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Recovery of Indium from LCD Displays

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LCD displays are the most widespread imaging technology at present. Their recycling becomes important due to containing rare indium. For experimental study displays after the manual dismantling of ten monitors (two monitors with LED backlighting) were used. After removal of polarizing foils, the granularity of the sample (<0.71 mm) was adjusted by milling in the vibration mill and sieving. Subsequently, the hydrometallurgical treatment was realized by application of acid non-oxidative, oxidative leaching and solvent extraction (SX). Optimal leaching conditions were: 1 M H_2SO_4 (400 ml), 100 g of sample, 80 °C, 2 hours, 850 rpm with 10 ml H_2O_2 (30 %). The most suitable conditions for SX were set up: 10 % D2EHPA + kerosene, A : O = 5 : 1

Wiedergewinnung von Indium aus LCD-Displays

LCD-Displays stellen die heute am weitesten verbreitete Bildschirmtechnologie dar. Deren Recycling nimmt wegen des Gehalts an seltenem Indium an Bedeutung zu. Zur experimentellen Untersuchung wurden nach manueller Zerlegung die Displays von zehn Monitoren verwendet, zwei davon mit LED-Backlight. Nach Entfernen der Polarisationsfolien wurde die Korngröße der Probe durch Mahlen in einer Schwingmühle und Sieben auf <0.71 mm eingestellt. Anschließend wurde die hydrometallurgische Behandlung mit saurer nicht-oxidierender, oxidierender Laugung und Flüssigextraktion (SX) durchgeführt. Als optimale Laugungsbedingungen ergaben sich: 1-molare H_2SO_4 (400 ml), 100 g Probenmaterial, 80 °C, zwei Stunden und 850 U/min mit 10 ml H_2O_2 (30 %). Die geeignetsten Bedingungen für die Flüssigextraktion waren 10 % D2EHPA + Kerosin, A : O =

Récupération d'indium provenant des écrans LCD

Recuperación de indio procedente de pantallas de LCD

1 Introduction

Indium was included into the list of critical raw materials created by the European Commission already in 2011 (COM/2011/0025) following the economic importance and supply risk [1]. Even the import dependence rate dropped down from 100 % in 2011 to 0 % in 2017 [2], the recycling rate (according to the COM/2017/0490) is at present still 0 %. Indium is a very scattered element in the earth-crust with the content in the ores between 10 and 20 ppm of In. Its total reserves and resources are estimated at approximately 50,000 t (up to 50 % in China) mainly in zinc and copper primary resources [3]. Due to these facts, it is very impor-

and for stripping process: 4 M HCl at the ratio O : A = 5 : 1. By use of SX a relatively high efficiencies were achieved (92 % for LCD-LED and 84 % for LCD), but the stripping process was less efficient for leachates without H_2O_2 (45 % and 50 %). Practically, stripping did not succeed in obtaining of In from both leaching liquors (LCD and LCD-LED) containing H_2O_2 . The experiment confirmed the possibility of mutual processing LCD and LCD-LED displays, however in this case As should be monitored.

Keywords:

Displays – Indium – Acid leaching – Oxidant – Solvent extraction

5 : 1 und für das Strippen 4-molare HCl im Verhältnis O : A = 5 : 1. Mit der Flüssigextraktion wurde ein relativ hohes Ausbringen erzielt (92 % für LCD-LED und 84 % für LCD), jedoch war das Strippen weniger effektiv bei Lösungen ohne H_2O_2 (45 % und 50 %). Praktisch gelang es nicht, durch Strippen aus beiden H_2O_2 enthaltenden Laugungs-lösungen (LCD und LCD-LED) Indium zu gewinnen. Die experimentelle Untersuchung bestätigte die Möglichkeit der gemeinsamen Verarbeitung von LCD- und LCD-LED-Displays, jedoch sollte in diesem Fall das Arsen kontrolliert werden.

Schlüsselwörter:

Displays – Indium – Saure Laugung – Oxidans – Flüssigextraktion

tant to recover indium effectively from secondary sources. In 2012 the production of indium from secondary sources represented 950 t compared to primary production of 550 t (Figure 1) [4]. On the other hand, other literature sources report the primary refined production of indium ~770 t in 2013 and secondary refined production capacity ~610 t [3]. The world's biggest indium producer is China, and the largest European producer is France [2, 5]. Japan and Republic of Korea are leading consumers of indium [6]. The Japanese National Institute for Materials Science estimated that in Japan alone more than 1700 t of indium exist in the form of consumer waste [3]. The important secondary sources of indium are LCD displays also because of their widespread

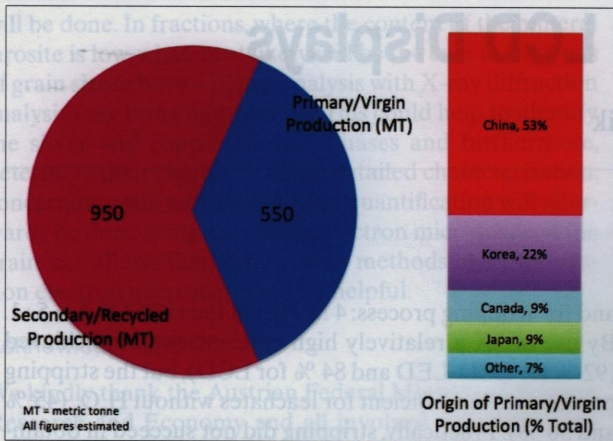


Fig. 1: Global refined indium production in 2012 [4]

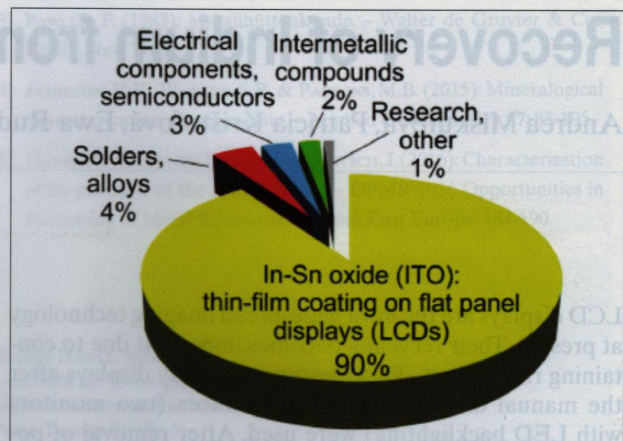


Fig. 2: Consumption of indium by end use in 2012 [8]

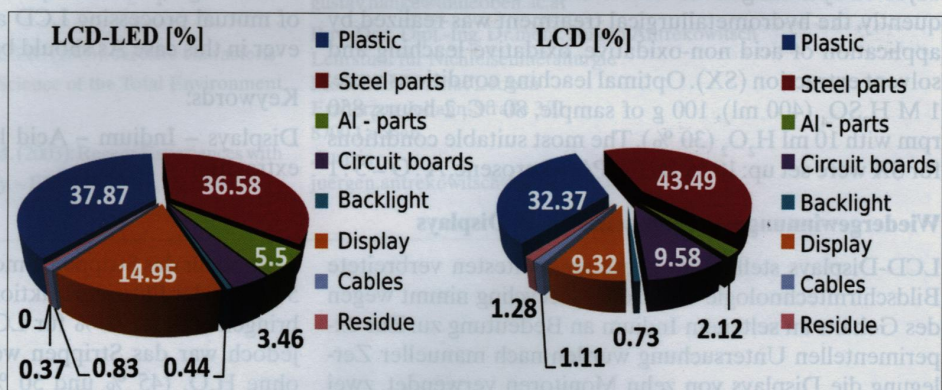


Fig. 3: Material balance of sample LCD and LCD-LED displays

production – the highest production from all types of monitors (LCD and LCD-LED) in the present. Indium occurs in LCD displays as ITO (indium tin oxide) layer film. The usage of indium in this form represented 90 % in 2012 in comparison to 84 % in the year 2008 (Figure 2) [7, 8].

The ITO film is a transparent and conductive layer that allows displaying the image on the projection screen of the monitor. In the LCD displays there are two ITO layers. The layer consists of indium oxide (90 %) and tin oxide (10 %). The research in recovery of indium from waste is focused mainly on hydrometallurgical processes. The advantages of a hydrometallurgical method are primarily lower energy costs, flexibility and a low indium content in a secondary source (for instance about 234 mg/m² of In for LCD) [9-13]. The first part of this work is aimed at a material balance of LCD and LCD-LED monitors, characterisation of display samples from a chemical composition point of view. The second part of this paper is dedicated to the leachability study of indium in acidic media and possibilities for indium recovery from the leaching solution by solvent extraction process.

1 Experimental

1.1 Materials and methods

For the experimental part, ten LCD monitors were used – TV, PC, and laptops, of which two were with LED backlighting. After disassembly, the material balance of both monitors' types was obtained, as shown in Figure 3. For

leaching experiments, displays from both types of monitors (LCD and LCD-LED) have been used.

Firstly, displays were annealed at 240 °C for 5 minutes in order to remove polarizing foils (Figure 4). The displays after foils removal were then crushed and milled in the vibration mill VM4 and sieved below 0.71 mm (Figures 5, 6).

Subsequently, representative samples (with granularity below 0.71 mm) were subjected to elemental analysis (for In and Sn an Atomic Absorption Spectrometry (AAS) using Solaar M5 and for other elements an Inductively Coupled Plasma Atomic Emission Spectrometry ICPS) and XRF semiquantitative analysis (Thermo Scientific™ Niton™ XL3t GOLDD+). The chemical composition of samples is

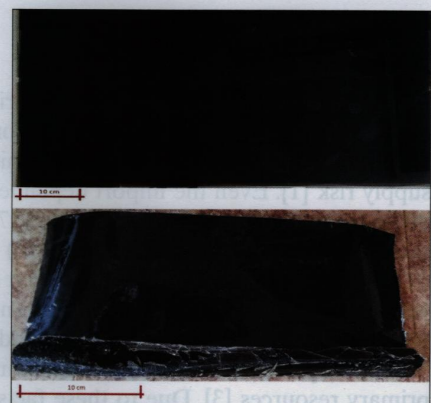


Fig. 4: Display before and after annealing at 240 °C, 5 minutes

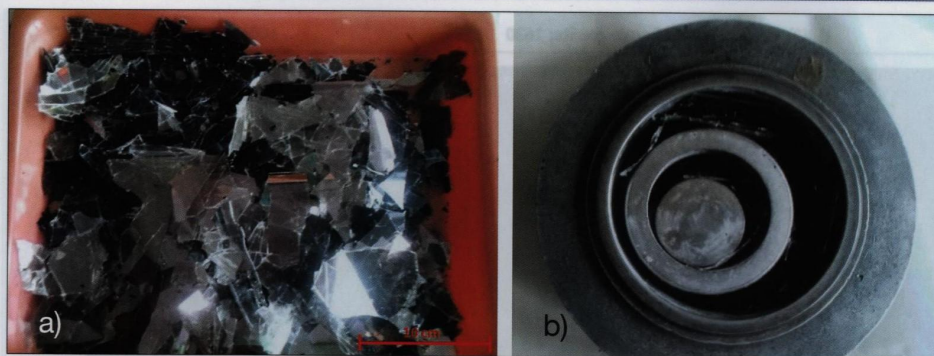


Fig. 5: a) Crushed sample after annealing (240, 5 min), b) vibration mill used for milling

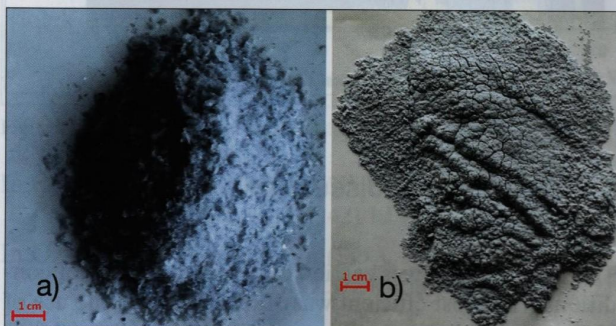


Fig. 6: Ground LCD display sample after annealing and sieving: a) above 0.71 mm, b) below 0.71 mm (experimental sample for hydrometallurgical treatment)

Table 1: Chemical composition of experimental samples (AAS and ICPS*)

Element	Content [%]		Element	Content [%]	
	LCD	LCD-LED		LCD	LCD-LED
In	0.0346	0.049	Zr	0.0127	0.0157
Ag	<0.00005	<0.00005	Au	-	<0.0002
Cu	0.0138	0.0358	Ca	-	5.46
Rh	0.00485	-	Mo	-	0.0139
Si	18.9	19.5	Ni	-	0.000873
Sn	0.0035	0.00482	Pd	-	<0.0002
Sr	1.02	0.622	Pt	-	<0.0002

* ICPS-analysis performed in accredited laboratory (ALS Czech Republic, s.r.o.)

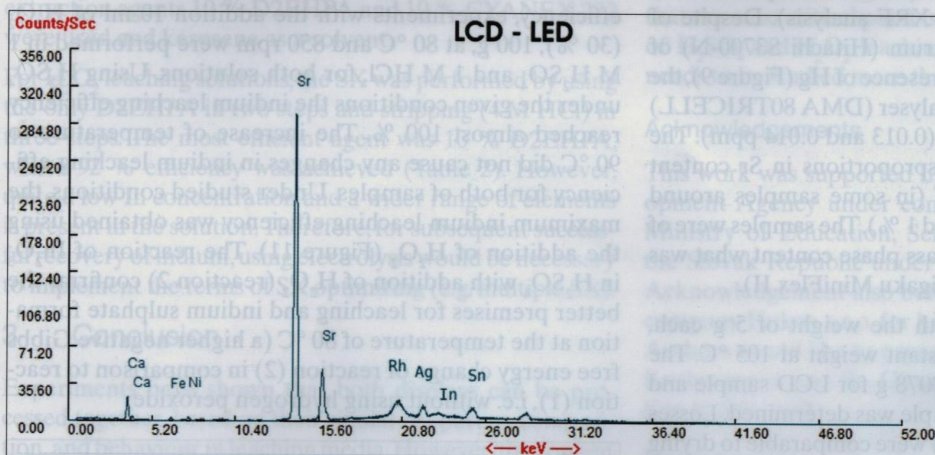


Fig. 7: Record from XRF analysis for LCD-LED display sample

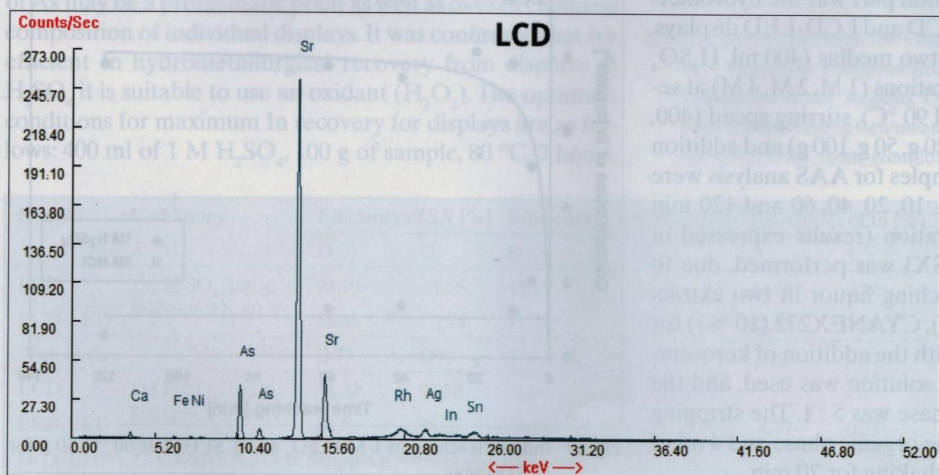


Fig. 8: Record from XRF analysis for LCD display sample

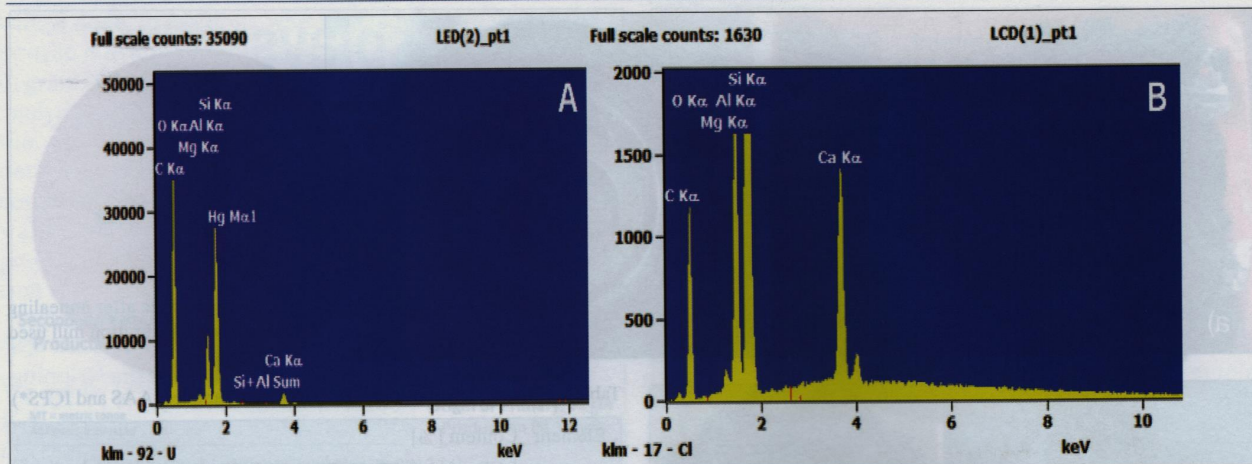


Fig. 9: SEM-EDS of LCD-LED (A) and LCD (B)

given in Table 1. From chemical composition in Table 1, it is obvious that the main components of displays are silicon and calcium oxides. Both of the samples have similar SiO₂ content. LED displays have a bit higher content of indium as well as tin and copper. Except of mentioned elements, displays also contain Sr, Mo, Rh, Fe, Ni, Zr, Ag, Ba, etc. XRF analysis (Figures 7, 8) confirms the similar composition of LCD and LCD-LED samples, with the exception of As content in LCD individual displays (from 0.002 up to 2.17 % measured by semiquantitative XRF analysis). Despite of the fact, that SEM-EDS spectrum (Hitachi S3700-N) of LCD sample did not show the presence of Hg (Figure 9), the Hg content measured by Hg analyser (DMA 80TRICELL) was similar in both of samples (0.013 and 0.014 ppm). The interesting fact was certain disproportions in Sr content in samples measured by XRF (in some samples around 40 %) and AAS analysis (around 1 %). The samples were of amorphous character due to glass phase content what was confirmed by XRD analysis (Rigaku MiniFlex II).

Three samples were taken with the weight of 5 g each, and subsequently dried to constant weight at 105 °C. The average total loss by drying 0.0078 g for LCD sample and 0.0095 g for the LCD-LED sample was determined. Losses on ignition (1150 °C, 1 g, 1 hour) were comparable to drying losses. The aim of the experimental part was the hydrometallurgical recovery of In from LCD and LCD-LED displays. Leaching of In was realized in two medias (400 ml, H₂SO₄ and HCl) with various concentrations (1 M, 2 M, 4 M) at selected temperatures (20, 80 and 90 °C), stirring speed (400, 850 rpm), with sample weight (20 g, 50 g, 100 g) and addition of H₂O₂ (30 %) for 2 hours. Samples for AAS analysis were collected at time intervals of 5, 10, 20, 40, 60 and 120 min and measured for In concentration (results expressed in mg/dm³). Solvent extraction (SX) was performed, due to low concentration of In in leaching liquor in two extraction reagents (D2EHPA (10 %), CYANEX272 (10 %)) for 5 min with a volume of 20 ml with the addition of kerosene. For SX 100 ml of the leaching solution was used, and the ratio of inorganic to organic phase was 5 : 1. The stripping was performed with 20 ml of the organic phase and 4 ml of 4 M HCl (O : A = 5 : 1) during shaking for 20 min.

2 Results and discussion

2.1 Leaching

The leaching step was carried out under a variety of conditions. The most efficient was H₂SO₄ (without the use of H₂O₂) under these conditions: 1 M H₂SO₄, 50 g, 80 °C, and 400 rpm (Figure 10). The concentration of In in leachate was very low under given conditions and leaching efficiency was about 15 %. For the increase of In leaching efficiency, experiments with the addition 10 ml of H₂O₂ (30 %), 100 g, at 80 °C and 850 rpm were performed in 1 M H₂SO₄ and 1 M HCl, for both solutions. Using H₂SO₄ under the given conditions the indium leaching efficiency reached almost 100 %. The increase of temperature to 90 °C did not cause any changes in indium leaching efficiency for both of samples. Under studied conditions, the maximum indium leaching efficiency was obtained using the addition of H₂O₂ (Figure 11). The reaction of In₂O₃ in H₂SO₄ with addition of H₂O₂ (reaction 2) confirms the better premises for leaching and indium sulphate formation at the temperature of 80 °C (a higher negative Gibbs free energy change of reaction (2) in comparison to reaction (1), i.e. without using hydrogen peroxide:

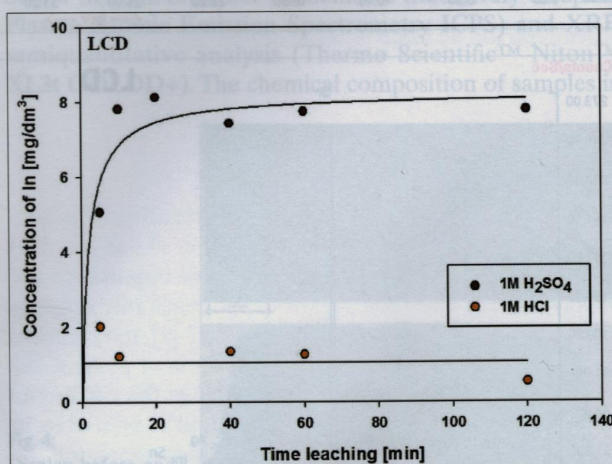


Fig. 10: Indium leaching in 1 M H₂SO₄ and 1 M HCl at 80 °C, 50 g for LCD sample

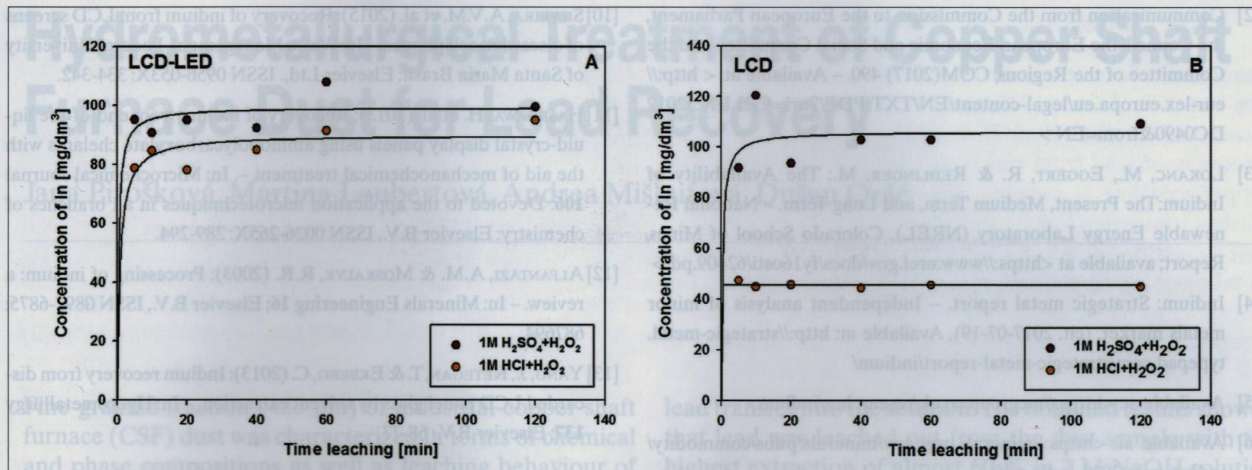
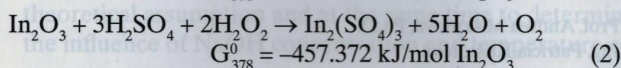
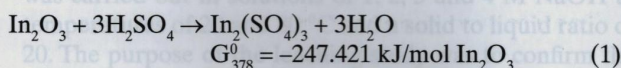


Fig. 11: Indium leaching in 1 M H₂SO₄ and 1 M HCl at 80 °C, 100 g: LCD-LED (A); LCD (B)



2.2 Solvent extraction

The SX was used for In concentration in the leaching solution with an aim to apply electrolysis in the next step. As extraction agents 10 % D2EHPA and 10 % CYANEX 272 were used and kerosene as a solvent.

For H₂O₂ leaching solutions, the SX was performed by using the only D2EHPA in two steps and stripping (4 M HCl) in three steps. The most efficient agent was 10 % D2EHPA, where 92 % efficiency was achieved (Table 2). However, quite a low In concentration and a wider range of elements is present in the solution. Therefore, for subsequent successful recovery of indium, using electrolysis would be necessary to implement the terms of SX optimizing (e.g. multiple SX).

3 Conclusion

Experiments have shown that both displays can be processed together, based on their similar properties, composition, and behaviour in leaching media. However, the content of As may be a problematic point as well as overall chemical composition of individual displays. It was confirmed that for efficient In hydrometallurgical recovery from displays in H₂SO₄ it is suitable to use an oxidant (H₂O₂). The optimum conditions for maximum In recovery for displays are as follows: 400 ml of 1 M H₂SO₄, 100 g of sample, 80 °C, 2 hours,

850 rpm, with 10 ml H₂O₂ (30 %). The change of acid concentration has practically no effect on In extraction. The most suitable conditions of SX were determined: 10 % D2EHPA + kerosene. Even multiple stripping process (carried out with 4 M HCl at ratio A : O = 5) was not efficient enough under given conditions. Intensification of the SX can be accomplished by using a more concentrated extraction/stripping agent, multistage extraction/stripping, homogeneous extraction, etc. The results also indicated an interesting fact, that the most critical point is stripping, especially in the case of H₂SO₄ and H₂O₂ leaching solutions. This phenomenon needs to be studied more thoroughly.

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Sample	Conditions	Efficiency of SX [%]		Efficiency of stripping [%]			Total profit of In [%]	
		D	C	D	C	S ³⁾	D	C
LCD	1M H ₂ SO ₄ , 100 g,	92.19	1.55	45.19	27.85		41.66	2.16
LCD-LED	850 rpm, 2 h, 80 °C	88.60	3.75	51.71	10.53		45.99	1.98
With H ₂ O ₂		D ¹⁾	D ²⁾	S ¹⁾	S ²⁾	S ³⁾	3.65	0.47
LCD	1M H ₂ SO ₄ , 100 g,	84.32	97.78	1.01	4.32	3.65		
LCD-LED	850 rpm, 2 h, 80 °C	82.5	96.37	4.18	5.79	4.77	4.77	0.52

D: D2EHPA; C: CYANEX 272; S: Stripping; ^{1),2),3)}: Stages of process

Table 2: Results of the SX experiments by use of leaching solutions with the highest In concentration

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