Value Recovery from Waste Liquid Crystal Display Glass Cullet through Leaching: Understanding the Correlation between Indium Leaching Behavior and Cullet Piece Size

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Abstract: For hydrometallurgical recovery of indium from glass cullet after dismantling a waste liquid crystal display (LCD), leaching is the rudimentary stage. Though size reduction of the cullet pieces adds convenience for recycling, from an efficiency and cost-effectiveness perspective regarding leaching process development, determining the proper cullet piece size is essential. Hence, in this study, leaching efficiency of indium as a function of cullet piece size was investigated, wherein the proper mechanical classification of crushed glass cullet could be addressed. The optimum conditions of 5 M mineral acid as the lixiviant, pulp density of 500 g/L, temperature of 75 °C, agitation speed of 500 rpm, 2 h process time were kept constant for the leaching studies. It was concluded that the size of the waste LCD cullet inversely affected the leaching efficiency of indium. For efficient leaching, a smaller cullet size is recommended; hence, waste LCD should be crushed to pieces 1 mm or smaller. Indium leaching behavior comparison using HCl, HNO3, H2SO4 revealed that all three mineral acids had similar leaching efficiencies. The reported process provides the missing link between physical dismantling and chemical processing for indium recovery via techno-economical-sustainable process development.

Keywords: indium leaching; critical metals; cullet classification; crushing and sieving; e-waste recycling

1. Introduction

Owing to better functionality, excellent optoelectronic properties, proficient design, in the past decade, flat panel displays (FPDs) have become the market leading design for display screens/monitors in both television and IT applications. FPD sales have been continuously increasing; in 2007, the number of liquid crystal display televisions (LCD TVs) sold surpassed that of conventional cathode ray tube (CRT) displays. Currently, first-generation CRT TVs are no longer produced, with second-generation FPDs mainly in use. Globally, about 200 million units of LCD TVs were produced in 2010 [1,2]. Considering an average 10-year lifespan of LCDs, in 2020, the number of waste LCD TV units should reach 200 million. The global market share of Korean-brand FPDs is at appreciable level, but the recycling rate is limited and associated technology for recycling are quite unorganized and primitive. Hence, the global e-waste share from FPDs is huge, thus these devices need to be eco-efficiently and cost-effectively recycled. To satisfy the current national/international urban mining interest, a mass production capable semi-automated dismantling process has been developed. Indium needs to be recovered from dismantled waste LCD glass, to fulfill the nation’s
environmental responsibility and to circularize the indium cycle for self-reliance. Valuable metals from these wastes should be recovered, not only to be in compliance with stringent policies such as the Waste Electrical and Electronic Equipment (WEEE), Restriction of Hazardous Substances (RoHS) in Electrical and Electronic Equipment (EEE), and Extended Producer Responsibility (EPR) Directives, but also from the perspectives of urban mining, circular economics, supply chain stability of critical and non-replaceable metals.

Excellent optoelectronic properties and superior transparent conducting properties of indium-tin-oxide (ITO) make it a superior transparent conduction oxide, which holds 84–90% of the market size of FPDs and thin-film coatings [3–6]. ITO is mainly applied in a thin layer for use as a transparent conducting oxide in LCD manufacturing [7,8]. Typically, ITO consists of 90% In$_2$O$_3$ and 10% SnO$_2$ by weight. The United Nations Environment Programme (UNEP) [9], US Department of Energy (DOE) [10], European Commission [11], US National Academy of Sciences (NAS) [12], and American Physical Society and Materials Research Society [13] consider indium a very critical metal. In addition, UNEP specifies that barely 1% of indium-bearing end-of-life (EOL) waste is being recycled [14,15]. Primary resources of indium only contain approximately 100 ppm [16], thus waste LCDs that contain 100–400 ppm of indium [4] could be better resources for indium recovery. Recycling of LCDs can address issues such as environmental impact from waste incineration and/or disposal in landfill sites, health hazard from ITO pollution, circular economy, supply chain instability, import dependency, urban mining, and supply stability of raw materials for nations that depend on imports [7,8,17,18]. It can also complement the WEEE (effective 14 February 2014) [19], RoHS [20], and EPR [21] Directives.

Various researchers have reported indium recovery from ITO, mainly via the hydrometallurgical process [22–25], from several waste resources, for example ITO scrap [24–26] and LCD etching waste [27,28]. To hydrometallurgically recover indium from any source, leaching is the first step, as has been reported by several researchers [4,17,29,30]. Zhang et al. [2] recently reviewed the research on the recycling of indium from waste LCDs, which clearly indicates hydrometallurgy is the preferred process followed by dismantling and pretreatment. Ueberschaar et al. [31] reviewed the recycling strategies for LCD panels from the WEEE and, in their report, indicated that mineral acid leaching is an important strategy for recycling LCD waste. Though Zhang et al. [32] reported leaching of indium from uncrushed waste LCD by HCl through ultrasonic waves could be an important strategy, our observation is quite clear that, without crushing, the leaching efficiency decreases significantly.

The purpose of the current investigation is to determine the missing link between the LCD dismantling process developed for metal beneficiation and the recovery of indium from LCD glass via the hydrometallurgy route [7,8,33]. Elsewhere our reported process indicates that dismantling of waste to LCD glass, leaching of indium followed by indium recovery from LCD waste has already been developed [7,8,33]. However, an important drawback of these studies is that whether size has a predominant effect on leaching efficiency has not been reported, which could be a determining factor for industrial valorization of waste LCD glass [33]. Hence, in the current investigation, the leaching efficiency of indium as a function of cullet piece size was investigated, wherein the proper mechanical classification of the crushed glass cullet could be addressed. From our earlier reported investigation, the optimum condition which were developed for indium leaching from LCD waste has been used for understanding of the purpose, that is, impact of cullet piece size [33]. The reported process is important and novel, as it provides the missing link between physical dismantling and chemical processing for techno-economical-sustainable indium recovery. The process can advance the WEEE, RoHS, and EPR Directives further by a step and lead to eco-efficient and sustainable recycling of LCD waste.

2. Materials and Methods

LCD waste glass was collected after dismantling followed by beneficiation of waste LCD panels. The size of the LCD glass was reduced through crushing. The LCD glass panels were cut into pieces with an average size of 4 cm × 4 cm followed by crushing using a 3.5 L grinder equipped with two stainless steel blades. About 300 g of the 4 × 4 cm$^2$ glass pieces and 150 mL of water were mixed
together in a grinder chamber and ground for 3 min. The ground glass cullet was separated using filter paper and dried overnight (24 h). The dried glass cullet was classified into five different sizes via sieving. Table 1 reflects the sieves that were used in this experiment and their aperture sizes. The flowchart in Figure 1 shows the sample sizes and classification procedure using the various sieve sizes presented in Table 1. As presented in Figure 1, five different classifications were produced through sieving, and the samples generated by such were used for subsequent leaching.

Table 1. Different sieve sizes used for classification of the sample.

<table>
<thead>
<tr>
<th>ASTM E11 Sieve</th>
<th>Aperture (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 7</td>
<td>2.8</td>
</tr>
<tr>
<td>No. 12</td>
<td>1.7</td>
</tr>
<tr>
<td>No. 18</td>
<td>1.0</td>
</tr>
<tr>
<td>No. 30</td>
<td>0.6</td>
</tr>
<tr>
<td>No. 50</td>
<td>0.3</td>
</tr>
</tbody>
</table>

![Flowchart](image)

**Figure 1.** Flowchart for classification of the crushed glass cullet from the waste liquid crystal display panels.

The lixiviants HCl, HNO₃, and H₂SO₄ were of analytical grade and supplied by the Daejung Chemical & Metals Co., Ltd., Siheung, Korea. Using the leaching reactor shown in Figure 2, the glass cullet was leached. The main reactor vessel was a 1000 mL round-bottom, three-neck, round-top beaker equipped with an overhead agitator driven by a variable-speed motor. A heating mantle was used for heating, with a thermostat attached to control the reactor temperature. A thermocouple equipped to digitally measure the temperature during continuous operation of the reactor was used to monitor the temperature during leaching. A reflux condenser was used to prevent vapor loss, heating was provided by an electrical mantle, and temperature was controlled via a temperature monitoring apparatus. The required volume of lixiviant was poured into the reactor and allowed to reach thermal equilibrium, and then 50 g of waste LCD glass cullet was added into the reactor. An agitation speed of 500 rpm was used for 2 h during the experiments. Finally, the leach liquor was filtered, and the metal content was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES; OPTIMA 4300DV, PerkinElmer, Richmond, CA, USA) after suitable dilution using 5% v/v HCl. The maximum deviations permitted during the ICP-AES analysis were about ±5%.
which can be (re)crushed to requisite size and leached.

(b) \[1.7 \geq S > 1.0 \text{ mm}\]; (c) \[1.0 \geq S > 0.6 \text{ mm}\]; (d) \[0.6 \geq S > 0.3 \text{ mm}\] and (e) \[S \leq 0.3 \text{ mm}\], where \(S\) stands for the size of the glass cullet pieces. Samples from each size classification of the waste LCD glass cullet were leached using mineral acids (HCl, HNO₃, H₂SO₄). Approximately 2750 g of crushed glass pieces was collected through 9 times of crushing. Table 2 presents the glass weight and proportion for the size of the glass cullet pieces. Samples from each size classification of the waste LCD glass were leached using mineral acids (HCl, HNO₃, H₂SO₄). Approximately 2750 g of crushed glass pieces was collected through 9 times of crushing. Table 2 presents the glass weight and proportion of each size category, which were obtained via classification by sieving as presented in Table 1 and Figure 1. Pieces of the glass cullet that were larger than 2.8 mm were sieved out during the first sieving, which can be (re)crushed to requisite size and leached.

### Table 2. Weight analysis of the different sizes of crushed glass pieces.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight (g)</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residue</td>
<td>921</td>
<td>33.6</td>
</tr>
<tr>
<td>Sample 2.8 ≥ S &gt; 1.7 mm</td>
<td>164</td>
<td>6.0</td>
</tr>
<tr>
<td>Sample 1.7 ≥ S &gt; 1.0 mm</td>
<td>301</td>
<td>11.0</td>
</tr>
<tr>
<td>Sample 1.0 ≥ S &gt; 0.6 mm</td>
<td>512</td>
<td>18.7</td>
</tr>
<tr>
<td>Sample 0.6 ≥ S &gt; 0.3 mm</td>
<td>390</td>
<td>14.3</td>
</tr>
<tr>
<td>Sample S ≤ 0.3 mm</td>
<td>450</td>
<td>16.4</td>
</tr>
</tbody>
</table>

1 Glass cullet pieces larger than 2.8 mm were sieved out during the first sieving.

### 3. Results and Discussion

#### 3.1. Classification of the Glass Cullet

After the dismantling and crushing, the crushed glass cullet was classified using various sizes of sieves. As shown in Figure 1, the sizes of the glass cullet pieces were classified as (a) \(2.8 \geq S > 1.7 \text{ mm}\); (b) \(1.7 \geq S > 1.0 \text{ mm}\); (c) \(1.0 \geq S > 0.6 \text{ mm}\); (d) \(0.6 \geq S > 0.3 \text{ mm}\) and (e) \(S \leq 0.3 \text{ mm}\), where \(S\) stands for the size of the glass cullet pieces. Samples from each size classification of the waste LCD glass cullet were leached using mineral acids (HCl, HNO₃, H₂SO₄). Approximately 2750 g of crushed glass pieces was collected through 9 times of crushing. Table 2 presents the glass weight and proportion of each size category, which were obtained via classification by sieving as presented in Table 1 and Figure 1. Pieces of the glass cullet that were larger than 2.8 mm were sieved out during the first sieving, which can be (re)crushed to requisite size and leached.

#### 3.2. Leaching of the Waste LCD Glass Cullet

Mass production that employs a semi-automated LCD dismantling process and an efficient ITO leaching process through optimization of various process parameters was developed by the authors’ research group [5,7,8,33]. The leaching behavior of indium from waste LCD glass has been investigated, optimized, and reported on in our earlier publication [33]. As reported, the optimum conditions for quantitative leaching of waste LCD glass were 5 M HCl, a pulp density of 500 g/L, a temperature of 75 °C, 10% \(v/v\) H₂O₂, an agitation speed of 500 rpm, and a process time of 120 min. However, an important drawback of that study is that whether size has a predominant effect on
leaching efficiency was not reported, which could be a factor for industrial valorization of waste LCD glass. A link is missing between the above-developed processes, that is, whether crushed or non-crushed waste LCD panels should be used for indium leaching. Hence, the leaching efficiency of indium as a function of cullet size needs to be understood for proper mechanical classification of crushed glass.

In the current investigation, how the size of waste LCD glass cullet can affect the leaching efficiency was investigated using three different lixiviants, that is, HCl, HNO₃, and H₂SO₄, under the optimum conditions reported elsewhere [33]. Figure 3 indicates the leaching behavior of indium and tin as a function of cullet size, as classified earlier using 5 M HCl as the lixiviant. Other leaching conditions obtained from the previously determined optimum conditions were a pulp density of 500 g/L, a temperature of 75 °C, an agitation speed of 500 rpm, and a process time of 2 h. The figure clearly indicates that when the size of the waste LCD cullet pieces are in the range 2.8 ≥ S > 1.7 mm, the smallest amounts, i.e., 18.92 ppm of indium and 8.95 ppm of tin, were leached even after 2 h of leaching under the optimum leaching conditions. The amount of indium and tin leached as a function of size were 57.79 and 5.73 ppm, respectively, for the size range of 1.7 ≥ S > 0.6 mm; and 81.94 and 11.99 ppm, respectively, for the size range of 0.6 ≥ S > 0.3 mm. When the size was S ≤ 0.3 mm, the highest amount, that is, 154.05 ppm of indium and 50.57 ppm of tin, leached under the optimum conditions. The amount of indium and tin leached as a function of size as classified earlier using 5 M HCl as the lixiviant (LCD: liquid crystal display).

Figure 4 indicates the leaching behavior of indium and tin as a function of the size of the cullet pieces, as classified by sieving using 5 M HCl as the lixiviant. Similar to above, the other optimum leaching conditions used, as determined from our previous research were a pulp density of 500 g/L, a temperature of 75 °C, an agitation speed of 500 rpm, and a process time of 2 h. The figure indicates that when the size of the waste LCD cullet pieces was in the class of 2.8 ≥ S > 1.7 mm, the least amounts, that is, 53.84 ppm of indium and 5.73 ppm of tin, leached under the optimum conditions. The amount of indium and tin leached as a function of size were 57.79 and 5.73 ppm, respectively, for the size range of 1.7 ≥ S > 1.0 mm; 61.89 and 7.08 ppm, respectively, for the size range 1.0 ≥ S > 0.6 mm; and 89.57 and 9.04 ppm, respectively, for the size range of 0.6 ≥ S > 0.3 mm. When the size was S ≤ 0.3 mm, the highest amounts, that is, 191.97 ppm of indium and 42.29 ppm of tin.
of tin, leached under the optimum conditions. Figure 4 indicates that, similar to the HCl lixiviant, the lixiviant HNO$_3$ leaching efficiencies increased steadily as the size of cullet pieces decreased.

![Figure 4](image4.png)

**Figure 4.** Leaching behavior of indium and tin as a function of the size of the cullet pieces, as classified by sieving using 5 M HNO$_3$ as the lixiviant.

Similar to Figures 3 and 4, Figure 5 indicates the leaching behavior of indium and tin as a function of size as classified earlier using 5 M H$_2$SO$_4$ as the lixiviant, a pulp density of 500 g/L, a temperature of 75 °C, an agitation speed of 500 rpm, and a process time of 2 h. The figure obviously shows that when the size of the waste LCD cullet pieces are in the range 2.8 ≥ S > 1.7 mm, the least amounts, that is, 47.92 and 6.49 ppm, respectively, for the size range of 1.7 ≥ S > 1.0 mm; 51.12 and 8.87 ppm, respectively, for the size range of 1.0 ≥ S > 0.6 mm; and 65.00 and 8.11 ppm, respectively, for the size range of 0.6 ≥ S > 0.3 mm. When the size was S ≤ 0.3 mm, the highest amount, that is, 190.67 ppm of indium and 44.51 ppm of tin, leached under the optimum conditions. Figure 5 indicates that similar to the HCl and HNO$_3$ lixiviants, the lixiviant H$_2$SO$_4$ leaching efficiencies increased steadily as the size of the cullet pieces decreased.

![Figure 5](image5.png)

**Figure 5.** Leaching behavior of indium and tin as a function of the size of the cullet pieces, as classified by sieving using 5 M H$_2$SO$_4$ as the lixiviant.
Figure 6 compares the leaching behavior of indium and tin as a function of the size of the LCD glass cullet pieces and various mineral acids, that is, HCl, H$_2$SO$_4$, and HNO$_3$. Figure 6a reflects the average sizes of the glass cullet pieces when different sizes of ASTM E11 sieves were used. Figure 6b shows that cullet piece size and indium leaching were inversely related. As the size of the glass cullet pieces increased, indium leaching increased. The same is true for all the mineral acids. Though indium leaching via H$_2$SO$_4$ and HNO$_3$ were higher than that with HCl when the average cullet piece size was 2.6 mm, the difference is marginal and could be due to the higher proton activity of H$_2$SO$_4$ or the oxidizing behavior of HNO$_3$. Similar to indium, Figure 6c shows that cullet piece size and tin leaching also were inversely correlated. As the size of the glass cullet pieces increased, tin leaching decreased. The same is true for all the mineral acids. However, considering subsequent indium purification and recovery, the HCl process is recommended as other acids are either adversely affect environment or the process itself. Figure 7 is a picture of the different sizes of the glass cullet following ITO leaching. From Figure 7a, it can be clearly understood that when the cullet size pieces are bigger, ITO remains on the LCD glass cullet and thus is not proficient for leaching of indium and tin. Figure 7b–e clearly indicates that the smaller the size of the cullet pieces of the LCD is, the clearer the leach residue, which means better leaching. Finally, Figure 7e shows that the LCD glass is quite clean and most of the ITO has been leached out. Per the glass cullet classification, as shown in Figure 1, the larger LCD cullet pieces had relatively smaller surface areas exposed to acid for leaching; hence, the ITO leaching efficiency was adversely affected. As the size of the cullet pieces decreases, the surface area exposed to acid increases, leading to proficient leaching, which accelerates the leaching efficiency of ITO. Hence, for efficient leaching, smaller pieces of cullet are recommended.

**Figure 6.** (a) Average sizes of the glass cullet pieces per different sizes of ASTM E11 sieves; (b) Relationship between indium leaching and cullet piece size; and (c) Relationship between tin leaching and cullet piece size.
4. Conclusions

The size of waste LCD cullet pieces has a significant effect on the leaching efficiency of indium and tin, which inversely affects the leaching behavior of ITO. As all the mineral acids tested had similar leaching efficiencies, 5 M HCl should be used for industrial application, considering subsequent indium purification and recovery. Lixiviant HCl recommended as other acids are either adversely affect environment or the process itself. For efficient leaching of indium from waste LCDs, the waste LCDs should be crushed to pieces 1 mm or smaller. Moreover, the optimum conditions for leaching should be as follows: lixiviant of 5 M HCl, a pulp density of 500 g/L, a temperature of 75 °C, an agitation speed of 500 rpm, and a process time of 2 h. The proposed leaching process can be a sustainable and eco-efficient process for the leaching of indium from LCD waste glass cullet. As larger pieces of LCD cullet have a relatively smaller surface area exposed to acid, the leaching efficiency is adversely affected. Hence, for efficient leaching, smaller pieces of cullet are recommended, as the smaller pieces have greater surface area exposure to acid, which leads to proficient leaching.

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Conflicts of Interest: The authors declare no conflict of interest.

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