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THE LEACHING BEHAVIOUR OF INDIUM AND IMPURITIES FROM THE LCD GLASS OF SMARTPHONES AND TABLETS

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Abstract: Primarily, the mechanical removal of LCD panels from smartphones was examined, and a relatively easy and quick manual method was established. The LCD panels can be separated from the rest of the screen in a few seconds. In the cases of more tightly packed applications, the whole screen can be directly ground to a fine powder. The separated LCD screens were leached in different concentrations of HCl and H_2SO_4. The latter was found as practically more advantageous. Leaching with slightly acidic solutions (0.1 M H_2SO_4) results in longer leaching time, however solutions with higher purity can be obtained. If further purification is required, a relatively straightforward method of selective hydrolytic precipitation has also been examined. The practically recoverable amounts of indium may be close to the 400 mg/kg level in a dilute sulphuric acid solution containing less than 10 mg/dm^3 of total impurities (Fe, Zn, Al, Cr, Ni and Cu).

Keywords: LCD, leaching, indium, recovery

INTRODUCTION

Modern flat screen applications rely on indium (In) metal, in the form of a thin coating of indium-tin oxide (ITO). This predominant application represents ~ 90% of the global consumption of this metal [1]. However, there are no individual indium ores, the metal is extracted mainly from the by-products of zinc metallurgy, and to a lesser extent from the refining of tin and lead. Yearly consumption of In is around 1,600 tonnes, with known reserves being only 16,000 tons [2], [3]. Moreover, indium compounds have been found to pose serious health hazards [4], [5]. Thus processing LCD waste has an increasingly strong double incentive. The world produces more than 50 million tonnes of e-waste every year and this value is growing steadily by 3-4% on the yearly bases [6]. It is said that screens, small IT-s, telecommunication devices account for 10% of the aforementioned amounts. In 2020 around 1.38 billion smartphones were sold alone [7]. Hence, this raw material is available abundantly.

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1. THE REMOVAL OF THE LCD PANELS

The removal of the indium bearing LCD screen from smart phones (iPhone, Samsung, HTC, and Sony), as well as tablets (iPad, Asus and Samsung) made around the years 2014–2016 were examined with the aim for developing a fast and easy recovery technique. The smartphones have a tightly packed and well-sealed structure, thus the dismantling of the entire phone may prove difficult. The easiest way was found to open up the screen of the devices to pry a screw driver below the top or bottom of the screen and lift up the entire screen package. In most cases, the layers of the screen could be separated easily, and the LCD components could be extracted. However, in the case of more tightly packed screens, the glass layers cannot be separated from each other, requiring a special handling. In this case, the raw material was crushed into a fine powder (<0.5 mm) in a commercial knife mill. Separated LCD panels were deemed good enough to be leached. This separation and preparation process is shown in *Figure 1*.

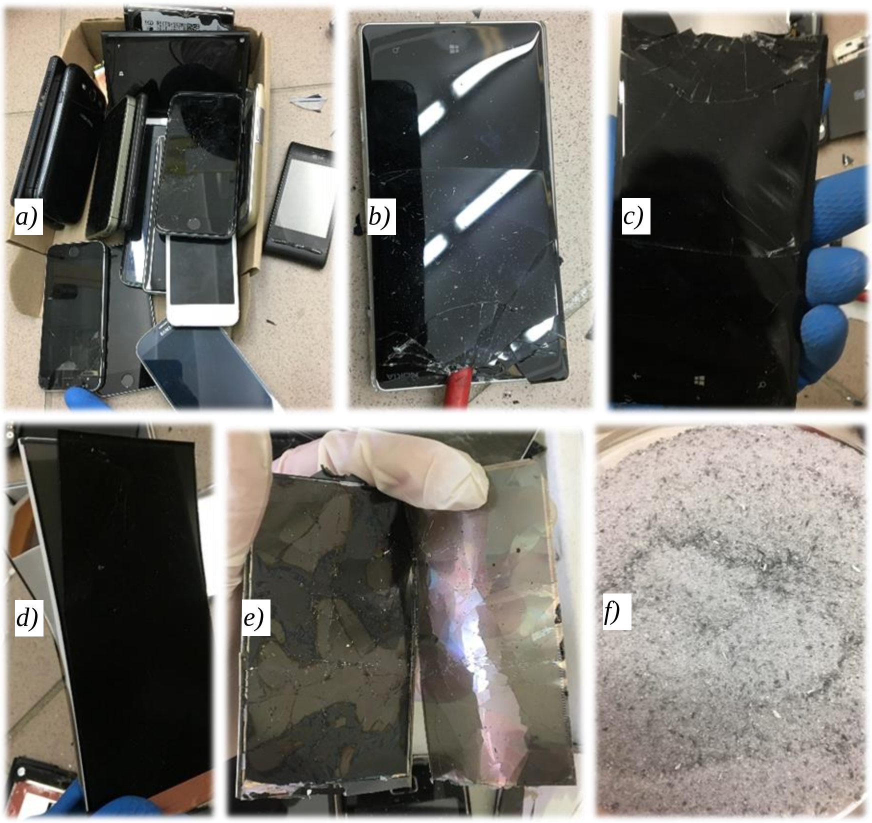

Figure 1

The process for extraction of LCD panels from smartphones: a) – the waste smartphones, b) – prying the screen open, c) – separated screen block, d) – the layers of the screen, e) – separated LCD screens, f) – ground glass powder from the inseparable screen packages

While the procedure requires manual labour, it takes only 30–60 seconds per applications to an untrained lab worker. A similar method was used for the removal of LCD panels from tablets. In this case, the outer glass shielding was simply cracked, and the LCD screens were simply lifted or cut from the frame. It is shown in *Figure 2*.

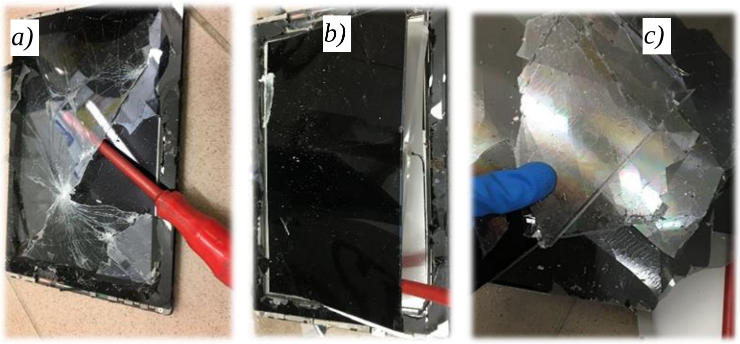

Figure 2

The removal of LCD panels from tablets: a) – removal of shielding glass, b) – lifting out the LCD screen, c) – separated LCD panels

2. THE EXPLORATORY LEACHING PROCEDURE AND RESULTS

The leaching experiments were carried out in heated conical beakers covered with watch glass lids. After proper dilution of the liquid samples, they were analysed by Atomic Absorption Spectrometry (Varian SpectrAA 300). The hydrolysis experiments were performed in open beakers at room temperature, applying 1 M NaOH neutralizing solution from a burette and stirring at a rate of 150 rpm.

The total leachable metal content of the LCD glass was determined by applying 3 M HCl acid at 90 °C for 2 hours with constant stirring at 350 rpm. The batch consisted of equal amounts of LCD screens extracted from different smartphones and tablets. The liquid/solid ratio was 1 cm^3/g. Results are shown in *Figure 3*.

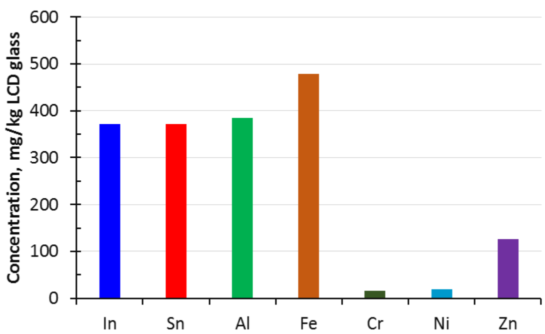

Figure 3

Average leachable metal content of the LCD panels as extracted from the examined smartphones (3 M HCl, 90 °C)

The average leachable indium content was found to be ~372 mg/kg, similar to that of tin and aluminium and iron. The kinetic behaviours associated with the leaching of In and the accompanying (impurity) elements were examined with a smaller batch of the same LCD mix but applying 2 cm^3/g lixiviant ratio at 55 °C. The relative recoveries or the ratios of dissolution – referring to the leachable contents – are shown in *Figure 4*.

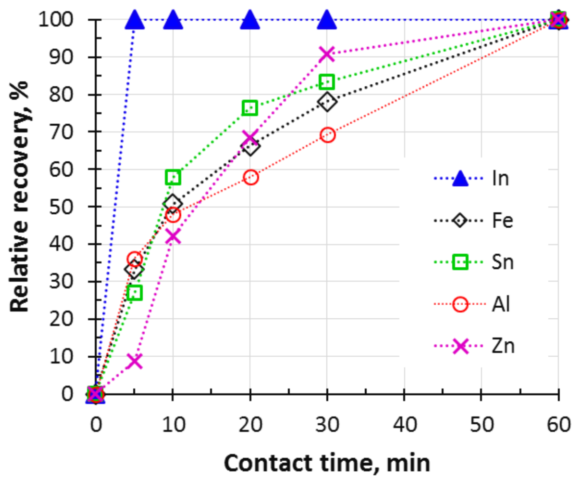

Figure 4

*The kinetics of LCD glass leaching (*3 M *HCl, 55 °C, 350 rpm.)*

It can be seen, that 3 M HCl at a mildly increased temperature can solubilize the indium content in 5 minutes, while the major portions of the impurities remain in the solid residue. The composition of the finally obtained solution is shown in *Table 1*.

Table 1

The elemental composition of the leachate obtained with 3 M HCl in 1 h time

	Concentration, mg/dm³						
In	**Fe**	**Sn**	**Zn**	**Al**	**Cr**	**Ni**	**Cu**
148.4	189.5	27.3	87.5	248.2	12.4	7.6	1.4

Although the leaching rate of indium is quite high, the impurity levels of the solution are also considerable. Thus it may be beneficial to use less acidic solutions to hinder the dissolution of the more refractory accompanying metals, or to include an efficient solution purification step after the intensive leaching. The latter option may be preferred for practical reasons. The known hydrolytic behaviour of the common accompanying elements [8] should be compared to the behaviour of indium. For this reason, we have gradually neutralized a 10 g/dm^3 indium solution while monitoring the pH during the addition of 1 M NaOH solution from a burette under close to equilibrium conditions. The results are shown in *Figure 5*.

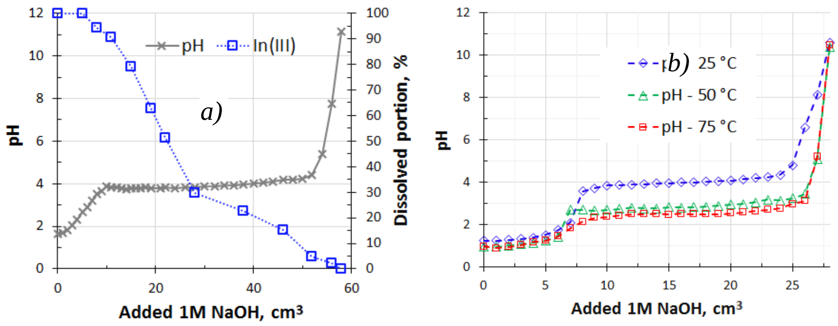

Figure 5

The equilibrium characteristics (a) and temperature dependence (b) of the hydrolytic precipitation of indium

The plateau in the pH curve indicates the metal precipitation by consuming the OH^- ions in the following hydrolysis reaction:

$$In^{3+} + 3OH^- = In(OH)_3\ ,\ \Delta G^\circ_{298} = 80.5\ \text{kJ/mol}\ In(OH)_3 \qquad (1)$$

Based on these results, a solution of pH 4 should be able to keep ~10g/dm^3 In in solution at 25 ^{o}C. It must be noted also, by increasing the temperature, the pH range of the hydrolysis also decreases and at 75 °C the reaction (1) starts already at not much above pH 2. Most of the base metals (Zn, Cr and Ni) are stable in the solution until the pH reaches significantly higher values than that of indium hydroxide precipitation, therefore they do not interfere with the indium precipitation. Copper is not dissolved from the LCD at any appreciable levels in HCl. Iron and tin can be separated from the solution with relatively good efficiency under reducing conditions at the lower valent states as indicated by the results shown in *Figure 6*.

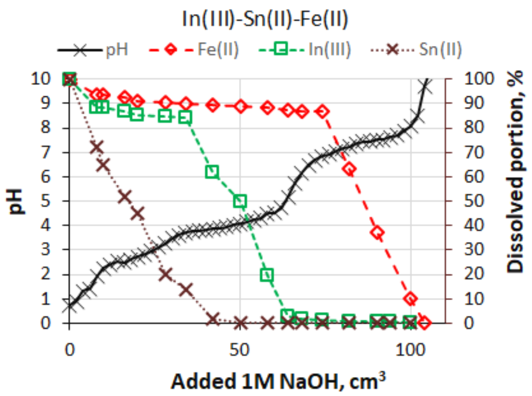

Figure 6

The equilibrium characteristics of the hydrolytic precipitation of In(III), Fe(II) and Sn(II) ions at 25 ^{o}C.

However, aluminium, which is an important impurity component according to *Table 1*, has been found to co-precipitate with indium from the leachate. Its separation is impossible by the conventional hydrolytic method. However, if indium is cemented, or cathodically deposited from the solution to obtain a metallic product, aluminium ions can be excluded as potential impurities because of having very negative electrode potential.

3. The optimization of leaching

Although the method of solution purification may be practically useful, we have tried to decrease the dissolving power of the leaching step. The effect of the pH on the leaching kinetics of In from pure In_2O_3 powder is presented in *Figure 7*.

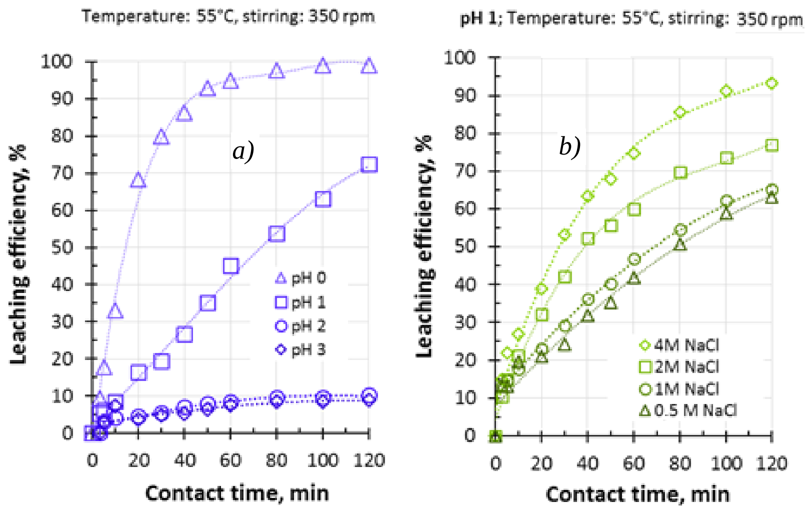

Figure 7
The effect of pH (a) and chloride ion concentration (b) on the leaching rate of indium (L/S = 300 cm^3/g)

It can be seen, that leaching at pH 2 and 3 cannot result in recoveries higher than 10%. However, virtually 100% recovery was reached with pH 0 in sulphuric acid (0.5 M H_2SO_4) relatively quickly. Also pH 1 seems to be able to produce satisfactory extraction with longer contact times. The effect of chloride ions was examined at pH 1. Results are shown in *Figure 7.b*. It can be noted, that Cl^- ion concentration in the range of 0.5–1 M did not increase the recoveries. However, in the presence of ~4 M NaCl, the recovery is noticeably higher than in the sulphate solution. It can be attributed to the extra solubilizing effect of the added chloride ions by the formation of chloride complex species.

Further leaching experiments with the LCD glass at milder conditions were conducted using diluted H_2SO_4 and HCl as lixiviants. The raw material was simply cut into pieces small enough to fit into the neck of the conical beaker. The leaching was conducted at 55 °C with a constant 350 min^{-1} stirring. Results are shown in *Figure 8.*

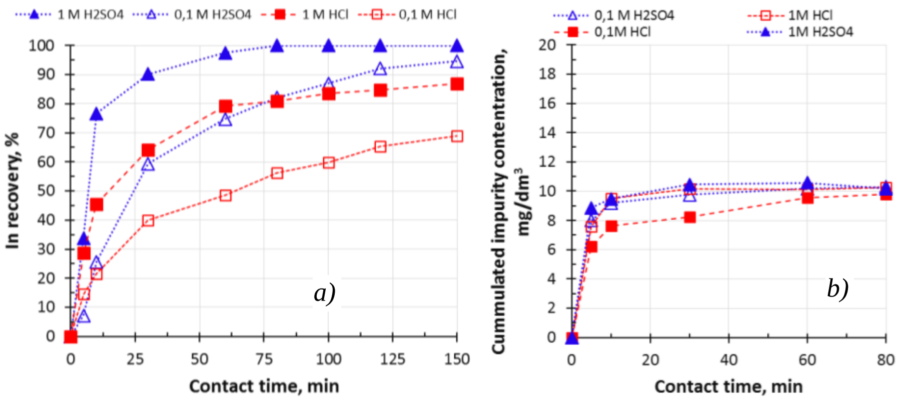

Figure 8

The kinetics curves for the dissolutions of In (a) and of the impurities (b) during the leaching of LCD glass with H_2SO_4 and HCl

The leaching seems to be significantly more effective with the same molarity of sulphuric acid than with HCl as the lixiviant, probably because of the stoichiometrically higher hydrogen ion concentration. The level of impurities in the solution seems to be roughly the same. The composition of the solution obtained by the mild (0.1 M H_2SO_4) leaching is shown in *Table 2*.

Table 2

The composition of the solution obtained by leaching LCD glass with 0.1 M H_2SO_4

	Concentration, mg/dm^3					
In	**Fe**	**Zn**	**Al**	**Cr**	**Ni**	**Cu**
138.9	6.76	1.28	0.43	0.13	0.06	0.01

Comparison of these results to those summarized in *Table 1* shows a definite advantage in terms of solution purity. Indium recovery is still almost complete as suggested by the saturation of the kinetic curve, although at a significantly longer processing time.

CONCLUSIONS

According to the circular economy concept, the smartphone and tablet waste could become a valuable secondary indium raw material. The LCD screens can be removed from the units with a sharp tool by a simple and quick manual operation. In most cases the LCD panels can be easily separated from the rest of the screen. However, more tightly packed screens need to be broken to small particles so as the lixiviant can access the ITO layer. Leaching of LCD panels were examined by HCl and H_2SO_4. The kinetics of the process is definitely improved by higher acid concentrations, but the impurity level is also increased significantly. A relatively simple solution purification by the conventional method of selective hydrolytic precipitation has been shown as practicable. However, the selectivity of the leaching step is advisable to be improved by applying less aggressive reagents. It was found that 0.1M H_2SO_4 was able to leach indium effectively in 120 minutes at 55 °C, with no Sn and relatively little dissolution of other accompanying metals from the initial waste material.

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