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Hydrometallurgical methods of indium recovery from obsolete LCD and LED panels

Hydrometalurgiczne metody odzysku indu z zużytych paneli LCD i LED

Abstract

This paper shows a review of literature data on the possibilities of indium recovery from ITO layers of waste LCD and LED displays. A short characterization of indium, its compounds, resources, production, and applications is presented. The structure and operation of LCD displays are shown. A detailed overview of the ITO leaching process is presented. Methods of indium(III) ion separation from the leachate solutions (SX, HoLLE, IX) as well as recovery of the final products (precipitation, cementation, electrowinning) are also shown.

Keywords: indium; LCD, LED, ITO, hydrometallurgy, recycling

Streszczenie

Artykuł przedstawia przegląd literatury na temat odzysku indu z warstw ITO w zużytych panelach LCD i LED. Przedstawiono krótką charakterystykę indu, jego związków chemicznych, zasobów, produkcji i zastosowań. Omówiono budowę i zasadę działania paneli LCD. W sposób szczegółowy opisano proces ługowania ITO. Przedyskutowano także metody rozdzielenia jonów indu(III) z roztworów po ługowaniu (SX, HoLLE, IX) oraz odzysku produktów końcowych (strącanie, cementacja, elektroliza).

Słowa kluczowe: ind, LCD, LED, ITO, hydrometalurgia, recykling

1. Introduction

1.1. Characterization of indium

Indium is a shiny silvery-white metal. It is one of the softest metal known, even softer than lead [1]. Table 1 summarizes the technical data for the metal. In the atmosphere, indium is relatively stable; only very slowly it is covered with a yellow-green layer of indium oxide In_2O_3 . An unusual property of indium is that it produces a “tin cry”; i.e., a scream-like sound made when the metal is bent.

Table 1. Technical data for metallic indium [2]

Technical data for indium		
Overview	Atomic number: Oxidation states: Atomic weight: Melting point: Boiling point: Color: Crystallographic structure: Discovery: Name origins:	49 +I, +II, +III 114.818 u 156.6°C 2072°C Silver tetragonal 1863 in Germany; F. Reich and T. Richter Named after the indigo line in its spectrum
Thermal properties	Melting point: Boiling point: Heat of fusion: Heat of vaporization: Specific heat: Thermal conductivity: Thermal expansion:	156.6°C 2072°C 3.26 kJ/mol 230 kJ/mol 233 J/kgK 82 W/(mK) 0,0000321 K ⁻¹
Electrical properties	Electrical conductivity: Resistivity: Superconducting point:	1,2·10 ⁷ S/m 8·10 ⁻⁸ mΩ 3.41
Magnetic properties	Magnetic type: Molar magnetic susceptibility: Volume magnetic susceptibility:	Diamagnetic -1.61·10 ⁻¹⁰ -0,0000102
Bulk physical properties	Density (solid): Density (liquid): Brinell hardness: Young modulus:	7.31 g/cm ³ 7.02 g/cm ³ 8.83 MPa 11 GPa
Reactivity	Electronegativity (Pauling): Electron affinity: Ionization energies:	1.78 28.9 kJ/mol 558,3; 1820,7; 2704; 5210 kJ/mol

Indium compounds in oxidation states I and II are highly unstable and decompose to indium(III) forms and elemental indium (oxidoreduction). In the compounds, it is most

common in oxidation state III. In an alkaline environment, it creates trivalent indium indates InO_2^- and hydroxoindates $\text{In}(\text{OH})_4^-$, while the acidic conditions yield indium simple cations In^{3+} .

1.2. Sources of indium

The average content of indium in the Earth's crust is 0.25 ppm [3]. Indium is a significantly chalcophilic element and concentrated as a blending component in heavy metal sulphides. The highest concentrations of indium are found in the veins and metasomatic deposits of tin ore. For industrial production, however, it has practical importance only if occurs in the form of solid solutions in sphalerite.

The highest content of all known indium minerals has dzhalindite, which contains 69.23% In. Specimens of indium metal have been found in a region of Russia, and an indium mineral has been found in Siberia; however, such a specimen is rare. Other minerals as well as their indium contents are listed in Table 2.

Table 2. Exemplary indium minerals [3]

Mineral name	Formula	In content [wt %]
Dzhalindite	$\text{In}(\text{OH})_3$	69.23
Indite	FeIn_2S_4	55.50
Damiaoite	PtIn_2	54.07
Cadmoindite	CdIn_2S_4	49.58
Roquesite	CuInS_2	47.35
Laforetite	AgInS_2	40.03
Yanomamite	$\text{In}(\text{AsO}_4) \cdot 2\text{H}_2\text{O}$	39.62
Sakuraiite	$(\text{Cu, Zn, Fe, In, Sn})_4\text{S}_4$	24.35
Yirunite	Pt_3In	16.40
Abramovite	$\text{Pb}_2\text{SnInBiS}_7$	11.41
Petrukite	$(\text{Cu, Fe, Zn})_2(\text{Sn, In})\text{S}_4$	6.05

Indium produced in industry comes as a by-product of smelting zinc and lead sulfide ores, some of which can contain 1% of indium. It is estimated that the indium supply will remain for fewer than 14 years based on the current rate of extraction, which demonstrates the need for additional recycling of this critical metal [4]. The lack of indium mineral deposits and the fact that indium is enriched in sulfidic lead, tin, copper, iron, and predominately zinc deposits makes zinc production the main source for indium. The indium is leached from the slag and dust of zinc production. Further purification is done by electrolysis. The process varies with the exact composition of the slag and dust [3].

1.3. Production

Leading producers of indium (1450 tons in 2015) are South Korea, China, Taiwan, and Japan [5]. The Teck Cominco refinery in Trail, British Columbia, is a large single-source indium producer. South American Silver Corporation's Malku Khota property in Bolivia is a large source of indium, with an indicated resource of 1481 tons and inferred resource of 935 tons. Adex Mining Inc.'s Mount Pleasant Mine in New Brunswick, Canada, manages some of the world's known indium resources [6].

The amount of indium consumed is largely a function of worldwide LCD production. Worldwide production of refined indium in 2012 was 550 tons per year from mining and a further 950 tons per year from secondary sources and recycling [4]. Demand has risen rapidly in recent years with the popularity of LCD computer monitors and television sets, which now account for 50% of indium consumption. Increased manufacturing efficiency and recycling (especially from ITO scrap in Japan and the Republic of Korea) help maintain a balance between demand and supply.

According to the UNEP (United Nations Environment Program), indium's end-of-life recycling rate is less than 1%. Demand increased, as the metal is used in LCDs and televisions, and supply decreased when a number of Chinese mining concerns stopped extracting indium from their zinc tailings.

In 2014, the price for indium was US \$700–780 per kilogram. The recent changes in demand and supply have resulted in the high and fluctuating prices of indium, and the prices of indium decreased to \$240–285 US/kg in November, 2015 [5].

1.4. Applications

Most indium is used to make indium tin oxide (ITO), which is an important part of touch screens, flatscreen TVs, and solar panels [5, 7]. This is because it conducts electricity, bonds strongly to glass, and is transparent. Indium nitride, phosphide, and antimonide are semiconductors used in transistors and microchips.

Indium metal sticks to glass and can be used to give a mirror finish to windows of tall buildings as well as a protective film on welder goggles. It has also been used to coat ball bearings in Formula 1 racing cars due to its low friction. An indium alloy has been used for fire-sprinkler systems in shops and warehouses because of its low melting point. Other uses are in engine mounts, flat screen, glass layers on touch screens (it captures infrared rays), medical technology, solar and photovoltaic technology, light emitting diodes, construction equipment, solder, batteries, and special coating layers.

2. LCD and LED panels

Liquid crystal display (LCD) and its various variants and modifications are currently the most-widely-used display means [7]. The imaging layer is comprised of a matrix of pixels

formed liquid crystal. These work as semiconductors – light is either released or it remains dark. Thanks to rotation, the crystal may release different amounts of light and (only to a limited extent) regulate local brightness, depending on the electrodes and a polarizing filter that is surrounded by a matrix or transistors allocated to each pixel. Each pixel consists of three sub-pixel primary colors – red, green, and blue. Their folding can achieve a wide array of colors. The light source is cold cathode fluorescent lamp (CCFL) or light-emitting diode (LED) backlighting. LCD panels also have difficulty displaying a faithful representation of black (which, in this case, is more like gray). It is therefore preferred LED backlight and contrast, while brightness, color reproduction, and viewing angles are about the same as in LCD. Another advantage of LED-LCD models are their smaller dimensions – particularly their thinness.

The theoretical composition of these monitors contains more resources in the following quantities: ferrous metals (25–44%); plastics (28–31%); glass (10–23%); printed circuit boards (6–10%); non-ferrous metal (3–9%); cables (4%); and other materials including fluorescent lamps or cold cathode and liquid crystals (<1%).

LCD and LED displays contain some amounts of indium, mainly as indium tin oxide (tin-doped indium oxide). ITO is a mixture of indium(III) oxide In_2O_3 and tin(IV) oxide SnO_2 , typically 90% In_2O_3 and 10% SnO_2 by weight. In LCD displays (Fig. 1), ITO can be found in two distinct layers: in active matrix liquid crystal displays as the common electrode in the color filter (CF) plane (on the front glass of the display) and coating AM-LCD used as a pixel electrode in the thin film transistor (TFT)-plane. It forms the contact to the transistor's active area [7].

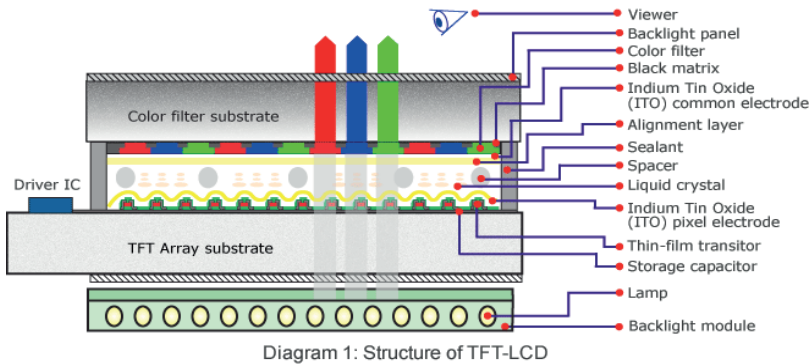


Fig. 1. Structure of TFT-LCD [8]

The microstructure of ITO strongly depends on the substrate temperature used during deposition. The coatings deposited on polymer film or directly applied to glass are applied at room temperature [7]. In these coatings tin admixture in ITO does not contribute to conductivity as the ITO conductivity purely relies on oxygen vacancies.

Less frequently, ITO can be incorporated in inks using an appropriate film-forming polymer resin and solvent system and deposited by screen printing – albeit, with lower transparency and conductivity when compared to a physical deposition process. Of the various transparent conductive oxides (TCOs), ITO is considered the premium TCO, having superior conductivity and transparency, stability, and ease of patterning to form transparent circuitry. ITO is used in a number of display technologies, such as LCD, OLED, plasma, electroluminescent, and electrochromatic displays as well as in a number of touch screen technologies [9].

Further uses of this versatile material include antistatic indium tin oxide coatings, EMI shielding, photovoltaic solar cells, aircraft windshields, and freezer case glass for demisting. Yet, further applications for ITO are as an infrared reflecting coating to reflect heat energy, such as in low-E glass and in low-pressure sodium lamps [9].

3. Leaching of waste LCD and LED displays

Obsolete LCD and LED displays are relatively new sources of indium recovery. Depending on the origin of the LCD panels, indium content is within a range of 53–410 ppm, but it typically reaches 110–200 ppm [10]. Literature data shows that hydrometallurgical treatment is the most-suitable and most-frequently-used method for indium recovery from waste panels, mainly due to the low percentages of the element [11]. Leaching of such waste is carried out in hydrochloric or sulfuric acids. Table 3 summarizes an overview of the different leaching conditions.

Table 3. Leaching conditions of indium from waste materials

Origin	Leachant	s/l ratio [g/mL]	Temperature [°C]	Time [min]	Final In(III) recovery	Reference
Waste LCDs	HCl:H ₂ O 3:2	0.2	80	60	317 mg In/kg LCD	[12]
ITO targets powders	1M H ₂ SO ₄	0.1	90	120	>99% recovered	[13]
glass substrate containing ITO	6M HCl	0.3	25	360	260 mg/kg glass	[14]
LCD scraps	2M H ₂ SO ₄	–	80	10	35 mg/L in solution	[15]
Shredded LCD glass	Aqua regia	0.1	20	2880 (2 days)	200 ± 50 g / t glass	[16]

Dissolution of indium from ITO is usually carried out at high temperatures (80–90°C), but final solutions contain only a dozen milligrams of indium ions per liter. This seems quite obvious, since the thickness of ITO layers reaches only a few nanometers in displays.

4. Separation of In(III) ions

Due to the very low concentration of indium ions in the solutions obtained in the leaching stage, special methods for metal separation with simultaneous concentration are required. For such purposes, ion exchanges in liquid-liquid or liquid-resin systems are the most-efficient techniques.

4.1. Solvent extraction

Solvent extraction (SX) consists of two contacting immiscible liquid phases in order to provide selective transfer of ionic species from the aqueous to organic phases. In a further step, ions are stripped from the loaded organic to aqueous phases, producing concentrated solutions. Scrubbing the organic phase can be also introduced as a middle-stage.

Solvent extraction of indium has been studied since the 1960's for the recovery of trace amounts of metal from primary (zinc ores) or secondary (residues or slags from zinc and lead circuits) sources. Currently, it is economically used on an industrial scale for the production of indium, mainly in zinc refineries (e.g., Mitsubishi's Akita, Japan; Kidd Creek, Canada) [17]. Typical extractants used for such purposes are bis(2-ethylhexyl) phosphoric acid D2EHPA (or DEHPA), tributyl phosphate TBP, bis(2,4,4-trimethylpentyl) phosphinic acid Cyanex 272, or a mixture of different phosphine oxides known as Cyanex 923. These are used for separating indium from liquors after the leaching of waste LCD – although, in recent years, some other organic extractants have also been investigated (e.g., di-2-ethylhexyl phosphoric acid P-204 or 9-ethylhexyl phosphonic acid mono-2-ethylhexyl ether PC-88A). Extraction of indium ions from acidic solutions was examined further using carboxylic acids (e.g., Versatic 10), hydroxyoxime derivates (e.g., LIX 984, LIX 973N, LIX 63), phosphine oxides (TOPO, TBPO), or methylisobutylketone (MIBK) as well as synergic mixtures (e.g., D2EHPA+TBP) [18]. Figure 2 shows the structural formulas of some extractants.

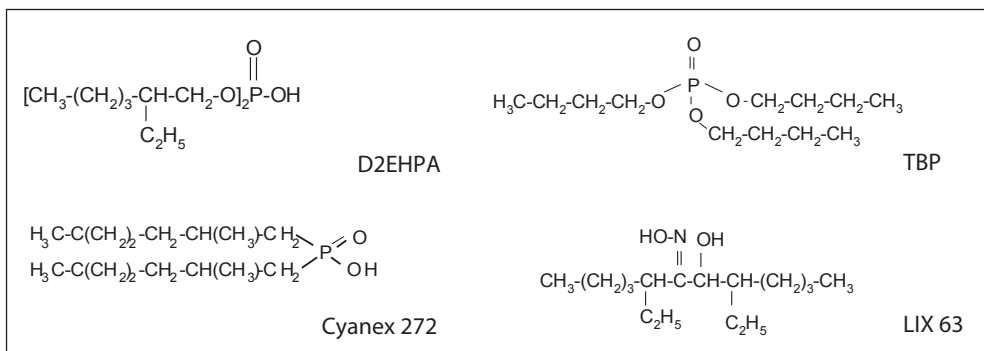
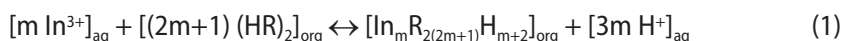


Fig. 2. Structures of selected extractants

Solvent extraction of indium ions is usually investigated using synthetic solutions simulating the composition of liquors obtained from the LCD leaching process. Table 4 (on the interleaf) summarizes the exemplary results reported by various authors.

D2EHPA is the most-popular acidic cationic extractant, having high loading capacity and good selectivity; however, the efficiency and kinetics of indium extraction depends on the type of acid in the aqueous phase. Sato and Sato [19] have found that In^{3+} extraction increased in the order of $\text{HCl} < \text{H}_2\text{SO}_4 < \text{HNO}_3$ for acid concentrations below 2M, while this order was reversed for more-acidic solutions. The results were confirmed by Lupi and Pilone [20], but Yang et al. [16] excluded HNO_3 as an aqueous phase due to the slow LCD leaching kinetics. Differences in extraction behavior were explained by the formation of various indium species. In sulfate or nitrate media, pure ion exchange with the formation of polymeric compounds in the organic phase was proposed:



In chloride systems, the formation of indium chlorocomplexes was dependent on the acid concentration; hence, the extraction mechanism can be described by the following scheme:



accompanied by a solvation reaction in more-concentrated HCl (above 1M):

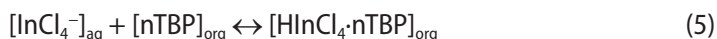


To improve extraction and selectivity, D2EHPA was also used in mixtures along with other organic extractants. Synergic effects were observed in the D2EHPA+TBP system, where high separation of indium was observed from tin ions [18, 21]. It was also found that the extraction kinetics of Sn(IV) ions are much slower than those for indium [18, 22]. It is worth noting that tin ions are co-extracted with indium by D2EHPA from acid sulfate solutions, but the selective recovery of indium from the loaded organic phase can be successful using HCl in the stripping stage.

TBP is a solvating extractant, but its selectivity for indium separation is not high as for cationic extractants, and it has good selectivity for tin over indium ions from HCl solutions. It forms various species with indium ions in the organic phase, and the indium distribution coefficient is enhanced by increased HCl concentration; hence, the following extraction reactions from chloride solutions have been proposed:



for HCl below 6M; and:



at higher acid concentrations [18].

Table 4. Indium solvent extraction – extraction stage

No.	Solution	Ions concentration in aqueous phase	Extractant	Diluent	O/A ratio	Contact time	Extraction	Stripping solution	A/O ratio	Contact time	Stripping efficiency	Comments	Reference
1	Simulated: ITO powder dissolved in 1M acids (H ₂ SO ₄ , HCl)	740 mg/dm ³ In ³⁺ 33 mg/dm ³ Sn ²⁺	1M D2EHPA 1M TBP 0.8M D2EHPA+0.2M TBP	ShellSol 2046 ExxsolD-80	1:1	3 h	In, Sn from H ₂ SO ₄ 97% Sn from min. 1.5M HCl 99% Sn from min. 1-2M HCl	min. 1.5M HCl no data no data	1:1 – –	3 h – –	94% In – –	Separation from Sn; 12 g/dm ³ In in final HCl H ₂ SO ₄ – low extraction, low selectivity 5% In co-extracted from HCl	[21]
2	Leaching TFT-LCD with H ₂ SO ₄	42 mg/dm ³ In ³⁺ 33 mg/dm ³ Sn ²⁺	30 vol % D2EHPA	kerosene	1:5	5 min	98.5% In from H ₂ SO ₄ (pH = 0.3)	4M HCl	1:5	no data	97% In	–	[24]
3	Simulated: InCl ₃ (Al, Cu, Fe, Zn, Sn salts) dissolved in acids (HNO ₃ , H ₂ SO ₄ , HCl)	200 mg/dm ³ In ³⁺ 20 mg/dm ³ Sn ²⁺ 150 mg/dm ³ (Al ³⁺ , Cu ²⁺ , Fe ³⁺ , Zn ²⁺)	1.75M TBP + 2% n-decanol 0.1M Cyanex 272 0.1M Cyanex 923 0.1M D2EHPA	Solvent 70 toluene n-octanol cyclohexanone	1:1	10 min	Selective In extraction (99.9%) only with D2EHPA diluted in kerosene (Solvent 70) from 0.1M H ₂ SO ₄	1M HCl	1:1	10 min	96% In	Slow extraction kinetics from HNO ₃	[16]
4	Simulated: In, Cu, Fe, Zn oxides dissolved in acids (HNO ₃ , H ₂ SO ₄ , HCl)	1300 mg/dm ³ In ³⁺ 3200 mg/dm ³ Fe ³⁺ 5300 mg/dm ³ Zn ²⁺ 1100 mg/dm ² Cu ²⁺	3–15 vol % D2EHPA 3 vol % Cyanex 272 3 vol % LIX 984 3–8 vol % IONQUEST 801	kerosene	1:1	No data	High In extraction with D2EHPA and Ionquest 801 at low extractant concentration and pH 0.8–1.2, but not selective from Fe ³⁺	I step – 0.05M H ₂ SO ₄ II step – 2M HCl	1:1	15 min	0% In 100% In	Reductive stripping of Fe ³⁺ with Zn from D2EHPA In stripping	[20]
5	Waste ITO target dissolved in HCl	154 g/dm ³ In ³⁺ 27 mg/dm ³ Sn ²⁺	PC88A Versatic acid Alamine 336 Cyanex 272 D2EHPA	Exsol D80	1:3	10–15 min	Selective separation of Sn from In in 2M acid with PC88A	I step – 3M HCl II step – 12M HCl	1:5 1:3	No data	– 100% Sn	In scrubbing from organic phase Sn stripping from organic phase	[25]

Cyanex 272 belongs to the acidic extractants, similarly as with D2EHPA. It characterizes with low solubility in the aqueous solutions, good recycling capacity, and miscibility with common diluents. It extracts indium from HNO_3 , H_2SO_4 , and HCl for acid concentrations up to 0.1M, and stripping can be performed with 1M HCl [23]. However, Yang [16] showed easy separation of tin from indium ions and other metals (Cu, Fe, Zn), while the separation of indium from Zn^{2+} and Fe^{3+} was poor.

Good separation of In(III) from Zn, Fe, Cu, and Al ions in H_2SO_4 can be obtained using Cyanex 923, but the main drawback is the co-extraction of tin [16].

Fontana et al. [14] studied indium extraction with an aqueous biphasic system (ABS) as an alternative for traditional solvent extraction in an oil-water system. Aqueous two-phase systems are formed when a water-soluble polymer (e.g., polyethylene glycol PEG) is mixed with some inorganic salts (e.g., Na_2SO_4 , Na_2CO_3 , KCl) at the proper concentrations. Dehydration of the polymer caused by the addition of the salt (the salting-out effect) leads to separation of the two immiscible aqueous phases. Metal ions are distributed between both phases (the "top phase" is a PEG phase, and the "bottom phase" is a salt phase) with the characteristic distribution coefficient.

Indium extraction was carried out from a 6M HCl solution (obtained from the LCD leaching stage) using a $\text{PEG}-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O}$ system and 1,10-phenantroline as a ligand for indium ions. It was reported that 80-95% of indium can be extracted in the "bottom phase." Concentration of In(III) in the "bottom phase" was 30% higher (110 ppm) than the initial concentration before extraction (85 ppm).

4.2. Homogenous liquid-liquid extraction

Homogenous liquid-liquid extraction (HoLLE) applies low-density organic solvents without employing centrifugation. In contrast to solvent extraction, aqueous and organic phases are in a homogenous state at the starting point of extraction of the target compound; therefore, mechanical intensive mixing for increasing the contact interface between both phases is not necessary. In laboratory practice, aqueous solutions containing metal chelates are used. Separation of the phases into water immiscible sediment containing the target substance (metal chelates) is stimulated by changes of pH, temperature, light, or the addition of some organic compounds like surfactants (e.g., perfluorooctanoic acid PFOA, Fig. 3a) or water-miscible organic solvents (e.g., acetone or tetrahydrofuran THF). This allows to achieve from 100- to 100,000-fold concentration of metal ions in microvolume in several minutes. Figure 4 shows a scheme of the HoLLE process.

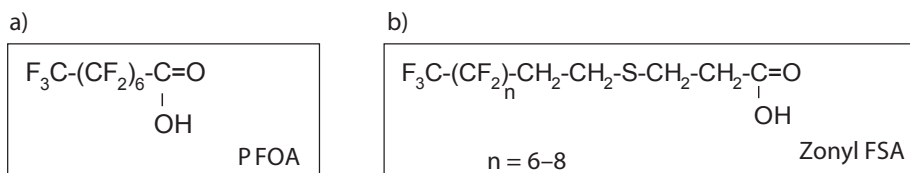


Fig. 3. Structural formulas of PFOA (a) and Zonyl FSA (b)

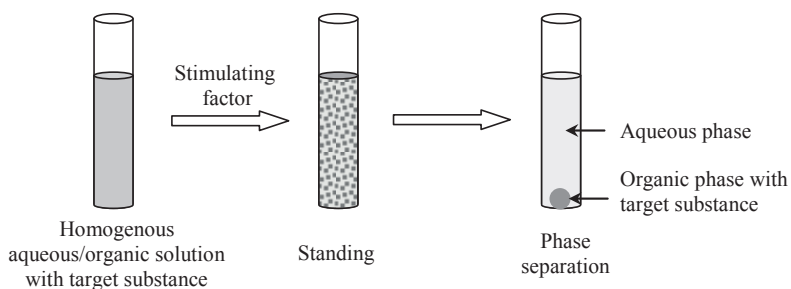


Fig. 4. Scheme of HoLLE process

The HoLLE method was studied for the separation and recycling of indium and other rare metals [26, 27]. Kato et al. [26] investigated the recovery of indium from LCD screens of mobile phones. On the basis of the LCD-screen leaching results, a simulated acid chloride solution (pH 2.0) was prepared. After the formation of metal chelates with 1,10-phenantroline, Zonyl FSA (3-[2-(perfluoroalkyl)ethylthio]propanoic acid) (Fig. 3b) and acetone were added. After phase separation, 96.7% of the indium extracted from the leachate was found in the sedimented liquid phase. The aqueous-phase-to-sedimented-phase volume ratio was 438. The concentration of indium in the final sedimented liquid phase was 10.4 wt%, while the concentration of In(III) in the initial solution was 15.2 mg/dm³.

The authors [26] also discussed the possibilities of indium recovery from the sedimented liquid phase. Perfluoro-surfactants can be removed from the sedimented liquid phase with heating in a vacuum by the decomposition method, recovered using chemically modified polymers or back-extracted by adding solvent. However, Kato et al. [26] proposed the dissolution of Zonyl FSA of the sedimented liquid phase in water at a pH level higher than 6.5 and adsorption of indium on the solid phase (e.g., Chelex-100). The solution containing Zonyl FSA could then be recycled for further HoLLE processes. No experimental verification of the procedure above was carried out.

Saito et al. [27] investigated the application of the HoLLE method for the separation of 62 elements from HNO₃, HCl, HF H₂SO₄ or KOH solutions of various concentrations. 1,10-phenantroline was applied as chelating compound. Zonyl FSA was used as a phase-separation agent, while acetone or THF were used as solubilizing agents. It was found that Pd(II), Pt(II), and rare metals can be extracted in the sedimented phase at very high percentages (usually above 95%), but no In(III) extraction was observed.

4.3. Ion exchange

Ion exchange (IX) includes the selective adsorption of ionic species from aqueous on the solid phase (resin). In a further step, ions are stripped from a loaded solid ion exchanger to the aqueous phase producing concentrated solutions.

Ion exchange resins are characterized by large capacities, high efficiency, and short reaction times; hence, they are more-often applied in recycling processes as an energy-saving technique. Inoune and Nishirua [28] used highly porous XRD-7 resins impregnated with Cyanex 923 and Aliquat 336 for the adsorption of metal ions from a HCl solution simulating the leachate of the spent LCD panels. The solution was passed across two columns packed with resins. In the first column (with the resin impregnated with Aliquat 336), the major impurities (iron, tin, and zinc) were removed, while in the second column (with the resin impregnated with Cyanex 923), indium was selectively adsorbed. The loaded indium was then eluted with diluted sulfuric acid. The final solution was enriched more than ten times as compared to the feed solution.

Diaz-Pavón et al. [29] investigated the influence of HCl and In(III) concentrations in an aqueous solution as well as the amount of added resin on the recovery of indium ions using a cationic ion exchange Lewatit K-2621 resin. It was found that In(III) was removed from the solution preferably to Cu(II) and Zn(II) ions, but not to Fe(III) ions. The best conditions of the process were obtained for a minimum of 2.5 g/dm³ of the resin in the feed solution (In[III] uptake 16 mg/g in 0.01M HCl) and the use of 0.5M HCl in the elution stage at an eluant/resin volume ratio of 100. The final indium concentration in the aqueous solution reached 291 g/dm³, and this corresponded to a total indium recovery of about 88%.

The application of ion exchange polymeric resins for the adsorption of In(III) from sulfate acidic media was studied by Fortes et al. [30]. They used three chelating resins (Ionac SR-5, Ionac SR-12, and S950) as well as a strong acid cation exchange resin (Amberlite IR-120P). It was recommended to use an Ionac SR-5 resin with iminodiacetic functional groups as the most-selective concerning iron ions.

5. Final product recovery

5.1. Chemical precipitation

The chemical precipitation of hardly soluble compounds is one of the oldest methods for metal removal from a solution. However, some metals like aluminum or iron show precipitation properties similar to indium, making the latter difficult to separate. Literature data and practical applications usually use ammonia NH_{3aq} or phosphoric acid H₃PO₄ for the precipitation of hydrated In₂O₃ or InPO_{4r}, respectively. Hydrated oxide is produced at a pH level of about 6, while phosphate is obtained at a pH of about 4 [22].

5.2. Cementation

Cementation is one of the methods often used for the separation of indium from a solution in a metallic state. This is based on the differences in the electrochemical potentials of indium ($E^{\circ}_{\text{In}/\text{In(III)}} = -0.34 \text{ V}$) and other metals used for such purposes (mainly magnesium $E^{\circ}_{\text{Mg}/\text{Mg(II)}} = -2.37 \text{ V}$, aluminum $E^{\circ}_{\text{Al}/\text{Al(III)}} = -1.66 \text{ V}$, zinc $E^{\circ}_{\text{Zn}/\text{Zn(II)}} = -0.77 \text{ V}$).

Li et al. [13] studied the recovery of indium from used ITO targets. They precipitated indium from a purified sulfate solution with zinc plates of high purity. The process was carried out at pH = 1.2 at a temperature of 65°C for 40 h. Sponge indium was obtained as the final product, and process efficiency was over 99% (corresponding to the decrease of indium concentration from 54 g/dm³ to 0.12 g/dm³). The low purity of cemented indium requires further treatment of the solid. It can be melted with caustic soda before casting it into raw indium ingots. The purity of the latter is improved to 99.99% by electrorefining.

A more-detailed work on indium cementation was presented by Rochetti et al. [15]. They determined the influence of a concentration of zinc powder (2–100 g/dm³), solution pH (1–4), and cementation time (10–240 min) on the efficiency and purity of the final indium metal. A sulfate solution containing 35 mg/dm³ of In³⁺ was used. The highest indium recovery (99.8%, indium purity about 62%) was obtained at pH = 2 at zinc powder concentration 100 g/dm³. Indium cementation was almost completed (98%) for 20–60 min at pH = 3 and 5 g/dm³ of zinc. However, purity of the product was low, and the indium content in the solid was usually within a range of 36–48 wt%.

5.3. Electrowinning

Electrolytic recovery of indium from an aqueous solution is often used for production of a final metal of high purity.

Lee and Oh [31] investigated the effects of variables on the current efficiency and cell voltage of indium electrowinning from an acid chloride solution. It was found that the initial pH of electrolyte, temperature, and current density had a negligible effect on the current efficiency, and the cell voltage increased linearly with increased current density. The authors reported that a current efficiency of 90% may be achieved at a current density of 100 mA/cm², but the initial concentration of indium ions and NaCl should be higher than 50 g/dm³.

Bisselink and Panjer [32] studied potentiostatic electrowinning of indium from 1M and 6M HCl solutions containing 10 g/dm³ In³⁺. It was observed that efficient electrolysis can be carried out at a potential of –0.8 V vs. SCE at 20°C. The purity of the indium deposits was over 99% (arsenic, zinc, and vanadium were not co-deposited).

6. Conclusions

This paper has shown a review of literature data on the possibilities of indium recovery from ITO layers of obsolete LCD and LED displays. An analysis of ITO acid leaching showed that the final In(III) ion concentration of a few dozen mg/L can be expected in the solution. This results in the application of a special method for selective ions separation and preconcentration before final metal extraction; namely, SX, HoLLE, or IX. Final products (metal or compounds) can be obtained by chemical precipitation, cementation with zinc, or electrowinning.

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