INFLUENCE OF VARIOUS MECHANICAL PREPARATION METHODS OF LCD ON THE LEACHABILITY OF CRITICAL ELEMENTS

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Abstract

As various electrical and electronic equipment pieces are frequently replaced due to technological development or changes, the recycling of the generating in huge amount e-wastes is of outstanding importance. The research in this field is inevitable in the spotlight of creating the circular economy. The recycling strategy is generally aiming at the recovery of materials like plastics and metals, as well as of valuable, even critical elements and compounds along with the satisfactory treatment of toxic ones. For this sake the mechanical treatment is combined with the chemical/bio/thermal techniques.

Due to the numerous elements used for their manufacturing, LCD (Liquid Crystal Displays) display panels provide a wide range of valuable and critical, but also toxic elements. Thus, instead of disposal of waste LCD panels, the recovery of such elements can not only prevent possible environmental hazards but endorse the utilisation of secondary raw materials.

It was proved that the mechanical pre-treatment is an important step, first of all, to recycle materials like plastics and common metals. Furthermore, the chemical mass transfer is governed by the concentration gradient, the area exposed and the retention time. Nevertheless, the presence of the "alien" components in the mass transfer can dramatically decrease the concentration gradient, the contact surface, as well as the diffusion rate. And finally, the lower the material flow to be submitted for the chemical processing, the lower the specific reagents requirement and, therefore the costs of the process (BOKÁNYI 2014).

Thus, the mechanical removal of LCD polarizing film seems to be highly advisable; however is not easy, needs 200–250 °C high temperature as well. At the same time, the ITO (Indium-Tin-Oxide) surface layer at favourable conditions can be exposed for the diffusion even without removing polarizing foil.

Therefore, one experimental series of our current research was focused on the comparison of acidic leaching of the stripped and ground LCD panel with and without the polarizing film. Another experimental series was devoted to the effect of fineness on the leachability of indium, tin and other elements. Thereafter, ground LCD was produced with different fineness in Retsch ZM 200 centrifugal mill. Based on the data obtained, important conclusions were drawn.

Keywords:*LCD panel, critical elements recycling, mechanical preparation, acidic leaching*

1. INTRODUCTION

Nowadays, e-waste is one of the fastest growing waste streams. It was estimated that ~44.7 million tonnes of e-waste were generated in 2016 and, with an annual growth rate of 3–4%, is expected to reach ~52.2 million tonnes in 2021 (BALDÉ et al. 2017).E-wastes are a potential resource for various valuable materials and critical metals such as indium, rare earth elements, precious metals, lithium and cobalt, as these are widely consumed in the production of electric and electronic equipment (ZHANG et al. 2017). Liquid crystal displays (LCDs) are widely used in TVs, laptops, desktops and any other device with a screen. Thus, with the emergence and replacement of a great amount of LCD electronic devices, the recovery of certain elements, i.e. indium or tin, from the waste LCDs is a relevant research topic.

Numerous studies have been reported on the research of indium production from waste ITO targets (HSIEH et al. 2009; LI et al. 2011), but only a few deals with the indium recovery from waste LCD displays. That is why it is became a very important task nowadays. In case of this latter, the first and very important part of the process is the pre-treatment method, which involves the separation of the polarizing film, as well as the liquid crystal from the surface of the glass substrate. LI J. et al. studied the separation of the polarizing film by thermal shock, and ultrasonic cleaning was used for the removal of liquid crystal. For the dissolution of indium a mixture of hydrochloric and nitric acids was applied at 60 °C for 30 min (LI et al. 2009). After the thermal treatment and ultrasonic washing the effect of a high energy ball grinding was studied by Lee et al. The leaching process was carried out with The ground product was then leached with a mixed acid solution (H_2O:HCl:HNO_3 = 50:45:5) solution for 30 min. It was concluded that higher recovery of indium was achieved at room temperature after using high energy ball mill, than by using a conventional shredding machine (LEE et al. 2013). Based on the experimental results of Yang et al. 1M HCl and 1M H_2SO_4 solution was also proved to be suitable for the dissolution of indium (YANG et al. 2013). The selective recovery of indium from the acidic solution is also a key factor for an effective and economical technology. Precipitation is one of the possible ways, but cementation of indium on Al or Zn particles was also investigated (MURATANI et al. 2010), as well as the solvent extraction (VIROLAINEN et al. 2011; RUAN et al. 2012) is also used widely for the selective separation of indium in the experimental studies.

The effect of different pre-treatments has been examined for the separation and recovery of glass, plastic and various metals, mainly indium. Among thermal treatments, the pyrolysis was mainly used to remove organic materials, the recovery rate of indium in leaching was examined (FERELLA et al. 2017; WANG and XU 2016; ZHANG et al. 2015).

During the experiments of HASEGAWA et al. (2013), ITO-glass was crushed into approximately 30 mm × 50 mm pieces, then the size of particles was reduced by milling in a ceramic pot mill combined with alumina balls of different sizes. When milling was performed for 6 h at 150 rpm, the fine particles facilitated the rate of indium extraction with amino-polycarboxylate chelats. SILVEIRA et al. (2015) investigated the effect of the particle size of the panels on the dissolution efficiency of indium. For their experiments, a knife mill, hammer mill, and porcelain ball mill were used before acid leaching with H_2SO_4. During leaching, the concentration, solid/liquid ratio, temperature and leaching time were also examined. It was concluded that one of the most important parameters affecting the dissolution efficiency is the size of the particles to be leached.

Thus, it can be concluded that mechanical pre-treatment is an important step in the processing of waste LCD panels.

For the experiments described in the article, an experimental series focused on the comparison of acidic leaching of the stripped and ground LCD panel with and without the polarizing film. Another experimental series was devoted to examining the effect of fineness on the leachability of indium, tin and other elements.

2. MATERIALS AND METHODS

A mixture of 12 LCD displays from various types and brands of dismantled televisions was used for each experiment. The structure and design of a standard LCD panel can be observed in Figure 1. An LCD panel consists of several layers in a sandwich structure:on the outside, polarising foils are adhered to 0.4-1.1 mm thick glass substrates, latteraccount for 40–50 wt.% of the panel. The inside of the panel, the liquid crystals and the conductive indium tin oxide (ITO) layer are enclosed in a colour filter (CF) and thin film transistor (TFT) layerwhich are approximately 140–150 nm thick. ITO is a mixture of indium(III) oxide (In_2O_3) and tin(IV) oxide (SnO_2), with 80–90 wt.% of In_2O_3, and 10–20 wt.% of SnO_2 (FAITLI and MAGYAR 2014; UEBERSCHAAR et al. 2017; WANG et al. 2017).

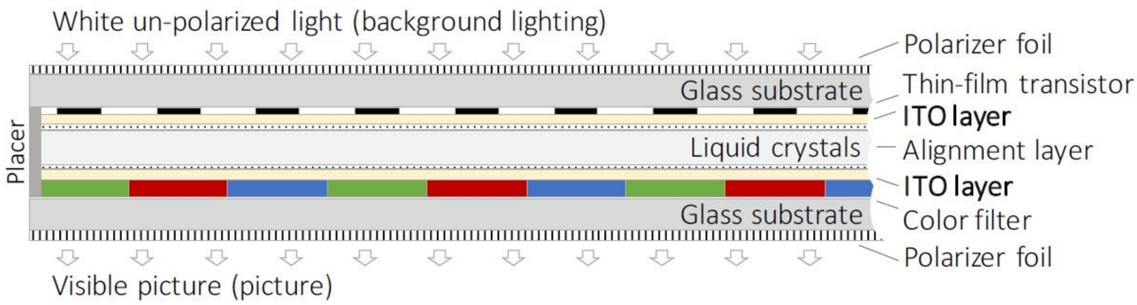

Figure 1
The structure of an LCD panel
(UEBERSCHAAR et al. 2017)

To compare the effect of the polarising foil on the properties of the ground panels and on the efficiency of acidic leaching, the experiments were carried out using LCD panels with (hereinafter LCD F) and without the polarising foil on (hereinafter LCD NF). *Figure 2* summarises the processing flow sheets of both experiments.

When the foil wasn't removed *(Figure 2.a)*, the stripped displays were first crushed using a hammer mill under 8 mm particle size, then ultrasonic washing at 40 Hz was carried out with a solution of surfactant at 40 °C for 30 minutes. The feed with particle size between 3.15–6.3 mm was further comminuted with Retsch SM 2000 cutting mill under 4 mm. Finally, before acidic leaching, the particle size was reduced below 1 and 0.5 mm with Retsch ZM 200 centrifugal mill at 14,000 rpm.

For the experiments with LCDs without foil *(Figure 2b)*, the film removal and the ultrasonic washing of the LCD panels were carried out in accordance with the literature (LI et al. 2009;

MIŠKUFOVÁ et al. 2018). First, the panels underwent an ~230 °C thermal shock treatment for 2-3 minutes to remove the polarising film. Next, after ultrasonic washing (40 °C, 40 Hz, 30 minutes) with a solution of surfactant to remove liquid crystals, the ITO glass was crushed in a hammer mill under 8 mm. Finaelly, the particle size of product of the hammer milling was further reduced under 1 mm and 0.5 mm with Retsch ZM 200 centrifugal mill at 14,000 rpm.

The acid leaching of all samples was carried out with a 1:1 (g/mL) dilution ratio with 1 M HCl in Erlenmayer flasks, using 150 min^{-1} intensive stirring in a shaking apparatus at 55 °C for 1 h using the elaborated earlier procedure (BOKÁNYI et al. 2014_1).

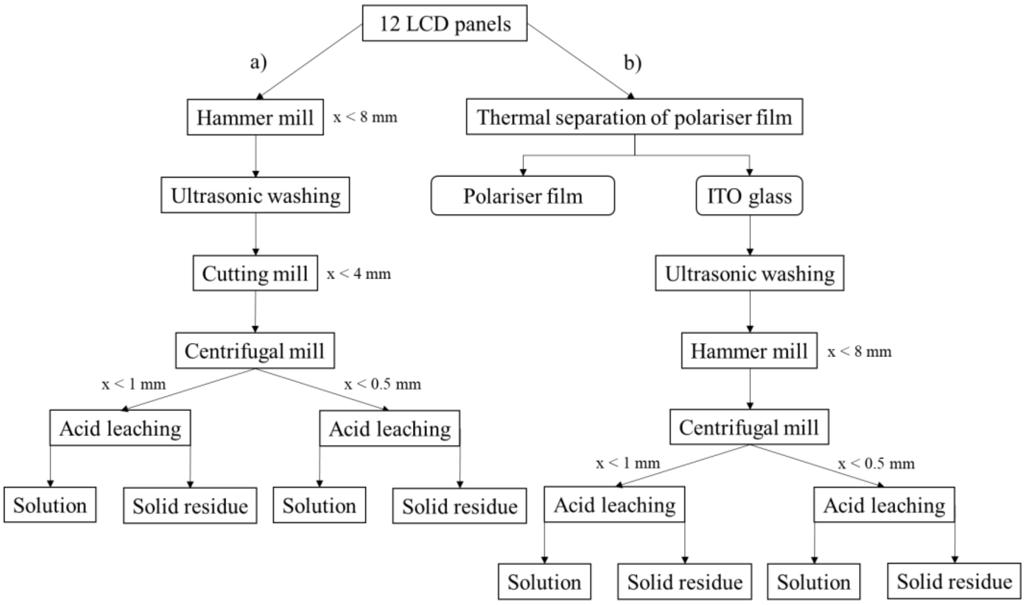

Figure 2
The processing flowsheet of LCD panels a) with and b) without polarising film

The particle size distributions were determined by sieve analysis (after hammer and cutting mill) and using a CAMSIZER X2 particle size and shape analyser (after centrifugal mill). The microscopic image was taken using a Zeiss Axioskop 2 MAT optical microscope.

The chemical analysis of the base materials and the acidic leachate solutions was carried out at the Institute of Chemistry, University of Miskolc, using ICP-OES analysis.

3. RESULTS AND DISCUSSION

3.1. Film separation

Both the CF and TFT layers of the various LCD panels *(Figure 3)* were used for the experiments. After the thermal treatment, most of the film could be removed from the glass and the pieces from which the film couldn't be separated were discarded. The mass balance of the panels after the foil removal with thermal shock treatment is summarised in *Table 1*.

Table 1
The mass balance after foil removal

Feed, wt.%	Glass, wt.%		Polarising film, wt.%		Discard, wt.%
	CF	TFT	CF	TFT	
100	43.36	42.03	6.21	5.68	2.62

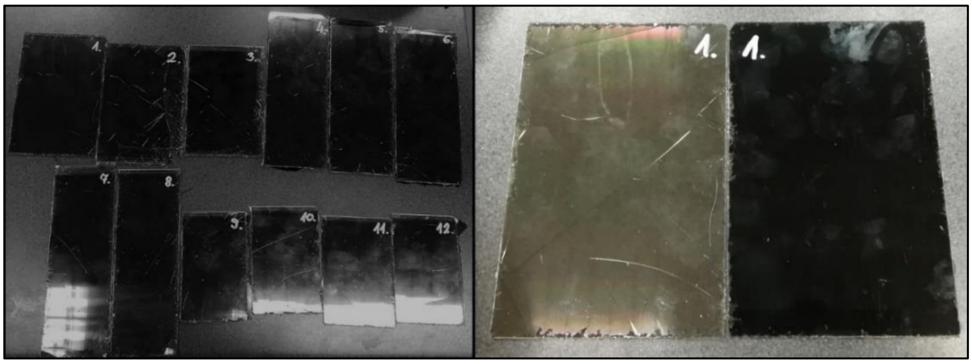

Figure 3
The 12 LCD displays (left) andthe TFT and CF layers of the panels (right)

3.2. Comminution

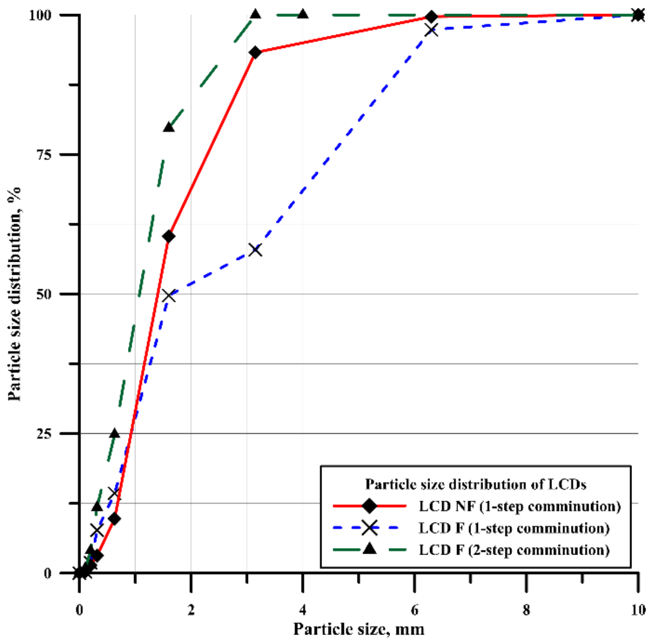

Figure 4
The particle size distributions of the LCDs after hammer and cutting milling

After film removal, the panels were crushed in a hammer mill with 8 mm sieve. Due to the different mechanical properties of the glass and the polarising film – the glass is brittle while the polarising film is flexible –, the particle size distribution of the hammer milled products were rather dissimilar. In case of the LCD F, over 40% of the particles were over 3.15 mm sized. On the other hand, the hammer milling of the LCD NF resulted in much finer particle size product, with only 6.7% of the particles over 3.15 mm and more than 80% between 0.63–3.15 mm.

To prepare an appropriate feed for the subsequent centrifugal milling, the LCD F panels were subjected to two-step comminution: the 3.15–6.3 mm LCD F particles were further ground using Retsch cutting mill under 4 mm. The acquired particle size distributions are illustrated in *Figure 4*.

Furthermore, some residual polarising film could be observed on certain >6.3 mm LCD NF particles; this was again confirmed by the optical microscopic analysis *(Figure 5)*. Thus, the preliminary crushing of the LCD NF panels is not only applicable for the size reduction, but also for the separation of larger particles with some polarising film still adhered to the glass.

Figure 5
The >6.3 mm LCD NF particles (top), and the remaining foil (white) on the CF layer (bottom)

The size reduction of the samples under 1 and 0.5 mm was carried out using Retsch ZM 200 centrifugal mill: the <1 mm samples went through a 1-step comminution, while the <0.5 mm samples were first ground to under 1 mm and then under the desired particle size. The products of the milling processes can be observed in *Figure 6*.

Figure 6
The products of the centrifugal milling

As it can be seen in *Figure 6*, the colour of the finer particle sized products was considerably darker than the <1 mm sized samples. After centrifugal milling, the particle size distribution of the samples was examined as well *(Figure 7)*.

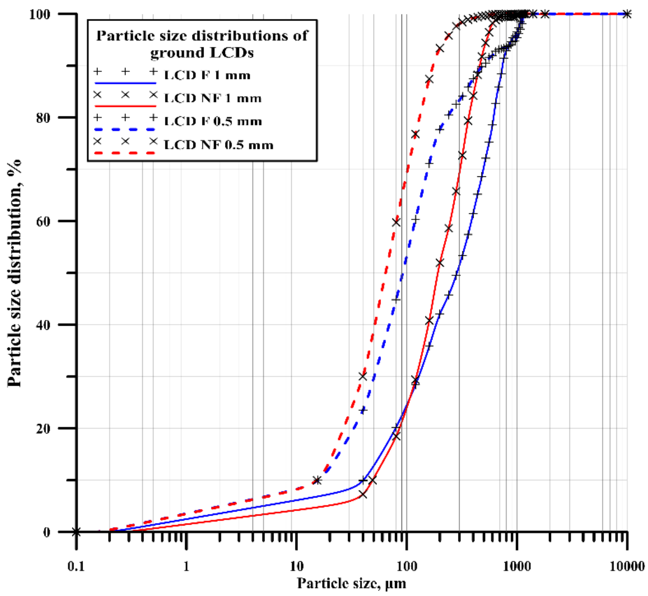

Figure 7
The particle size distributions of the LCDs ground in centrifugal mill

The examination of the particle size distributions revealed that the x_{10} values of the same-sized samples were almost identical, x_{10} = 40.25 µm and x_{10} = 48.86 µm for the <1 mm F and NF LCDs, and x_{10} = 15.66 µm and x_{10} = 15.30 µm for the <0.5 mm F and NF LCDs. However, the different trends of the particle size distributions get prominent as the particle size is increased. The median particle sizes of the LCDs without the polariser film are lower in both the <1 mm and <0.5 mm particle size ranges (x_{50} = 192.09 µm and x_{50} = 64.93µm, respectively), then the LCDs with the film on (x_{50} = 284.76 µm and x_{50} = 91.22 µm, respectively). Moreover, the two LCD NF curves indicate that the yield of coarse particles is similar in both samples. Thus, it can be stated that due to the film is still attached to the glass, the LCD NF samples have finer particle size distributions than the LCD F samples.

3.3. Chemical processing

After acid leaching with 1 M HCl solution, the acquired leachate solutions of the <0.5 mm samples showed a strong green discolouration in case of both the LCD F and LCD NF samples *(Figure 8)*. The material composition of the leachate solutions is summarised in *Table 2*.

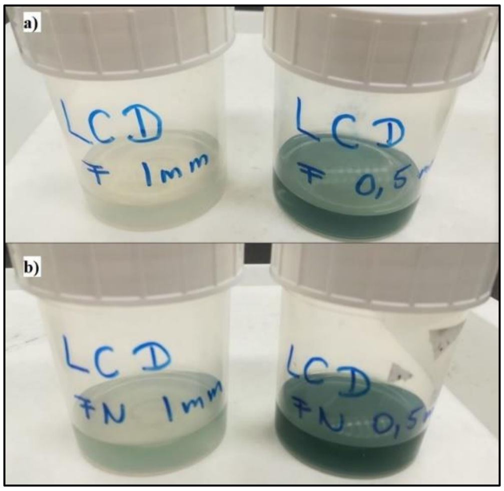

Figure 8
The acquired acidic leachate solutions of the a) LCD F and b) LCD NF samples

Table 2
The material composition of the acidic leachate solutions

Examined material	**As**	**Cu**	**Fe**	**In**	**Mn**	**Sn**	**Sr**
	mg/L						
LCD F <1 mm	0.124	8.15	731	40.9	22.2	11.8	233
LCD F <0.5 mm	0.213	2.08	4310	33.7	95.1	11.1	369
LCD NF <1 mm	0.220	2.34	1553	139.0	35.9	19.2	285
LCD NF <0.5 mm	0.602	2.32	6866	122.0	156.0	15.1	465

Based on our earlier results (BOKÁNYI et al. 2014_2) and chemical analyses, it was clearly revealed, that the mass transport is definitely hindered by the foil in both examined particle size ranges. The enrichment of the presented metals was in every case higher, when the foil was removed before the leaching tests, with one exception in case of the copper, when the recovery was almost 4 times higher from the sample LCD F <1mm compared to the other experiments. For example, in case of Mn, In, Fe and As, the leachability was much higher without the foil, about twice as many. In case of Sr, and Sn the effect of the foil removal showed not so remarkable changes in enrichment values. The effect of particle size reduction for the efficiency of the leaching was not the same comparing the recovery of the presented metals. In case of Sr, Mn, Fe and As it is proved, that the finer particle size enhanced the metal dissolution. Nevertheless, regarding the results related to Sn and In it is clear, that the further particle size reduction was maleficent. The explanation for this phenomena can be found, considering that the In and Sn is presented in the ITO layer on the surface of the glass substrate. The best results were obtained for In, in LCD NF< 1mm case, when the indium dissolution was complete.

4. CONCLUSIONS

The examination of the effect of mechanical preparation of LCD panels on metal recovery with acidic leaching is presented in the article. The effect of both removing and keeping the polarising film on the metal recovery was also taken into consideration. Using thermal treatment, most of the polarising film can be removed from the panels. In case of LCD NF samples, the mechanical treatment of the panels was less complicated than the comminution of LCD F samples. The comminution of LCD F samples required two-step crushing to produce the appropriate particle size for the centrifugal milling. Based on the particle size distribution of the product of the centrifugal mill, it can be concluded that the LCD F samples have more coarse particles than the LCD NF samples.

Thus, the polarising film not only affects the comminution procedure to be used, but the parameters of the ground products as well.

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