98.0
L4	40	1.5	Panel b, Plasma + roller	82.8	94.3	86.7
L5	60	1.5	Panel b, Plasma + roller	80.0	89.3	88.9

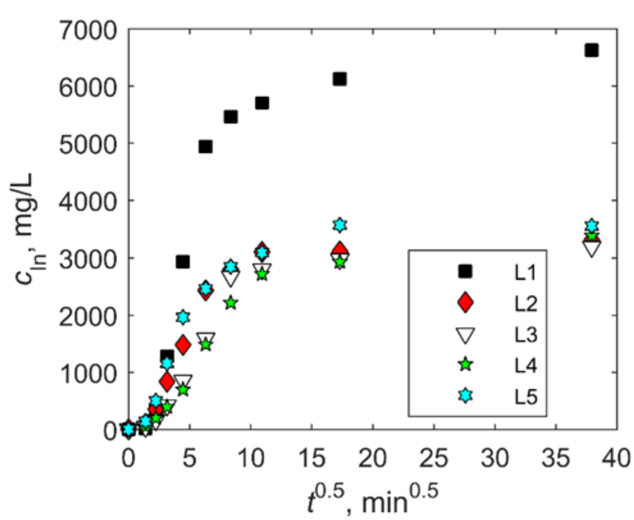

Fig. 6. Kinetics of indium leaching of the collected indium rich materials from physical treatment. See experimental details in Table 5.

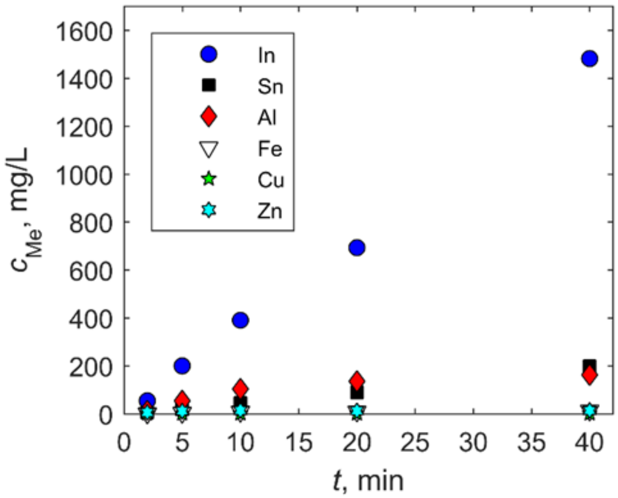

Fig. 7. Kinetics of the leaching of metals from the collected indium rich material from physical treatment. The dust collected from the plasma treatment followed by deep brushing was used as a raw material. T = 40 °C, $c(H_2SO_4)$ = 1.5 mol/L.

The difference in the metal leaching kinetics is not significant enough to improve the selectivity and purity of indium. The leaching rate is almost constant for the metals that are leached in significant concentrations (In, Sn, Al), which indicates that there are mass transfer resistances hindering the leaching (Fig. 7). The same conclusion can be drawn from the indium leaching results under different conditions (Fig. 6) as the shapes of the c vs. $t_{0.5}$ curves are typical for systems where the mass transfer dominates kinetics. This may be attributed to the physical appearance of the dust raw material, which is light, and small in particle size. Therefore, in further development of the suggested process, the process engineering aspects must be taken into account to overcome the mass transfer resistance issues.

Two indium rich aqueous solutions obtained from the leaching experiments above were subjected to zinc cementation to precipitate pure indium metal. One solution was from the plasma + roller brushing dust leaching experiment (Feed 1) and the other from the direct sanding abrasion dust leaching experiment (Feed 2). Table 6 presents the concentrations of the feed solutions.

Table 6. Feed solutions to the two cementation experiments. Concentrations in mg/L.

	In	**Sn**	**Al**	**Fe**	**Cu**	**Zn**
Feed 1	4280	565	357	27.8	29.6	21.1
Feed 2	6620	146	86.8	35.7	9.8	58.9

Before adding zinc powder (3.66 g/L) to start the cementation, the pH of the solutions was adjusted with NaOH to 2.90 and 2.79 for Feed 1 and Feed 2, respectively. As also Rochetti et al. (2016) have observed, significant portions of all of the metals are precipitated as hydroxides during the pH adjustment. The precipitated amounts were 22.4–69.2% for indium, tin, aluminum and iron, as Fig. 8 display. The cementation of indium was initially slow or did not occur at all during the first 40–70 min of the process. During this time, Fe^{3+} was reduced to Fe^{2+} (E° = 0.77 V) and protons to hydrogen gas (E° = 0 V). These reactions have a higher E° than the reduction of In^{3+} to In^0 (E° = –0.34 V), which means that they are preferred. After the 40–70 min interval the indium yield started to increase. With the lower-concentration Feed 1, the indium cementation was complete in 150 min, and with the higher-concentration Feed 2, the yield was 97.0% in 360 min. This is consistent with the results previously published by Barakat (1998), who obtained a 98.8% yield at 30 °C in 6 h.

Tin (E° for $Sn^{2+} \rightarrow Sn^0$ = –0.13 V) cemented faster than indium from Feed 1, which had a significantly higher tin concentration compared to Feed 2, from which, on the contrary, the cementation of tin was slower than that of indium. E° for the reduction of Fe^{2+} to Fe^0 is –0.44 V, and as expected, iron is removed more slowly than indium. On the other hand, the initial pH is quite high, making the direct precipitation of Fe^{3+} to $Fe(OH)_3$ possible. E° for the reduction of Al^{3+} to Al^0 (–1.66 V) is higher than that of Zn^{2+} to Zn^0 (–0.76 V), and therefore, the removal of aluminum from the system (Fig. 8) is likely due to some other mechanism than cementation. (These standard reduction potentials are from Habashi (1999)).

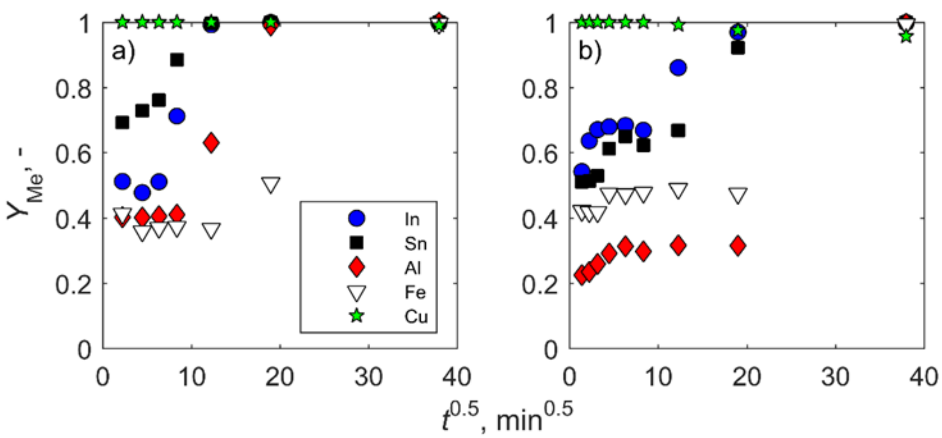

Fig. 8. Cementation of metals from the dust leachate. a) Feed 1 and b) Feed 2 in Table 6. T = 25 °C. The amount of zinc powder used: 3.66 g per 1 L of solution.

The cementation is not capable of producing high purity (*i.e.* 4N) indium from an impure feed solution as all the impurities were removed from the solution in the cementation experiments (Fig. 8). Even if the cementation time were optimized for selectivity, at least tin would still be co-cemented. Moreover, the precipitation of all of the metals is significant during the necessary pH adjustment before adding the zinc powder cementation agent. Therefore, an additional purification unit process, e.g. ion exchange or liquid-liquid extraction, would be needed.

Another option to recover metallic indium would be electrowinning, which has been demonstrated by Maslin et al. (1998) from sulfuric acid solutions and by Lee and Sohn (2003) from acidic chloride solutions. However, there is no evidence whether electrowinning would be selective, and solution purification would still be needed. On the other hand, it would be possible to perform electrowinning directly without increasing the pH, which would enable avoiding the unwanted mixed hydroxide precipitates. In the article by Maslin et al. (1998), electrowinning was successful from 1.5–2.4 g/L indium containing a 50–90 g/L H_2SO_4 solution, which closely resembles the solution obtained from the leaching of the dust in this work.

The results obtained with the pre-treatment methods indicate a significant and promising purity and yield. The content wt.% values with plasma pre-treatment, heat pre-treatment, and mechanical abrasion were 8.86, 14.68, and 7.14–15.58, respectively. In addition, the mechanical process reduces the mass of material fed to the hydrometallurgical recovery process and consequently the equipment sizes, and chemical and water usage are reduced. Previously, studies of mechanical exfoliation and mechanical stripping have been similar, and indium recovery can be comparable with the results in this study. The mechanical exfoliation utilized a negative vacuum lapping polisher on liquid crystal free substrate, achieving 7.26 wt.% of indium (Wang et al. 2017). Indium rich glass was treated first by pyrolytic decomposition before chemical extraction in the mechanical stripping, achieving 7.95 wt.% of indium (Zhang et al. 2017).

3.4 Economic feasibility analysis of the suggested recovery processes

Preliminary comparison in terms of energy consumption between the studied mechanical recovery methods is presented in Table 7. The analysis of mechanical abrasion method include industrial scale wide belt sander and dust blotter with powers of 5.5 kW and 4.0 kW, respectively. The capacity of mechanical abrasion was 0.84 m^2/min. The analysis of heat treatment was based on treatment of substrate for 30 min at the selected temperatures in a 12 kW oven that can attain maximum temperature of 1350 °C. Plasma treatment consisted a separate instrument providing compressed air, and the both equipment had a power of 1 kW. Times for heat treatment and plasma treatment were 0.5 h and 0.025 h, respectively.

Table 7. The energy consumptions and cost estimations for the studied mechanical processes.

	Treatment			
Apparatus	Mechanical abrasion	Heat treatment at 300 °C	Heat treatment at 600 °C	Plasma Treatment
	Consumption (kWh) / Cost (€/m^2)	Consumption (kWh) / Cost (€/m^2)	Consumption (kWh) / Cost (€/m^2)	Consumption (kWh) / Cost (€/m^2)
Sanding machine	0.110 / 0.013	0.110 / 0.013	0.110 / 0.013	0.110 / 0.013
Blotter	0.080 / 0.010	0.080 / 0.010	0.080 / 0.010	0.080 / 0.010
Oven	-	1.333 / 0.160	2.667 / 0.320	-
Plasma devices	-	-	-	0.050 / 0.006
TOTAL (kWh / €/m^2)	0.190 / 0.023	1.523 / 0.183	2.857 / 0.343	0.240 / 0.029

From the economic viewpoint, the mechanical abrasion method is the most cost-effective, but plasma treatment was almost as effective (Table 7). The plasma treatment before the mechanical abrasion increases the energy consumption from 0.190 to 0.240 kWh/m^2, but it does not give any added value from technical point of view. The energy consumption of heat treatment is excessively high, and the treatment did not improve the process from technical point of view either. Therefore the direct mechanical abrasion was deemed to be the most efficient method with energy costs of 117 €/kg produced indium.

Preliminary calculations of energy and chemical costs of the hydrometallurgical part of the process (leaching + cementation) are discussed below. The reactor used for leaching and cementation experiments in this study was very small and the impeller was not of industrially common type. Therefore, a typical value for mixing power in hydrometallurgical leaching (1 kW/m^3) was used in the calculations for both unit processes.

The cementation process was done here at 25 °C and, according to Barakat (1998), the temperature does not have a significant effect. Therefore, there is no cost for heating in cementation. The energy consumption of the leaching reactor was calculated with the heat capacity of 1.17 kWh/(m^3 °C) for 9.82%

of sulfuric acid (Kunzler and Giauque, 1952) and the leaching conditions according to the experiment L1 in Table 5. In order to link the calculations for the leaching step to those of the mechanical recovery part of the process (Table 7), the former were scaled to unit area of the panel. Therefore, the density of the glass panel (1.6 kg/m^2) was measured with six parallel determinations. In these calculations, the indium content of the glass panel and of the recovered black mass taken as the averages of the values shown in Table 3, i.e. 122 mg/kg and 12.2 wt.-%, respectively.

100% yield for the leaching was used as it was achieved with the certain physical treatment, which can be chosen for further development of the process. Energy consumption of 10.9 kWh/kg produced indium was obtained for 24 h reaction time. Such a long time was chosen as the energy consumption is largerly independent of leaching time but the value of the indium is higher when the yield can be increased from 90.8% in 2 h leaching to 100% in 24 h leaching. As a cost for sulfuric acid 0.044 €/kg was used (Hayes et al., 2018). Here the calculation is based on the non-optimized assumption that all the sulfuric acid is neutralized when pH is increased in the cementation and therefore the whole 1.5 M should be added as a make up to the recovered and recycled water from the cementation. The costs of this sulfuric acid addition are 1.33 €/kg produced indium.

In cementation, 6 h reaction time was used and the energy consumption was calculated to be 1.44 kWh/kg produced indium. Costs for 3.66 g/L zinc powder consumption at a price of 10 €/kg (estimate based on market value of bulk zinc metal) are 7.5 €/kg produced indium. As the pH was increased to 2.79, is it assumed for simplicity that all the 1.5 M sulfuric acid is neutralized with sodium hydroxide. With the price of 0.220 €/kg (Palencia et al., 1999), the neutralization costs are 5.41 €/kg produced indium.

As observed from these results, the energy costs of the hydrometallurgical part, 1.48 €/kg produced indium are negligible. Also the total chemicals cost, 14.2 €/kg produced indium, is small compared to the value of indium 181 €/kg (Asian Metal, 2019). Combined with the energy costs of the mechanical abrasion recovery method, the total process costs are 133 €/kg produced indium. Frenzel et al. (2017) present the inflation-adjusted indium price data from 1973 to 2013. The highest values have been over 1000 $/kg and the lowest ones under 200 $/kg, but these have been exceptions and it is fair to assume that the price would be 200–700 $/kg for the most of the time. In 2015–2018 the annual average prices were 410, 240, 225 and 310 $/kg, respectively (USGS 2019). As a reference, in a pilot scale tests run by Rochetti et al. (2016), the energy consumption was 0.13 kW/kg treated LCD glass, which counts for 128 €/kg produced indium when calculated with same indium content and energy price as above. The difference in these processes is that in the novel process described here the capital costs in the hydrometallurgical part would be significantly lower as the amount of treated solid raw material is significantly less. In the process described here, the capital costs of the mechanical process equipment can be assumed to be in the same range with Rochetti's et al. (2016) process, in which the glass panels are crushed. The other significant difference is that the purity of the indium product would be much higher in the process described here than the 62% obtained by Rochetti et al. (2016). However, due to the precipitation of all the metals and co-cementation of tin, optimization of the cementation is needed to obtain the market grade indium (> 99.99%). Alternatively, the solution could be purified before cementation by ion exchange or solvent extraction, the impure cementation product could be electrorefined (Alfantazi and Moskalyk 2003), or electrolysis could be used instead of cementation to give higher purity product. Costs in industrial large scale solvent extraction are at most, in case of difficult REE separation, 10 €/kg produced metal (Ritcey 2006), and in electrorefining typically under 1€/kg (Schlesinger et al. 2011). Costs of treatment or recycling of the effluent solution, which can be considered as concentrated brine here, are estimated to be ca. 1

€/m^3 being < 1 €/kg produced metal (ca. 5 g/L indium concentration). Even though the process suggested here is small and the costs can be assumed to be slightly higher, it is safe to state that adding the additional purification would not increase the production costs over the indium price.

Considering the feasibility of producing recycled indium in general, and particularly with the process proposed here, it has been estimated by Lokanc et al. (2015) that most of the primary indium producers are able to produce indium with 150–300 $/kg price. This is a reasonable goal also to the novel process described in this article. However, in addition to just economical feasibility, producing recycled indium may have environmental benefits. According to Ciacci et al. (2018) the environmental feasibility of the recycled indium is not certain as the processes are not yet explored in enough details, but according to the calculations of Rocchetti et al. (2015) the environmental footprint of recycled indium would be 600 kg CO_2/kg lower than for the primary indium.

The above discussion shows that the novel mechanical recovery based indium recovery process from waste LCD panels is promising also from economic point of view. Although the economic evaluation was preliminary, and not all the costs (e.g. capital and labor) were taken into account, the process can also be further optimized.

While this study focused on indium recovery from LCDs, it is worth noting that the generation of different types of indium-bearing waste may increase remarkably in the future due to new applications, such as solar panels. The technologies presented in this study could be available as installed automated apparatus for indium recovery from other potential new raw materials also. Attention should also be paid to the portability of the apparatus, as moving the process to the raw materials may be more economical than moving the raw materials to the process (Rocchetti et al. 2013). Based on the annual worldwide amount of WEEE produced (Baldé et al. 2017), the share of LCD panels from that amount (Lee and Cooper 2008), and indium content in the glass panels, it is possible to calculate the worldwide annual amount of indium available in urban mines (125 t). When comparing this to the primary production of 800 t, it is fair to assume that a global perspective should be considered as a business model. As it is impossible to transport feasibly waste panels to a permanently located plant, a mobile plant would be the preferable choice from business model point of view also.

4. Conclusions

This work studied novel mechanical pre-treatment and recovery methods followed by hydrometallurgical indium recovery processes. Brushing with sanding abrasion was shown to remove the ITO layer efficiently from the LCD glass, recovering 96.2% of the indium and yielding a 15.6 wt.-% content in the black mass product. The latter was roughly double compared to the roller abrasion (7.14 wt.-%). In addition, the purity was greater with the sanding abrasion. Heat or plasma treatment did not affect the yield or purity in the following brushing. With laser treatment, the ITO layer evaporated, and therefore, laser treatment is an interesting option as a recovery process.

After the mechanical recovery of the black mass, indium was leached to 0.5–2.5 M sulfuric acid at 40–60 °C. Indium yields of 88.7–100% were obtained in 24 h, and in 2 h the yields were roughly 10 percentage points lower. With sanding instead of roller pre-treatment, the collected black mass gave a significantly higher yield in leaching. The indium purities in the obtained leachates were 86.3–98.0%, and a lower acid concentration led to higher purities. Increasing the temperature and acid concentration led to slightly faster kinetics. Cementation could not produce pure indium from the leachate due to the complete co-cementation of the impurity metals (Sn, Fe, Al, Cu). Moreover, the needed pH increment before the cementation caused significant precipitation in all of the metals in the system. Therefore, solution purification or some other precipitation method would be necessary before the cementation to obtain high purity indium metal.

Overall, the studied process is a feasible option for indium recycling from waste LCD screens. The conducted preliminary economic analysis revealed commercial potential of the suggested process. Operational costs related to energy and chemicals consumption were calculated to be 133 €/kg produced indium, while the current market price is 181 €/kg, although the purity of the produced indium did not reach marketable level. Additional costs of product purification and effluent treatment are consider to be such that the overall process would be still profitable with the current price.

To further develop the suggested process, the challenges of pure indium precipitation, automation of the mechanical recovery, optimization of the overall process, recycling the other materials (glass, plastics and other organic materials, impurity metals), and economic potential should be studied in more detail. For example, from hazardous metals, free glass material could be utilized as a raw material in glass-ceramics products.

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REFERENCES:

Alfantazi, A.M., Moskalyk, R.R., 2003. Processing of indium: a review. Miner. Eng. 16, 687–694.

Amato, A., Rocchetti, L., Beolchini, F., 2017. Environmental impact assessment of different end-of-life LCD management strategies. Waste. Manage. 59, 432–441.

Ardente, F., Mathieux, F., Recchioni, M., 2014. Recycling of electronic displays: Analysis of pre-processing and potential eco-design improvements. Resour. Conserv. Recy. 92, 158–171.

Argenta, A.B., Reis, C.M., Mello, G.P., Dotto, G.L., Tanabe, E.H., Bertuol, D.A., 2017. Supercritical CO_2 extraction of indium present in liquid crystal displays from discarded cell phones using organic acids. J. Supercrit. Fluid. 120, 95–101.

Asian Metal, 2019. http://www.asianmetal.com/indexEn.shtml?s=1&r=/news/data/1471488/ (accessed 7 February2019).

Assefi, M., Maroufi, S., Nekouei, R.K., Sahajwalla, V., 2018. Selective recovery of indium from scrap LCD panels using macroporous resins. J. Clean. Prod. 180, 814–822.

Ayres, R.U., Talens Peiró, L., 2013. Material efficiency: rare and critical metal. Philos. T. Roy. Soc. A. 371, 1–21.

Babbitt, C.W., Althaf, S., Chen, R., 2017. Sustainable materials management for the evolving consumer technology ecosystem. Rochester Institute of Technology. https://www.rit.edu/gis/ssil/docs/Sustainable%20Materials%20Management%20for%20the%20Evolving%20Consumer%20Technology%20Ecosystem.pdf (accessed 12 January 2018)

Baldé, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P., 2017. The Global E-waste Monitor – 2017, United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna.

Barakat, M.A., 1998. Recovery of lead, tin and indium from alloy wire scrap. Hydrometallurgy 49, 63–73.

Boundy, T., Boyton, M., Taylor, P., 2017. Attrition scrubbing for recovery of indium from waste liquid crystal display glass via selective comminution. J. Clean. Prod. 154, 436–444.

Burke, M., 2007. The gadget scrap heap. Chem. World-UK. June 2007, 44–48.

Böni, H., Widmer, R., 2011. Disposal of Flat Panel Display Monitors in Switzerland. EMPA, St. Gallen.

Chen, P-H., Chang, T-C., Chang, K-C., Tsai, T-M., Pan, C-H., Shih, C-C., Wu, C-H., Yang, C-C., Chen, W-C., Lin, J-C., Wang, M-H., Zheng, H-X., Chen, M-C., Sze, SM., 2017. Effect of plasma treatment time on surface characteristics of indium-tin-oxide film for resistive switching storage applications. Appl. Surf. Sci. 414, 224–229.

Choi, C.H., Eun, J., Cao, J., Lee, S., Zhao, F., 2018. Global strategic level supply planning of materials critical to clean energy technologies – A case study on indium. Energy. 147, 950-964.

Ciacci, L., Wernerm T.T., Vassura, I., Passarini, F., 2018. Backlighting the European indium recycling potentials. J. Ind. Ecol. DOI: 10.1111/jiec.12744.

Dang, M.T., Wantz, G., Hirsch, L., Wuest, J.D., 2017. Recycling indium tin oxide (ITO) anodes for use in organic light-emitting diodes (OLEDs). Thin Solid Films. 638, 236–243.

EC (European Commission), 2017. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the regions on the 2017 list of Critical Raw Materials for the EU, Brussels, 13.9.2017 COM(2017) 490 final. http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52017DC0490&from=EN (accessed 30 January 2018).

EU (European Union), 2012. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32012L0019&from=EN (accessed 24 January 2018).

Eurostat, 2018. File: Electricity prices for non-household consumers, first half 2018 (EUR per kWh). https://ec.europa.eu/eurostat/statistics-explained/index.php?title=File:Electricity_prices_for_non-household_consumers,_first_half_2018_(EUR_per_kWh).png (accessed 7 February 2019).

Ferella, F., Belardi, G., Marsilii, A., De Michelis, I., Vegliò, F., 2017. Separation and recovery of glass, plastic and indium from spent LCD panels, Waste Manage. 60, 569–581.

Frenzel, M., Mikolajczak, C., Reuter, M.A., Gutzmer, J., 2017. Quantifying the relative availability of high-tech by-product metals – The cases of gallium, germanium and indium. Resour. Policy 52, 327–335.

Graedel, T.E., Allwood, J., Birat, J-P., Buchert, M., Hakalüken, C., Reck, B.K., 2011. Recycling rates of metals: A status report. International Resource Panel, United Nations Environment Programme (UNEP).

Habashi, F., 1999. A textbook of hydrometallurgy. Métallurgie Extractive Québec, Quebec City.

Hayes, M., Alshibli, A., Howell, J., Eakes, J., 2018. Economic Analysis of Phosphoric Acid Extraction. University of Tennessee Honors Thesis Projects.

He, Y., Ma, E., Xu, Z., 2014. Recycling indium from waste liquid crystal display panel by vacuum carbon-reduction. J. Hazard. Mater. 268, 185–190.

Iliev, S.P., Gommer, F., Tagarielli, V.T., 2018. Measurement of an indentation size effect for Indium as a function of temperature. Mater. Sci. Eng. A. 733, 232-234.

Kunzler, J.E., Giauque, W.F., 1952. Aqueous Sulfuric Acid. Heat Capacity. Partial Specific Heat Content of Water at 25 and -20°1. J. Am. Chem. Soc. 74, 3472–3476.

Lee, S., Cooper, J., 2008. Estimating regional material flows for LCDs, proceedings of the IEEE international symposium on electronics and the environment ISEE (May 2008). IEEE Int. Symp. Electron. Environ., San Francisco.

Lee, C-H., Jeong, M-K., Kilicaslan, M.F., Lee, J-H., Hong, H-S., Hong, S-J., 2013. Recovery of indium from used LCD panel by a time efficient and environmentally sound method assisted HEBM. Waste Manage. 33, 730–734.

Lee, M.-S., Sohn, K.-Y., 2003. Comparison of indium purification between vacuum refining and electrowinning. J. Mater. Sci. 38, 4843–4848.

Lokanc, M., Eggert, R., Redlinger, M., 2015. The Availability of Indium: The Present, Medium Term, and Long Term. National Renewable Energy Laboratory (NREL), United States.

Ma, E., Xu, Z., 2013. Technological process and optimum design of organic materials vacuum pyrolysis and indium chlorinated separation from waste liquid crystal display panels, J. Hazard. Mater. 263, 610–617.

Maslin, A.I., Belobaba, A.G., Vais, A.A., 1999. Electrowinning of indium from concentrated sulfuric acid solutions. Khim. Prom-st., Moscow.

Ohajinwa, C.M., Van Bodegom, P.M., Vijver, M.G., Peijnenburg, W.J.G.M., 2017. Health Risks Awareness of Electronic Waste Workers in the Informal Sector in Nigeria. Int. J. Env. Res. Pub. He. 14, 1–16.

Palencia, I., Romero, R., Iglesias, N., Carranza, F., 1999. Recycling EAF dust leaching residue to the furnace: A simulation study. JOM 51, 28–32.

Pavel, C.C., Marmier, A., Tzimas, E., Schleicher, T., Schüler, D., Buchert, M., Blagoeva, D., 2016. Critical raw materials in lightning applications: Substitution opportunities and implication on their demand. Phys. Status Solidi A. 11, 2937–2946.

Ritcey, G.M., 2006. Solvent Extraction: Principles and Applications to Process Metallurgy, Solvent Extraction: Principles and Applications to Process Metallurgy. G.M. Ritcey & Associates.

Rocchetti, L., Amato, A., Beolchini, F., 2016. Recovery of indium from liquid crystal displays, J. Clean. Prod. 116, 299–305.

Rocchetti, L., Amato, A., Fonti, V., Ubaldini, S., Michelis, I.D., Kopacek, B., Veglio, F., Beolchini, F., 2015. Cross-current leaching of indium from end-of-life LCD panels. Waste Manage. 42, 180–187.

Rocchetti, L., Vegliò, F., Kopacek, B., Beolchini, F., 2013. Environmental impact assessment of hydrometallurgial processes for metal recovery from WEEE residues using a portable prototype plant. Environ. Sci. Technol. 47, 1581–1588.

Schlesinger, M.E., King, M.J., Sole, K.C., Davenport, W.G., 2011. Extractive Metallurgy of Copper. Elsevier Science.

Swain, B., Mishra, C., Hong, H.S., Cho, S-S., 2016. Beneficiation and recovery of indium from liquid-crystal-display glass by hydrometallurgy. Waste Manage. 57, 207-214.

UBA, 2016. Lifetime of electrical appliances becoming shorter and shorter – Press releases. https://www.umweltbundesamt.de/en/press/pressinformation/lifetime-of-electrical-appliances-becoming-shorter (accessed 25 January 2018).

Ueberchaar, M., Schlummer, M., Jalalpoor, D., Kaup, N., Rotter, V.S., 2017. Potential and Recycling Strategies for LCD Panels from WEEE. Recycling 2, 1-19.

USGS, 2019. Mineral commodity summaries 2019. https://minerals.usgs.gov/minerals/pubs/commodity/indium/mcs-2019-indiu.pdf (accessed 19 March 2019).

Wang, H., Gu, Y., Wu, Y., Zhang, Y-N., Wang, W., 2015. An evaluation of the potential yield of indium recycled from end-of-life LCDs: A case study in China. Waste Manage. 46, 480–487.

Wang, S., He, Y., Zhang, T., Zhang, G., 2017. Recovery of valuable components from waste LCD panel through a dry physical method. Waste Manage. 64, 255–262.

Werner, T.T., Mudd, G.M., Jowitt, S.M., 2017. The world's by-product and critical metal resources part III: A global assessment of indium. Ore Geol. Rev. 86, 939-956.

Werner, T.T., Ciacci, L., Mudd, G.M., Reck, B.K., Northey, S.A., 2018. Looking down under for a circular economy of indium. Environ. Sci. Technol. 52, 2055-2062.

Won, M-S., Amanov, A., Kim, H-J., Yun, W-S., Joo, W-G., Kim, D-E., 2014. Evaluation of the mechanical and tribological properties of a TFT-LCD panel. Tribol. Int. 73, 95-100.

Yang, J., Ekberg, C., Retegan, T., 2014. Optimization of Indium Recovery and Separation from LCD Waste by Solvent Extraction with Bis(2-ethylhexyl) Phosphate (D2EHPA), Int. J. Chem. Eng. DOI: 10.1155/2014/186768

Yoshida, H., Izhar, S., Nishio, E., Utsumi, Y., Kakimori, N., Asghari, F.S., 2015. Recovery of indium from TFT and CF glasses of LCD wastes using NaOH-enhanced sub-critical water. J. Supercritical Fluid. 104, 40–48.

Yoshida, H., Izhar, S., Nishio, E., Utsumi, Y., Kakimori, N., Feridoun, S.A., 2014. Recovery of indium from TFT and CF glasses in LCD panel wastes using sub-critical water. Sol. Energ. Mat. Sol. C. 125, 14–19.

Zhang, L., Wu, B., Chen, Y., Xu, Z., 2017. Treatment of liquid crystals and recycling indium for stripping product gained by mechanical stripping process from waste liquid crystal display panels. J. Clean. Prod. 162, 1472–1481.

Zhang, K., Wu, Y., Wang, W., Li, B., Zhang, Y., Zuo, T., 2015. Recycling indium from waste LCDs: A review. Resour. Conserv. Recy. 104, 276–290.

Zhao, K., Liu, Z., Wang, Y., Jiang, H., 2013. Study on recycling process for EOL liquid crystal display panel. Int. J. Precis. Eng. Man. 14, 1043–1047.

Zhuang, X., He, W., Li, G., Huang, J., Ye, Y., 2012. Materials separation from waste liquid crystal displays using combined physical methods. Pol. J. Environ. Stud. 21, 1921–1927.

Zuser, A., Rechberger, H., 2011. Considerations of resource availability in technology development strategies: The case study of photovoltaics. Resour. Conserv. Recy. 56, 56–65.