Recovery of indium from scrap TFT-LCDs by solvent extraction

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Abstract

Recovery of indium from scrap LCDs, which contain indium in the form of indium tin oxide (ITO) films, is becoming economically and environmentally justified. Indium is a precious metal and the present study was aimed to recover indium from scrap TFT-LCDs by solvent extraction which was based upon H2SO4 acid leaching–D2EHPA extraction–HCl back extraction. The results showed that indium could be better leached in H2SO4 (1:1, v/v) acid solution in the optimal liquid/solid ratio of 1:1 while other metals’ leaching concentrations were relatively low. Indium could be selectively extracted from its H2SO4 solutions by 30% D2EHPA with O/A ratio of 1:5 within 5 min, and be completely stripped by 4M HCl from D2EHPA with A/O ratio of 1:5, the final extraction efficiency achieved more than 97%.

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Keywords: scrap TFT-LCDs; indium; solvent extraction; D2EHPA; back-extraction; strip

1. Introduction

In recent years, with the market share’s rapid growth, liquid crystal displays (LCDs) have held the mainstream of display products. Under the popularity of the LCDs, large number of scrap LCDs gradually becomes an important part of electronic waste. The panel is one of the core components of LCDs, which contains many kinds of rare, precious metals and heavy metals, also includes rare metal indium. Indium is a rare and valuable metal, which is mainly used as indium tin oxide (ITO) films in LCDs [1]. There is 0.37 mg indium per gram circuit board, and the price of it is around the 3600RMB/kg currently, so recovery of indium from LCDs is rather attractive.

Today the amount of waste LCD screens is accumulating fast owing to the popularity of their usage, thus the development of recovery methods for indium from these wastes is growing as well. Since 2007 more indium has been produced from secondary than from primary raw materials, the most important

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secondary raw material has been the waste from the sputtering process in the deposition of ITO onto the LCDs [1-2]. From ITO indium can be recovered by dissolving it in HCl and then precipitating it with NaOH. A few methods have been patented for recovering indium from secondary ITO waste (used LCDs).

Solvent extraction is a commonly used method for the purification of indium in process metallurgy particularly in zinc refineries, where indium is usually recovered from sulfate solutions [3]. Several extractant types have been used in the extraction of indium including carboxylic acids, phosphoric acid derivatives, chelating compounds like hydroxyoximes and azoles, and solvating extractants such as tributyl phosphate (TBP), trioctylphosphine oxide (TOPO) and methylisobutyl ketone (MIBK). Bis(2-ethylhexyl) phosphate, usually known as di-2-ethylhexyl phosphoric acid (D2EHPA), is by far the most popular extractant and it is almost always used in practical applications since it has a high loading capacity for indium and good selectivity for indium over many other metal ions such as, for example, Zn(II), Fe(II), Cd(II), As(III) and Cu(II) [4-6]. Sato and Sato [7] researched about the extraction of indium with D2EHPA and another organophosphorus extractant, 2-ethylhexyl 2-ethylhexyl-phosphonic acid (EHEHPA), separately from H2SO4, HNO3 and HCl solutions. They found that the order of the extraction of indium was HNO3 > H2SO4 > HCl while acid concentrations are below 2 M, but in concentrated acids, the order is reversed. Sami[8] et al. studied the recovery of indium when tin is present in solution both using D2EHPA and the mixture of D2EHPA and TBP by pure ITO nano-powder, found that indium and tin could be extracted by both of them, but D2EHPA has a higher loading capacity for indium, and with two countercurrent stages (A/O=1:8) of extraction and two countercurrent stages (A/O=2:1) of stripping, almost complete indium is recovered from the leaching solution and high In/Sn selectivity in stripping could be achieved.

Although there are several articles on the solvent extraction of indium using D2EHPA, few of them applied it to scrap LCDs but to ITO. The purpose of the present study was to explore the most appropriate experimental conditions for the acidic leaching of scrap LCDs and then to use solvent extraction with D2EHPA as extractants to extract indium from its acidic solutions and HCl as stripping agent to extract indium from the organic solutions, considering the effect of concomitant ions in leaching solutions.

2. Experimental

2.1. Materials

The sample was obtained from waste TFT-LCD panel after being frozen in liquid nitrogen, stripped polarizing film and initially broken to -1mm by Heavy-duty cutting mill SM2000. The elemental composition of the sample by XRF analysis was listed in Tables 1.

Bis(2-ethylhexyl) hydrogen phosphate (D2EHPA, assay 95%, Acros Organics); sulfuric, nitric and hydrochloric acids. All acids were of pro analysis purity and distilled water was used in experiment. Unless otherwise stated, D2EHPA was dissolved in kerosene (30% volume fraction of D2EHPA) before use.

Table 1. Percentage of main elements of waste TFT-LCD after normalization (%) by XRF

<table>
<thead>
<tr>
<th>elements</th>
<th>Si</th>
<th>Al</th>
<th>Ca</th>
<th>Sr</th>
<th>Ba</th>
<th>Fe</th>
<th>As</th>
<th>K</th>
<th>Zn</th>
<th>Ti</th>
<th>In</th>
<th>Cu</th>
<th>Sn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass(%)</td>
<td>69.78</td>
<td>14.37</td>
<td>9.58</td>
<td>3.43</td>
<td>0.85</td>
<td>0.34</td>
<td>0.90</td>
<td>0.34</td>
<td>0.18</td>
<td>0.13</td>
<td>0.06</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>
2.2. Analytical techniques

Metal analysis of leaching samples were carried out using ICP-AES. Indium and Iron analysis of extraction raffinate and strip liquor were carried out using AAS.

2.3. Elemental composition analysis of waste TFT-LCD under treatment with different acids

For the study of the elemental composition analysis of waste TFT-LCD under treatment with different acids, the digestion experiments were carried out in a glass reactor by leaching 1 g waste TFT-LCD with 20mL acid treatment solutions of concentrated hydrochloric acid, concentrated hydrochloric acid-hydrogen peroxide(4:1,v/v), concentrated nitric acid, aqua regia, sulfuric acid(1:1,v/v), hydrochloric acid-nitric acid-distilled water(1:0.1:1,v/v/v), heated by electronic hot plate at 160°C for 0.5h with a glass-surface vessel. Samples were filtrated by air pump, and filtrate were diluted in water to 100mL and conducted chemical analysis of elemental contents.

2.4. Leaching

The leaching experiments were carried out in glass reactors with different L/S ratio of 3:4 and 1:1by dissolving 10 g of waste TFT-LCD separately into 7.5mL and 10mL sulfuric acid(1:1,v/v), heated by electronic hot plate at 160°C for 1h covered with a glass-surface vessel. Samples were filtrated by air pump, and filtrate were diluted in water to 100mL and conducted chemical analysis of indium contents.

2.5. Solvent extraction

The extraction studies were carried out in either separatory funnels and the equilibrating time was 5 min at room temperature, considering two main factors, respectively volume fraction of extractant (20%, 25%, 30%, 40% D2EHPA )and ratio of organic phase and aqueous phase (O/A=1:3, 1:5, 1:6, 1:9, 1:12, 1:15).

2.6. Stripping

For the extraction with D2EHPA the selective stripping with HCl was also explored. In these experiments D2EHPA was first loaded with optimal A/O(result from above) from leaching solution above and then stripped with A/O=1:5 using HCl solutions of various concentrations(2M, 4M, 6M, 8M). The contact time for stripping was 5 min.

3. Results and discussion

3.1. Elemental composition analysis of waste TFT-LCD under treatment with different acid

Results of different digestion methods of waste TFT-LCD sample reflected the dissolution character of its main elements in different acid systems (Table 2 and 3).

In these acid systems, dissolution concentrations of zinc, titanium, copper, tin and chromium were relatively low, and the dissolution ratios changed significantly. Dissolution concentrations of aluminum and strontium in concentrated HCl systems were quitely higher than in single concentrated HNO₃ and H₂SO₄(1:1) systems. In the TFT-LCD panel, arsenic exists in the form of highly toxic material As₂O₃, in order to control its concentration in the effluent, there should choose the acid system in which arsenic has low dissolution concentration as far as possible while the target element has high dissolution concentration. The dissolution concentration of iron and indium changed slightly in different acid systems, so iron is the concomitant ion at indium’s leaching solution. Comprehensively considering the above reasons, this study chose H₂SO₄(1:1) as the acid system to leach indium, and took measures to eliminate the effects of iron.
Table 2 Dissolution concentration of main elements of waste TFT-LCD in different acid systems (mg/L)

<table>
<thead>
<tr>
<th>acid systems</th>
<th>elements</th>
<th>Al</th>
<th>Sr</th>
<th>Fe</th>
<th>As</th>
<th>Zn</th>
<th>Ti</th>
<th>In</th>
<th>Cu</th>
<th>Sn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td></td>
<td>52.69</td>
<td>21.89</td>
<td>5.66</td>
<td>0.27</td>
<td>0.61</td>
<td>0.08</td>
<td>2.83</td>
<td>0.22</td>
<td>0.88</td>
<td>0.88</td>
</tr>
<tr>
<td>HCl-H2O2</td>
<td></td>
<td>49.27</td>
<td>20.15</td>
<td>7.18</td>
<td>0.16</td>
<td>0.65</td>
<td>0.11</td>
<td>2.91</td>
<td>0.44</td>
<td>0.54</td>
<td>0.84</td>
</tr>
<tr>
<td>HNO3</td>
<td></td>
<td>8.15</td>
<td>3.02</td>
<td>7.69</td>
<td>1.48</td>
<td>0.41</td>
<td>0.04</td>
<td>3.03</td>
<td>0.48</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>aqua regia</td>
<td></td>
<td>51.39</td>
<td>21.68</td>
<td>6.07</td>
<td>5.47</td>
<td>0.54</td>
<td>0.1</td>
<td>3.06</td>
<td>0.3</td>
<td>0.57</td>
<td>0.15</td>
</tr>
<tr>
<td>H2SO4</td>
<td></td>
<td>3.14</td>
<td>1.01</td>
<td>6.12</td>
<td>0.37</td>
<td>0.1</td>
<td>0.06</td>
<td>2.8</td>
<td>0.19</td>
<td>0.13</td>
<td>0.89</td>
</tr>
<tr>
<td>HCl-HNO3-H2O</td>
<td></td>
<td>40.99</td>
<td>18.49</td>
<td>5.04</td>
<td>3.76</td>
<td>0.43</td>
<td>0.08</td>
<td>2.93</td>
<td>0.34</td>
<td>0.63</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 3 Dissolution ratio of main elements of waste TFT-LCD in different acid systems (%)

<table>
<thead>
<tr>
<th>acid systems</th>
<th>elements</th>
<th>Al</th>
<th>Sr</th>
<th>Fe</th>
<th>As</th>
<th>Zn</th>
<th>Ti</th>
<th>In</th>
<th>Cu</th>
<th>Sn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrated HCl</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>HCl-H2O2</td>
<td></td>
<td>102.5</td>
<td>101</td>
<td>93.3</td>
<td>4.94</td>
<td>113</td>
<td>80</td>
<td>92.5</td>
<td>73.3</td>
<td>154.39</td>
<td>586.67</td>
</tr>
<tr>
<td>Concentrated HNO3</td>
<td></td>
<td>95.87</td>
<td>92.94</td>
<td>118</td>
<td>2.93</td>
<td>120</td>
<td>110</td>
<td>95.1</td>
<td>147</td>
<td>94.74</td>
<td>560</td>
</tr>
<tr>
<td>aqua regia</td>
<td></td>
<td>15.86</td>
<td>13.93</td>
<td>127</td>
<td>27.1</td>
<td>75.9</td>
<td>40</td>
<td>99</td>
<td>160</td>
<td>19.3</td>
<td>146.67</td>
</tr>
<tr>
<td>H2SO4(1:1)</td>
<td></td>
<td>6.11</td>
<td>4.66</td>
<td>101</td>
<td>6.76</td>
<td>18.5</td>
<td>60</td>
<td>91.5</td>
<td>63.3</td>
<td>22.81</td>
<td>593.33</td>
</tr>
<tr>
<td>HCl-HNO3-H2O</td>
<td></td>
<td>79.76</td>
<td>85.29</td>
<td>83</td>
<td>68.7</td>
<td>79.6</td>
<td>80</td>
<td>95.8</td>
<td>113</td>
<td>110.53</td>
<td>120</td>
</tr>
</tbody>
</table>

3.2. Leaching

The results revealed that the change of the liquid/solid ratio had no obvious influence on the leaching of indium (Table 4). Indium could be leached completely in both two L/S ratios, however, it would be not conducive to mix solid sample with acid fully and difficult to filtrate leaching solutions when increase the amount of solid sample in L/S ratio of 3:4. For this reason, the liquid/solid ratio of 1:1 was chosen.

Table 4 Concentration of In in H2SO4 solutions with different L/S ratio (mg/L)

<table>
<thead>
<tr>
<th>Element</th>
<th>L/S ratio</th>
<th>1:1</th>
<th>3:4</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td></td>
<td>30.24</td>
<td>30.20</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>58.86</td>
<td>62.88</td>
</tr>
</tbody>
</table>

3.3. Solvent extraction

As iron is the concomitant ion in leaching solutions, the effect of it should be considered while extracting indium by D2EHPA. Laishou Long et al. [9] studied the effect of iron on the extraction of indium from annealed zinc sediment, results suggested equilibrating time of indium was about 5 min
while that of iron was much longer, so 5 min was chose as equilibrating time in the extraction to minish the effect of iron.

Fig.1(a) showed the extraction of indium in various volume fractions of D2EHPA used. All extraction tests were carried out for 5 min. The results show that the extraction efficiency of indium increased with the increase of D2EHPA volume fraction. The extraction efficiency achieved more than 95% when mass fraction of D2EHPA was 20% and quantitative extraction could be taken. Considering the viscosity of the organic phase, character of impurities and experiment costs, 30% D2EHPA-70% kerosene was chose for extracting indium from sulfuric acid leaching solution of waste TFT-LCD.

Fig.1 (a) Effect of volume fraction of D2EHPA on the extraction of indium from leaching solution (pH =0.3), O/A=1:5, co,In =42.32mg/L; (b) Effect of O/A on the extraction of indium from leaching solution (pH =0.3) with 30% D2EHPA, co,In =44.83mg/L.

Fig.1(b) showed the effect of various O/A ratios used on extraction of indium. The results suggest that the extraction efficiency of indium decreased with the decrease of O/A ratio. When the O/A ratio was in the range of 1:3~1:6, the extraction efficiency of indium was relatively high, especially when O/A ratio was 1:3, it achieved more than 99%. This is because two phases could be mixed fully and it would be not easy to achieve the saturation concentration of indium in D2EHPA when the fraction of organic is high. When O/A ratio was less than 1:12, the extraction efficiency of indium was below 90%, and organic phase occurred emulsification. Large O/A ratio would cause wastage of extractant and introduce more concomitant ions while getting high extraction efficiency of indium, cost increased and concentration of indium in organic phase dropped which increased the difficulty of separation of indium and foreign metal ions as well. Therefore, O/A of 1:5 was chosen as the optimal phase ratio here.

3.4. Stripping

The stripping experiment of indium from D2EHPA with various concentration of HCl was also constructed. As shown in Fig.2, more than 97% stripping efficiency for indium was achieved with HCl concentrations of 2 M and above. However, due to the high concentration of stripping agent, it would cause lots of impurities’ stripping and stripping agent’s waste, so the most appropriate concentration of stripping agent was selected in 4mol / L.
4. Conclusions

Recycling scrap LCDs was an important part of the indium market. However, little work has been done to dispose of used LCDs. The difficult problem was how to effectively strip indium from other metals and most of the previous studies were putting their focus on pure ITO or plant residues. Based on this situation, a novel hydrometallurgical process of treating used scrap TFT-LCDs to recover indium has been developed based upon H2SO4 acid leaching – D2EHPA extraction – HCl back extraction.

(1) Indium could be better leached in H2SO4 (1:1, v/v) acid solution in the optimal liquid/solid ratio of 1:1 while other metals’ leaching concentrations were relatively low.

(2) Indium could be selectively extracted from its H2SO4 solutions by 30% D2EHPA with O/A ratio of 1:5 within 5 min, and be completely stripped by 4M HCl from D2EHPA with A/O ratio of 1:5, the final extraction efficiency achieved 97%.

These results show that solvent extraction is an effective method of concentrating indium and separating it from other metals of scrap TFT-LCDs which is applicable for recovering indium from scrap LCDs.

Acknowledgments

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References