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MATERIALS RECOVERY FROM WASTE LIQUID CRYSTALS DISPLAYS: A FOCUS ON INDIUM

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Alla mia famiglia,

sostegno vero.

ABSTRACT

The aim of this research project is to develop a hydrometallurgical technique to recover valuable materials from waste LCDs (Liquid Crystal Displays).

The interest in this field is mainly related to the fact that the current treatment and recovery techniques are only partially developed: whilst for some components separated after primary dismantling (metallic fractions and metal rich-components such as printed circuit boards and cables) the recovery paths are quite well established, some others, such as the LCD glass panel, require further investigation.

The LCD panels contain a number of valuable materials (indium, glass, polarizing films) and their recovery could lead to both economic and environmental advantages.

Indium, in particular, present in the LCD panel as indium tin oxide layer (ITO, i.e. *indium tin oxide*), has been recently included in a list of “critical raw materials” by the European Commission and its recovery from secondary sources is gaining increasing attention among the scientific community.

The first step of the recovery process here proposed is aimed at removing the polarizing film from the glass substrate. Different treatment options were tested, such as thermal and chemical ones. Thermal treatments were performed both at high (T=100-240°C, 20°C/h) and at low temperature, the latter by employing liquid nitrogen (T = -196°C). Chemical treatments were carried out by soaking the waste LCDs into a number of organic solvents such as acetone, limonene, ethyl acetate and isopropyl alcohol; the influence of the ultrasound treatment was also investigated.

The best results were achieved by liquid nitrogen, since approximately 20 minutes were sufficient to remove the polarizing film completely; moreover, the obtained product did not show significant degradation.

The second step of the recovery process is the leaching (or solid/liquid extraction), aimed at dissolving the valuable metals from the glass substrate. In order to evaluate the best operative conditions, a number of leaching tests were performed on a pure reagent (indium tin oxide, -325 mesh, ≥99.99% trace metals basis, Sigma Aldrich) by varying the leaching agent, the contact time and the liquid/solid ratio.

The best results were achieved by employing HCl 6N as a lixiviant, since in a relatively short time (6h) 90% indium was extracted. The operative conditions thus defined (HCl 6N, t=6h) were then employed for the leaching of the LCD glass substrate, i.e. the solid residue obtained after the removal of the polarizing film.

The last step is aimed at recovering indium from the leachate. In order to do that, different separation techniques can be employed, such as solvent extraction, precipitation and ion exchange. Solvent extraction is widely used due to its characteristic of selectivity and high recovery efficiency; however organic extractants, which are potentially hazardous for human health and the environment, are often employed. In this work, indium recovery was investigated through solvent extraction with aqueous-biphasic systems (ABSs), which are now gradually emerging as an environmentally-sound alternative to the classical "oil-water" extraction systems due to their characteristics of low cost, reduced flammability and reduced toxicity.

Indium extraction tests in an aqueous biphasic system PEG-ammonium sulfate-water based were performed as a function of PEG concentration, salt concentration and molecular weight of PEG (PEG 3,350 and PEG 10,000), using 1,10 phenantroline as a ligand.

Experimental data showed that indium partitioning between the lower and the upper phase is quite independent from the composition of the system, since 80-90% indium is extracted in the lower phase and 10-20% in the upper phase. By increasing PEG concentration, the ratio between the lower and the upper phase volume decreases; since the percentage of indium extracted in the lower phase is invariable, this leads to a concentration of the species of interest.

Indium extraction is quite similar by employing PEG 3,350 as well as PEG 10,000, however the volume ratio decrease is more significant if PEG 3,350 is employed: in correspondence of [PEG]=18% w/w, the ratio between the lower and the upper phase volume is ~1.1 and indium concentration in the lower phase is 1.5 times the initial one.

Further extraction tests should be performed on the leachate (i.e. the aqueous phase coming from the leaching of the glass substrate with HCl 6N) in order to verify the selectivity of the recovery technique compared to other ions (mainly tin).

Moreover, techno-economic evaluations should be carried out in order to verify the possibility to apply the proposed process in a full-scale treatment plant.

SOMMARIO

L’attività di ricerca svolta nell’ambito della presente tesi ha avuto come obiettivo lo sviluppo di tecnologie di recupero di materiali da schermi LCD (Liquid Crystal Displays) a fine vita.

L’interesse nel settore nasce dalla constatazione che, allo stato attuale, tali tecnologie sono sviluppate in maniera soltanto parziale: mentre per alcune componenti separate a valle del trattamento primario (frazioni metalliche, cavi e schede elettroniche) si dispone di tecnologie di recupero consolidate, altre, quali ad esempio i pannelli in vetro contenenti i cristalli liquidi, necessitano di maggiore approfondimento.

All’interno dei pannelli LCD sono presenti componenti di valore (indio, vetro, film polarizzante), il cui recupero potrebbe tradursi in considerevoli vantaggi sia di tipo economico sia di tipo ambientale. L’indio, ad esempio, ivi presente sotto forma di sottile strato di ossido di indio e stagno (ITO, ossia *indium tin oxide*), è stato di recente incluso dalla Commissione Europea nell’elenco dei cosiddetti “materiali critici” ed il suo recupero a partire da fonti secondarie sta ricevendo interesse crescente da parte della comunità scientifica.

La prima fase del processo di recupero proposto è finalizzata alla rimozione del film polarizzante dal substrato in vetro; a tale scopo sono state messe a confronto tecniche differenti, di tipo termico e di tipo chimico. Le prove termiche sono state effettuate sia a temperatura elevata (T=100-240°C, 20°C/h) sia a bassissima temperatura, mediante contatto con azoto liquido (T=-196°C). Il trattamento di tipo chimico è stato condotto mettendo a contatto i pannelli LCD con una serie di solventi organici (acetone, limonene, acetato di etile e alcool isopropilico); è stata inoltre confrontata l’efficienza di rimozione con e senza l’ausilio del trattamento ad ultrasuoni. I risultati ottimali sono stati raggiunti mediante trattamento con azoto liquido in quanto il tempo necessario al distacco del film è inferiore a 20 minuti ed il prodotto ottenuto non presenta sensibili fenomeni di degradazione.

La seconda fase del processo di recupero è la lisciviazione (o estrazione solido/liquido), finalizzata a portare in soluzione i metalli di interesse. Al fine di poter definire le condizioni operative ottimali, sono state in primo luogo effettuate prove di lisciviazione su un reagente puro (ossido di indio e stagno) al variare di una serie di parametri operativi quali agente lisciviante, tempo di contatto e rapporto liquido/solido.

I risultati migliori sono stati ottenuti impiegando acido cloridrico quale agente lisciviante, in quanto risultato in grado di portare in soluzione circa il 90% di indio in un tempo relativamente breve (6 ore).

Le condizioni ottimali così definite (HCl 6N, t=6h) sono state impiegate per la lisciviazione del substrato in vetro, ossia il residuo solido ottenuto a valle della rimozione del film polarizzante.

L'ultima fase del processo è finalizzata al recupero dell'indio dalla fase acquosa. A tale scopo possono essere impiegate tecniche di separazione differenti, quali precipitazione, estrazione con solvente, scambio ionico. Benché l'estrazione con solvente tradizionale (estrazione *oil-water*) sia considerata una tecnologia particolarmente efficiente per la rimozione selettiva di ioni metallici da soluzioni acquose, la ricerca si sta orientando verso lo sviluppo di sistemi di estrazione alternativi, in seguito alla crescente consapevolezza della necessità di limitare la produzione, l'impiego e lo smaltimento di solventi organici.

L'estrazione mediante i cosiddetti Sistemi Acquosi Bifasici (ABSs) risulta essere una delle tecniche maggiormente promettenti in tal senso: a differenza dei solventi organici, essi non sono infiammabili né tossici e sono inoltre disponibili sul mercato ad un costo contenuto.

Sono state condotte prove di estrazione dell'indio mediante un sistema bifasico costituito da PEG-solfato di ammonio-acqua in presenza di 1,10 fenantrolina quale agente complessante, al variare della concentrazione del PEG e del solfato di ammonio nonché della tipologia di PEG impiegato (PEG 3,350 e PEG 10,000).

I risultati sperimentali ottenuti hanno evidenziato che la ripartizione dell'indio è pressoché indipendente dalla composizione del sistema, in quanto l'80-90% è estratto nella fase pesante ed il 10-20% nella fase leggera; poiché in tale sistema il rapporto volumetrico tra la fase pesante e quella leggera diminuisce all'aumentare della concentrazione del PEG, tale aumento di concentrazione contribuisce all'arricchimento dell'indio nella fase pesante.

I risultati ottenuti con il PEG 3,350 sono, infine, confrontabili con quelli ottenuti con il PEG 10,000; tuttavia la diminuzione del rapporto volumetrico è maggiormente significativa se si impiega il PEG 3,350. In particolare, se la concentrazione del PEG è pari al 18%, il rapporto volumetrico tra le fasi è pari a circa 1.1 e la concentrazione dell'indio nella fase inferiore è 1.5 volte quella iniziale.

Ulteriori prove di estrazione dovranno essere condotte sulla liscivia (ossia sulla fase acquosa che si ottiene a valle della lisciviazione del substrato in vetro con HCl 6N), al fine di verificare la selettività del processo proposto rispetto ad altri ioni presenti nella liscivia stessa (fondamentalmente stagno).

Dovranno, infine, essere effettuate valutazioni di tipo impiantistico ed economico per valutare l'effettiva applicabilità di tale processo su scala industriale.

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1. INTRODUCTION

1.1 THESIS CONTENT

The thesis is composed of six chapters:

- Chapter 1 defines the aim of the research project;
- in Chapter 2 a focus on critical raw materials contained in waste flat panel displays is provided;
- Chapter 3 describes the current treatment technologies for waste flat panel displays; moreover a literature review on material recovery from the LCD panel is provided;
- in Chapter 4 the materials and methods employed during the experimentation are illustrated;
- Chapter 5 presents the results of the experimental tests carried out on waste liquid crystal displays;
- Chapter 6 shows the overall outcome of the work and gives suggestions and recommendations for further research.

Part of the work presented in this thesis is included in two papers:

- Fontana, D., Forte, F., De Carolis, R., Grosso, M. Indium recovery from waste liquid crystal displays. Symposium on Urban Mining, SUM 2014. May 19th-21th 2014, Bergamo; submitted to Waste Management (Special Issue: Urban Mining);
- Biganzoli, L., Falbo, A., Forte, F., Rigamonti, L., Grosso, M. LCA of the WEEE management system in Lombardia. 4th International Conference on industrial and hazardous waste management. September 2nd-5th 2014, Chania, Crete.

1.2 AIM OF THE RESEARCH PROJECT

Flat panel displays (FPDs) are becoming more and more popular in technological applications as they are definitely replacing the cathode ray tube devices. Among flat panel displays, the liquid crystal display technology currently holds the mainstream position and is widely used in notebook computers, desktop computer monitors and televisions (Li et al., 2009; Bucher et al., 2012).

Due to the presence of hazardous components, that require adequate treatment and disposal operations, and to the relatively high content of critical raw materials that can be recovered, treatment of waste FPDs has been gaining increasing attention among the scientific community in recent years.

In EU flat panel displays are fed into a separate recycling process after collection (Buchert et al., 2012). Treatment process generally consists in a disassembly step aimed at removing the hazardous components and the valuable ones for further treatment and recovery. The LCD glass panels (i.e. the inner part of a LCD TV/monitor after primary dismantling) are currently stocked at the plant or incinerated, since no recycling process is available yet at the industrial scale; this practice obviously leads to a loss of resources potentially recoverable, such as the critical metal indium as well as the glass fraction and the polarizing films.

In the last decades a number of works have been focusing on material recovery from end-of-life LCDs. The main driver for waste LCDs treatment lies in indium recovery; to this aim hydrometallurgical techniques are usually employed, consisting in a leaching step, aimed at dissolving the metals of interests, followed by a separation step that can be performed through different techniques (such as precipitation, cementation, solvent extraction, ion exchange, adsorption and electro-winning). Some pretreatments can be performed before the leaching aimed at removing the polarizing film and/or the liquid crystals.

In most cases thermal treatment at high temperature is employed for the removal of the polarizing film from the glass substrate (Li et al., 2009; Lee et al. 2013; Ma et al., 2012), which implies high energy consumption and potential atmospheric emissions.

Regarding the leaching, the analysis of the available literature showed that it is often carried out by employing acid mixtures with inhomogeneous concentration values (Li et al., 2009; Lee et al., 2013; Ruan et al., 2012; Yang et al., 2013; Virolainen et al., 2011) so that a comparison among the lixiviants (in terms of leaching efficiency) is not always straightforward.

In most cases solvent extraction is used as separation step, due to its characteristics of high selectivity and high recovery efficiency; however, organic extractants are often employed, which are potentially hazardous for human health and the environment (Virolainen et al., 2011; Ruan et al., 2012; Yang et al., 2013).

In this work material recovery from waste liquid crystal displays was experimentally investigated at the laboratory scale.

The polarizing film was first of all removed from the glass substrate; to this aim different treatment options were tested (thermal and chemical).

Indium leaching was then investigated in a more appropriately way, since the experiments were performed by keeping the acid concentration constant (6N). Leaching tests were first carried out on a pure reagent (indium tin oxide, -325 mesh, ≥99.99% trace metals basis, Sigma Aldrich) in order to define the best operative conditions; then, leaching of the LCD glass substrate was performed.

Indium recovery from the aqueous phase was then investigated through solvent extraction with aqueous biphasic systems (ABSs), a relatively new kind of extraction media which is gradually emerging as an environmentally-sound alternative to the classical “oil-water” solvent extraction.

2. CRITICAL RAW MATERIALS IN WEEE: THE CASE OF INDIUM

2.1 INTRODUCTION

“Raw materials” are “*fundamental to Europe’s economy, growth and jobs and essential for maintaining and improving our quality of life*” (European Commission, 2010).

Besides energy carriers (such as oil and gas) a key rule is played by metals, minerals and biotic materials. “High-tech metals”, in particular, are essential for the manufacturing of modern technological devices such as flat panel displays, mobile phones, photovoltaic cells and electric cars; the list includes cobalt, lithium, tantalum, indium and molybdenum, just to number a few.

European economy is highly dependent on raw materials imports. Even if Europe can rely on valuable deposits, mining processes face a number of complex challenges, related to project economics, sound management of environmental impacts, permitting, access to finance and the establishment of a marketing channel for the mined product (ERECON, Conference Draft, 2014). Currently raw materials production and supply occur mainly in non-European countries: as reported in Figure 1, 61% of the world platinum group metals (PGMs[1]) production comes from South Africa, while China provides the majority of the world’s supply of rare-earths (European Commission, 2014).

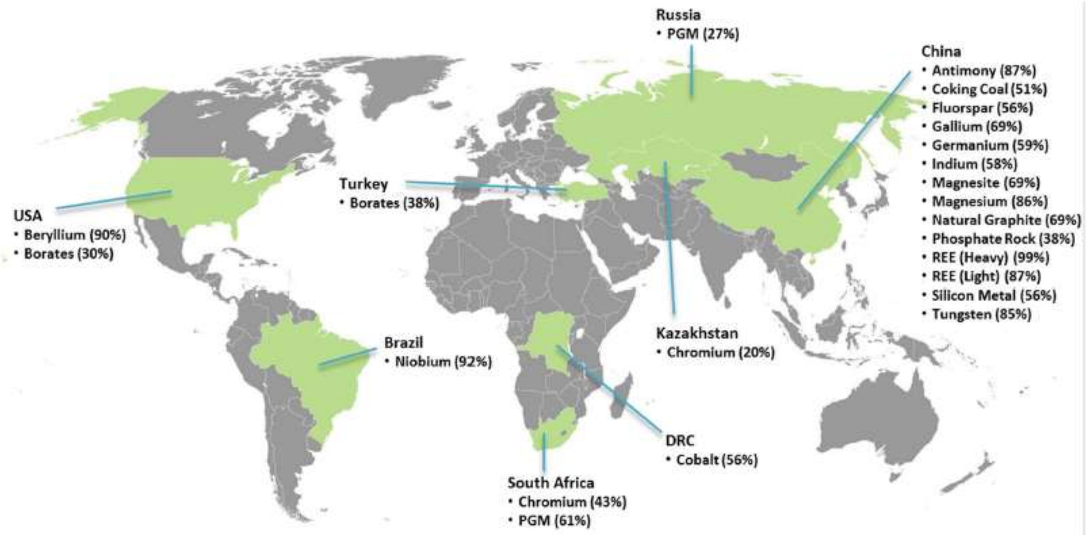

Figure 1. Major supplying countries of the EU Critical Raw Materials (European Commission, 2014)

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[1] PGMs: Platinum Group Metals (palladium, platinum, rhodium, ruthenium, iridium, osmium)

In order to turn this trend and to secure a reliable and sustainable access to non-energy raw materials, the European Commission launched an integrated strategy in 2008, called “EU Raw Materials Initiative”: the objective is to define a list of “critical” raw materials at the European level and to propose targets for their extraction and recycling.

According to the EU experts working group, a raw material is defined “critical” when “*the risks of supply shortage and their impacts on the economy are higher compared with most of the other raw materials*”.

In order to assess this “criticality”, two main components were used in the EU methodology:

1. *Economic importance*

It is independent from the raw material market price and it focuses on the benefit that it has for the manufacturing economy. This index is measured by breaking down the raw material main uses and attributing to each of them the value added of the economic sector that it has as input.

2. *Supply risk - Poor governance*

It takes into account three factors: substitutability, end-of-life recycling rates and high concentration of producing countries with poor governance. Substitutability measures the difficulty to substitute the material, scored and weighted across all applications; the end-of-life recycling rate measures the proportion of metal and metal products produced from end-of-life scrap and metal-bearing low grade residues; poor governance takes into account a number of different parameters, such as political stability, government effectiveness and regulatory quality.

The first criticality analysis was published in 2010 (European Commission, 2010): fourteen critical raw materials were identified from a candidate list of forty-one.

The updated version (European Commission, 2014) includes thirteen of the fourteen materials identified in the previous report; six new materials enter the list (borates, chromium, coking coal, magnesite, phosphate rock and silicon metal) and greater detail is provided for the rare earth elements, by splitting them into ‘light’[2] and ‘heavy[3]’ categories.

Twenty raw materials were thus selected; they are included in the red-colored threshold reported in Figure 2.

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[2] Light rare earths (LREE): the elements lanthanum to samarium, including scandium

[3] Heavy rare earths (HREE): the elements europium to lutetium, including ytttrium

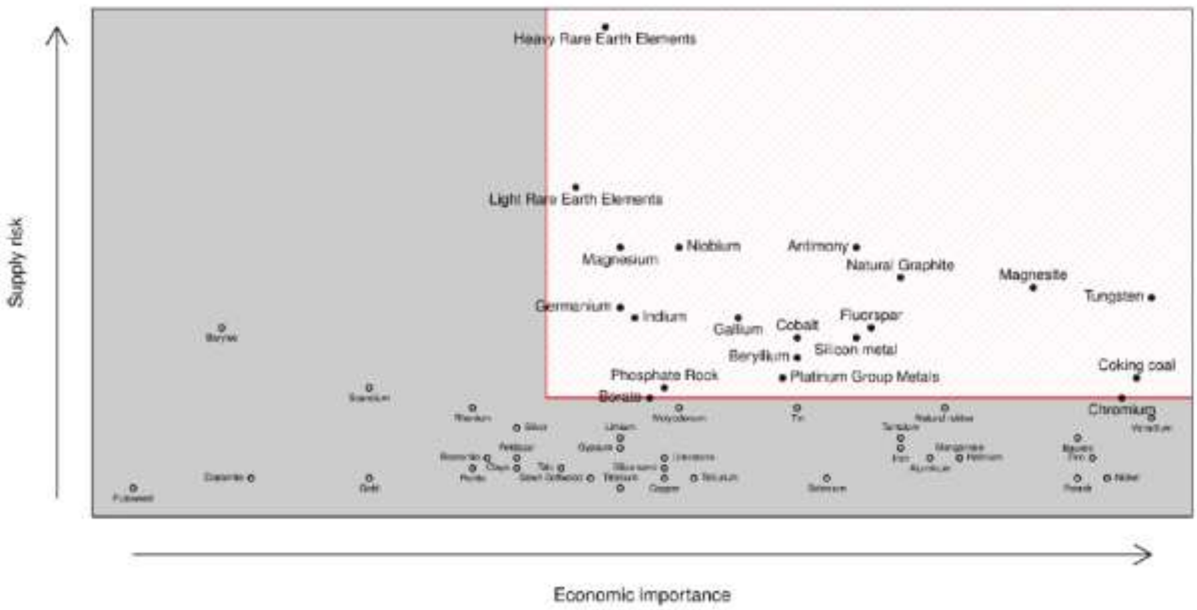

Figure 2. Critical Raw Materials for the EU (European Commission, 2014)

The identified critical raw materials are also listed in Table 1:

Table 1. Critical raw materials for the EU (European Commission, 2014)

Antimony	Beryllium	Borates	Chromium
Cobalt	Coking coal	Fluorspar	Gallium
Germanium	Indium	Magnesite	Magnesium
Natural Graphite	Niobium	PGMs	Phosphate Rocks
REEs (Heavy)	REEs (Lights)	Silicon Metal	Tungsten

2.2 URBAN MINING FROM WEEE

Most of the materials identified by the European Commission can be found in secondary sources such as end-of-life products (EoL) and production residues. In this perspective the concept of “Urban Mining”, defined as “the process of reclaiming compounds and elements from products, buildings and waste” (Graedel, 2011) is growing in importance. Recovery and recycling practices are now strongly encouraged and policy actions are suggested in order to make them more efficient. These measures should limit the demand for new supplies of elements, increasing the lifetime of our reserves infinitesimally (Dodson et al., 2012).

Waste from electrical and electronic equipment (WEEE, or e-waste) can be regarded as a valuable source of raw materials for the European economy. They are a “strategic waste” due to the presence of both hazardous components, which require adequate treatment before safe disposal, and valuable ones, which can potentially be recovered. As an example, in Table 2 the mean content of critical raw materials in notebooks are reported (Buchert et al., 2012):

Table 2. Mean content of critical raw materials in notebooks (incl. LCD monitors) (Buchert et al., 2012)

Metal	**Content per notebook (CCFL[4])**	**Content per notebook (LED[5])**	**Occurrence**
	[mg]	[mg]	
Cobalt	65,000	65,000	Lithium-ion batteries (100%)
Neodymium	2,100	2,100	Spindle motors (37%), voice coil accelerators (34%), loudspeakers (30%)
Tantalum	1,700	1,700	Capacitors on the motherboard (90%), capacitors on other PCBs (10%)
Silver	440	440	Motherboard (57%), other PCBs (43%)
Praseodymium	270	270	Voice coil accelerators (53%), loudspeakers (47%)
Gold	100	100	Motherboard (54%), other PCBs (46%)
Dysprosium	60	60	Voice coil accelerators (100%)
Indium	40	40	Display & background illumination (100%)
Palladium	40	40	Motherboard (64%), other PCBs (36%)
Platinum	4	4	Hard disk drive platters (100%)
Yttrium	1.80	1.60	Background illumination (100%)
Gallium	-	1.60	LED background illumination (100%)
Gadolinium	0.01	0.75	Background illumination (100%)
Cerium	0.08	0.10	Background illumination (100%)

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[4] CCFL: cold cathode fluorescent lamp

[5] LED: light emitting diode

Europium	0.13	0.03	Background illumination (100%)
Lanthanum	0.11	-	CCFL background illumination (100%)
Terbium	0.04	-	CCFL background illumination (100%)

WEEE production is continuously growing: it was estimated that approximately 8.3 million to 9.1 million tonnes of e-waste were generated in 2005 in EU and by 2020 this figure will rise to 12.3 million tonnes (United Nations University, 2008).

However the current treatment and recovery technologies can only recover a small part of metals and most of the valuable “strategic metals” are getting lost (Dodson et al, 2012).

2.3 WASTE FPDs: A SOURCE OF VALUABLE MATERIALS

Among WEEE, waste flat panel displays (FPDs) play a key rule: they are among the fastest growing waste stream in the European Union, with a 3-5% annual growth rate (Dodson et al., 2012).

Due to presence of the critical element indium, waste FPDs management is gaining increasing attention among the scientific community and a number of research projects are now focusing on the development of a holistic strategy aimed at recovering valuable materials from this kind of waste stream.

2.3.1 PRINCIPLE OF OPERATION AND MATERIAL COMPOSITION OF FPDs

Flat panel displays are increasingly used in modern appliances, including notebooks, desktop computer monitors and televisions. Compared to cathode ray tubes devices (CRTs), FPDs show a number of advantages, such as less volume, lighter weight and lower power consumption (Yang et al., 2012).

The main FPDs producer is South Korea (Tangjeong Crystal Valley); in Italy there is no direct manufacturing of FPD appliances, the main companies (such as Mivar s.a.s.) being only focused on the assembling of electronic components produced abroad.

Three different flat panel display technologies are currently in use (Bucher et al., 2012):

- Liquid crystal displays (LCDs)
- Plasma display panels (PDPs)
- Organic light emitting diode panels (OLEDs)

Liquid crystal displays

Liquid crystal displays is a non-emissive technology using a backlight as a light source.

The principle of operation of an LCD device (Figure 3) can be described as follows: a backlight passes through a polarized glass; at the same time, electrical currents cause alignment of the liquid crystal materials to form the variations of light passing into a second polarized glass, which occurs during the formation of colors and images (Jucknesky et al., 2013). Thin Film Transistor (TFT) technology is used to drive or control the orientation of the liquid crystals (pixels).

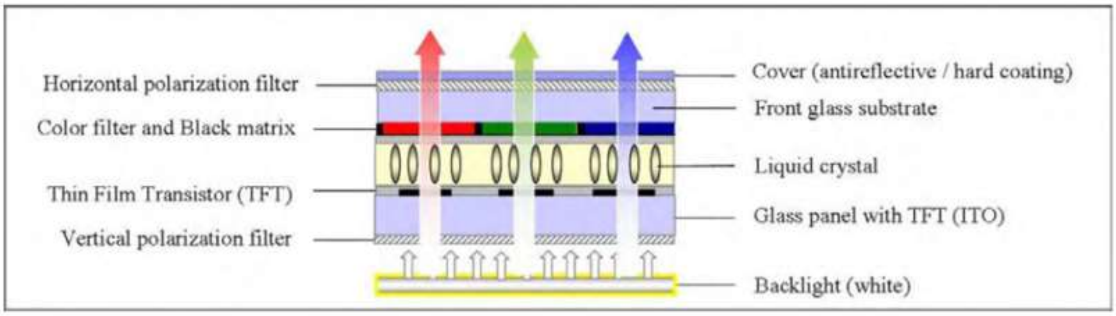

Figure 3. Principle design of a Liquid Crystal Display (Fraunhofer IZM, 2007)

Besides the cold cathode fluorescent lamps (CCFLs) mainly used in the past, light emitting diodes technology (LEDs) is now growing in importance (Buchert et al., 2012).

Plasma displays

Plasma display panel (Figure 4) is a self-emissive technology where light is created in a cell by phosphors excited by a plasma discharge between two glass substrates. Each cell is filled with a gas (neon and xenon) and sandwiched between layers of electrodes (Fraunhofer IZM, 2007):

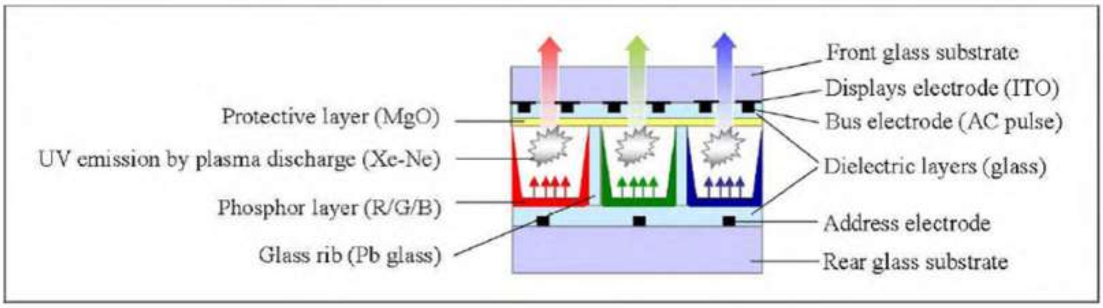

Figure 4. Principle design of a Plasma Display (Fraunhofer IZM, 2007)

Plasma screens are currently not used as PC monitors. They are usually produced for diagonals of around 37 inches and above and are therefore employed almost exclusively in the TV sector (Bucher et al., 2012). The illuminant effectiveness (brightness) is reduced if cell size is smaller as gas volume is also reduced.

Today only five PDPs are competing in the market: LG and Samsung, from Korea, and Panasonic, Pioneer and Fujitsu-Hitachi-Plasma, from Japan (Fraunhofer IZM, 2007).

OLED displays

OLED displays operate on the attraction between positively and negatively charged particles. When voltage is applied, one layer becomes negatively charged with respect to another transparent layer; as energy passes from the negatively charged layer (cathode) to the other one (anode), it stimulates the organic material between the two, which emits light visible through an outermost layer of glass.

Differently from LCD displays, OLEDs do not require backlighting, so power consumption is lower. They are mainly employed for the manufacturing of small-size color video displays, such as mobile phones and digital camera screens. It was estimated that full computer displays with OLED technologies was 4-5 years away in 2005 (European Commission DG TREN, 2005), but this statement is still valid.

LCD technology has been currently holding the mainstream position of the flat panel displays (Li et al., 2009; Bucher et al., 2012).

As reported in Figure 5, a LCD monitor is composed of a front frame, the LCD panel, plastic housing, film set, back frame, backlight assembly, a power supply and controller, a rear cover and a base/stand (Socolof et al., 2001; O'Mara, 1993; den Boer, 2005; Franke et al., 2006).

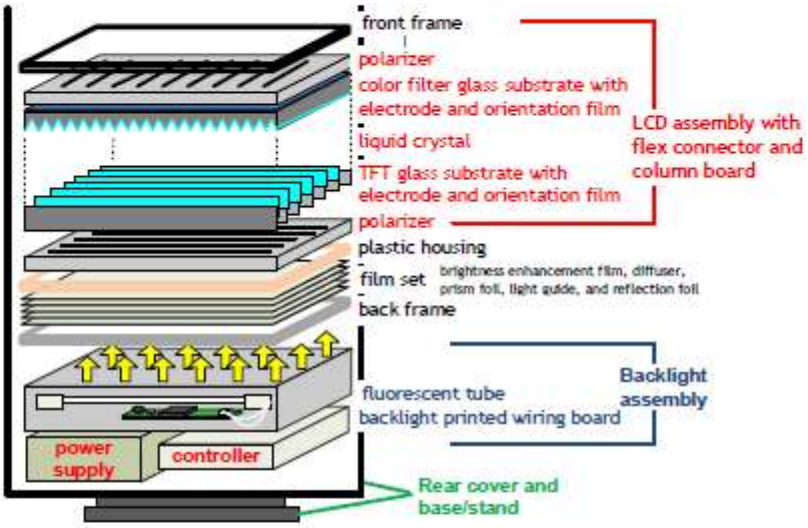

Figure 5. Structure of an LCD monitor (Lee and Cooper, 2008)

The structure of the LCD panel (i.e. the inner part of a LCD monitor/TV after primary dismantling) is shown in Figure 6:

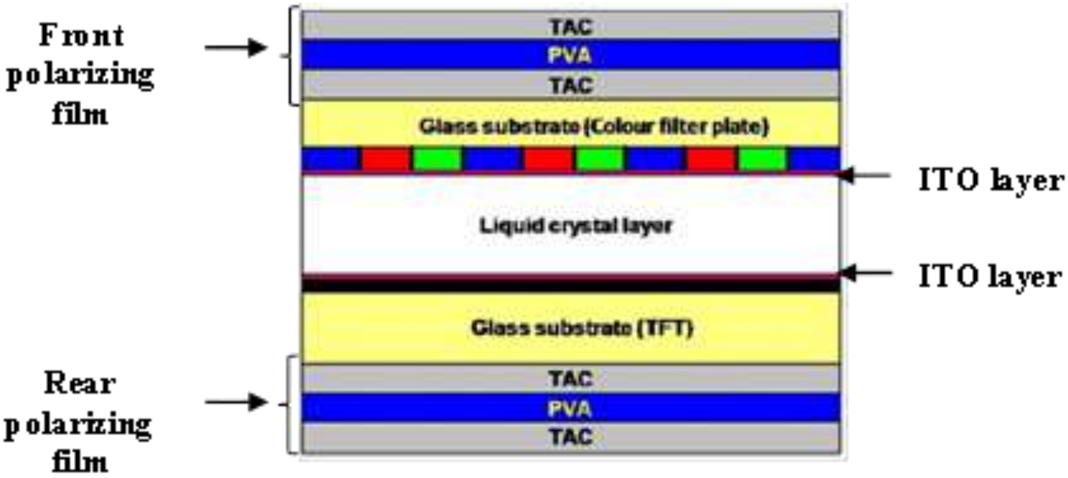

Figure 6. LCD panel structure (adapted from Dodson et al., 2012)

It is constituted of two polarizing films, two glass layers coated with indium tin oxide (ITO) film and the liquid crystals layer (Wang et al., 2013; Dodson, 2012).

Indium tin oxide

Indium is present in FPD devices as transparent conductive indium tin oxide film; these ITO layers are composed of 80-90% In_2O_3 and 10-20% SnO_2 (Virolainen et al., 2011; Lee et al., 2013). In the LCD devices two layers of ITO are applied, while OLED displays only have one layer.

Several methods can be used for ITO deposition on the glass substrate, but DC[6] and RF[7] magnetron sputtering are the most attractive because of high deposition rate, good reproducibility and possibility of using commercially available large area sputtering systems (Lee et al., 2004; Park et al., 2005). Typically, magnetron sputtering processes are performed at high substrate temperatures ($\geqslant$200 °C), as these allow the best results in terms of layer transparency and conductivity (Kurdesau, 2004).

In LCD displays with LED background illumination, indium is used not only as ITO layer, but also as a component of the LED semiconductor chip (mainly constituted by indium gallium nitride).

Literature data about ITO film thickness and indium content in FPDs are very different, as reported in Table 3.

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[6] DC: diode

[7] RF: radio frequency

Table 3. Published values on film thickness and indium content of LCD displays

Ref.	**mg ITO/m^2**	**nm/layer**	**mg In/m^2**
ISI, 2009	4,000	1,667	3,120
Socolof et al., 2003	7,176	2,990	5,597
Martin, 2007	700	292	150
Beker and Hettich, 2003	192/240	80/100	150/187
Bogdanski, 2009	72/192	30/80	56/150
Boni and Widmer, 2011	300	125	234

Wang (2009) reported a value of 102 mg/kg as indium content in the glass substrate, while Fem and Iuta (2011) determined a mean indium content of 174 mg/kg of waste display.

Glass substrate

The glass substrate accounts for 85% w/w of the LCD panel (Zhuang et al., 2012). Several types of materials can be used, such as alkaline-earth aluminosilicate, alkaline earth boro-aluminosilicate, barium aluminoborosilicate, barium borosilicate and soda lime. The current leader in glass technology is Corning Inc. (O'Mara, 1993); their latest innovation is represented by the EAGLE XGTM glass substrate, which is free of arsenic, antinomy and barium (Corning Display Technologies, 2008).

On the front glass substrate is the color filter layer; it consists of a black matrix, colorants and binders, an overcoat layer and the ITO layer (Yen and Tso, 2004). Material composition is reported in Table 4:

Table 4. Materials for color filter layer (Yen and Tso, 2004; Watanabe et al., 1996)

Color Filter Layer	**Materials identified**
Black matrix	Cr, Ni, black polymer resin, black chrome (Cr/CrO or Cr/CrO$_2$), Fe/FeOx, Mo/MoOx
Color filter colorants	Dyes or pigments
Photopolymers/binders	Gelatin, casein, acrylic, polyimide, polyvinyl alcohol, epoxy, melamine, polyester
Overcoat layer	Transparent acryl resin, polyimide resin or polyurethane resin
Conductive electrode	Indium tin oxide

On the rear glass substrate is the TFT layer; as reported in Table 5, it contains three terminals, a gate insulator, a semiconductor, an ohmic contact, a passivation layer and the conductive electrode.

Table 5. Materials for TFT layer (Socolof et al., 2001; O'Mara, 1993; den Boer, 2005; Katayama, 1999; Luo, 1997; Kuo et al., 1999; Tsukada, 1996)

TFT layer	**Materials identified**
Gate electrode and source/drain electrode	Refractory metals (Ta, Cr, Mo, W), Ti, Cu, Al, Al alloys, Ta-Mo, Mo-W, Cr-Ni, Ti-Mo, Mo-Al, Ti-Al-Ti, other dual or triple layers
Gate insulator (dielectric)	SiN, SiO, SiN_x, SiO_2, SiO_xN_y, Si_3N_4, Ta_2O_5, Al_2O_3, dual dielectrics
Semiconductor	a-Si:H
Ohmic contact	n^+ a-Si:H
Passivation layer	SiN, Polymer overcoat
Conductive electrode	Indium tin oxide

Polarizing films

Polarizing films account for 15% w/w of the LCD panel (Zhuang et al, 2012). They are generally constituted by a layer of iodine doped-polyvinyl-alcohol (PVA) sandwiched between two protective layers of cellulose triacetate (TAC) (Dodson et al., 2012). This complex multilayer film is assembled on the glass substrate by using a pressure sensitive adhesive (PSA) composed of acrylic polymers (Nam et al., 2001; Jin et al., 2009; Passamani, 2011), as shown in Figure 7:

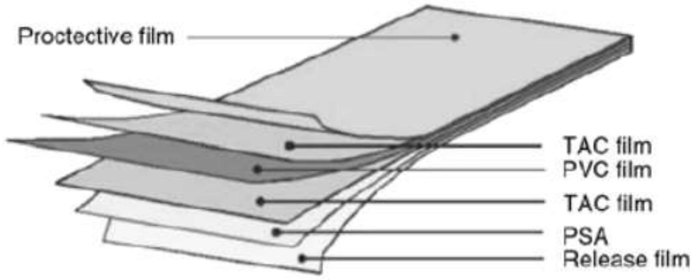


Figure 7. Polarizing film (Jin et al., 2009)

PVA layer is used to produce the polarized light. TAC layer is employed as protective film thanks to its characteristics of high transmittance (>93%), low birefringence and high thermal stability. PSA is also used a ligand between the several layers of the polarizing film; its properties are strongly affected by chemical composition, surface treatment, thickness and type of manufacturing process. Release film is rolled away when the polarizing film is assembled on the glass substrate (Passamani, 2011).

The polarizing film market is currently dominated by Nitto Denko, who has captured 35% of the total market share for several years. The rest of the market is dominated by Optimax, Sumitomo, LG Chemical and Santriz (Lee and Cooper, 2008).

Liquid crystals

The inner part of the LCD module is filled with liquid crystals, a mixture of aromatic-based polymers which account for 0.1% w/w of the LCD panel (Zhuang et al., 2012). The main liquid crystal compositions are biphenyl, azomethine, pyrimidine or difluorophenylene, with a 10:25 mixture of the individual components (Beker and Hettich, 2003; Zuang et al., 2012). Today 69% of liquid crystals are prepared by Merck KGaA (Germany), holding approximately 2,500 patents on liquid crystals and mixtures (Lee and Cooper, 2008).

2.4 INDIUM

2.4.1 CHEMICAL PROPERTIES AND ABUNDANCE

Indium (atomic number 49) is a malleable, silvery-white element in subgroup IIIA of the periodic table (USGS, 2004). It was discovered in 1863 by F. Reich and T. H. Richter during spectrometric analysis of sphalerite ores at the Freiberg School of Mines in Germany (Reich and Richter, 1863); its name derives from the indigo blue spectral lines that led to its identification (Felix, 2000).

Some physical properties are reported in Table 6:

Table 6. Indium physical properties (Felix, 2000)

Electronic configuration	[Kr] $4d^{10}\ 5s^2\ 5p^1$
A_r	114.82
Crystal structure	tetragonal A 6
Density at 293.15 K	7.310 g/cm^3
Enthalpy of fusion	3.26 kJ/mol
Enthalpy of vaporization	231.2 kJ/mol
Thermal conductivity (273.15 – 373.15 K)	71.1 Wm^{-1} K^{-1}

The most common valence of indium is three; monovalent and bivalent indium compounds with oxygen sulfur and halogens are also known (Felix, 2000).

Indium abundance in the continental crust is estimated to be approximately 0.05 ppm. It is most commonly recovered from the zinc-sulfide ore mineral sphalerite (ZnS), with an average content from less than 1 ppm to 100 ppm (USGS, 2011). Other important indium-containing minerals are lead and copper sulfides (Table 7).

Table 7. Indium contents of some minerals (Roskill, 1987)

Mineral	**Composition**	**Indium content [ppm]**
Sphalerite	ZnS	0.5-10,000
Galena	PbS	0.5-100
Chalcopyrite	$CuFeS_2$	0-1,500
Enargyte	Cu_3AsS_4	0-100
Bornite	Cu_5FeS_4	1-1,000
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	0.1-160
Covellite	CuS	0-500
Chalcocite	Cu_2S	0-100
Pyrite	FeS_2	0-50
Stannite	Cu_2FeSnS_4	0-1,500
Cassiterite	SnO_2	0.5-13,500
Wolframite	$(Fe,Mn)WO_4$	0-16
Arsenopyrite	FeAsS	0.3-20

2.4.2 PRIMARY PRODUCTION AND CONSUPTION BY END-USE

Indium deposits are located in China (Dachang district and Yunnan), Peru, Canada, United States and Australia (Schwarz-Schampera and Herzig, 2002).

The majority of global indium supply is currently from China: it was estimated that in 2010 more than 81% of the EU's indium imports originated from China (European Commission, 2010) which is responsible for more than 50% of global production (Polinares, 2012).

The main world producing countries are listed in Table 8 (USGS, 2013):

Table 8. Indium world refinery production (USGS, 2013)

	Refinery production [t]	
	2011	2012
China	380	390
Canada	75	70
Japan	70	70
Korea	70	70
Belgium	30	30
Brazil	5	5
Republic of Russia	5	5
Other countries	27	30
World total (rounded)	662	670

Indium is usually recovered as a by-product of zinc production and refining. The calcined ore is dissolved in sulphuric acid; then iron is removed as jarosite or oxide and zinc powder is added to remove other impurities including indium. These impurities are selectively re-dissolved in hydrochloric acid and selectively re-precipitated with copper dust. Indium is finally refined electrolytically; the obtained product is 99.9999% purity-grade (UK Energy Research Centre).

Japan is the largest consumer of primary indium, accounting for about a third of global consumption, followed by United States and China (USGS, 2011).

The majority of global indium consumption is represented by indium tin oxide (ITO) thin film (USGS, 2011), widely used in the manufacturing of flat panel displays and solar cells (Li et al., 2011). Alloys and solders are the second leading end use of indium globally; another important use is represented by semiconductor materials for light-emitting diodes (LEDs) and laser diodes (USGS, 2013). Indium consumption by end-use is shown in Figure 8:

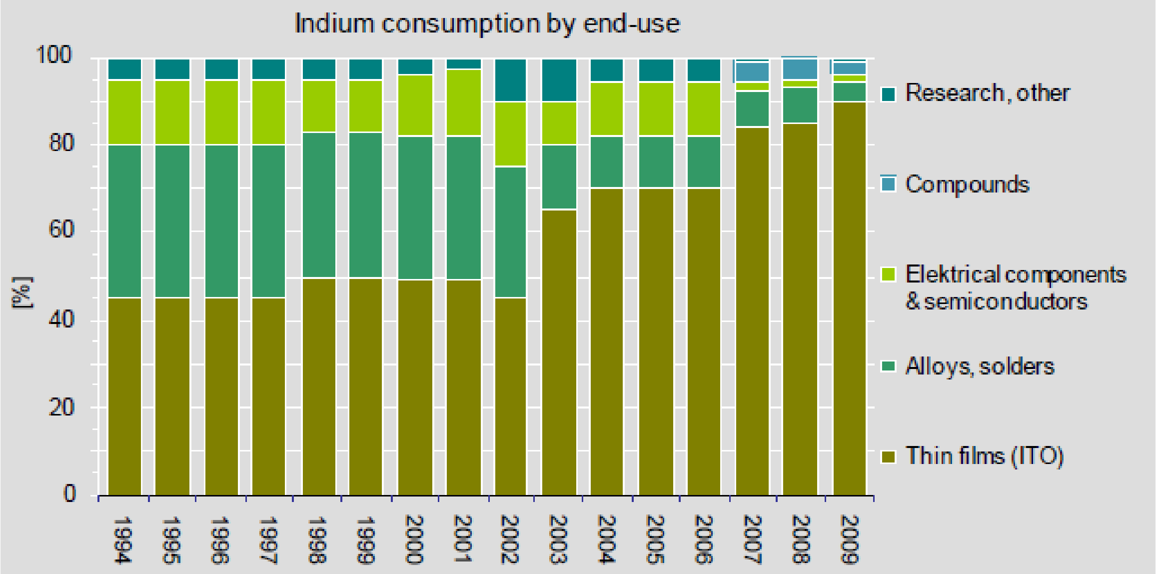


Figure 8. Indium consumption by end-use (Polinares, 2012)

2.4.3 SECONDARY PRODUCTION

Indium recovery processes from secondary sources are only applied at the ITO sputtering waste: during this process only 30% ITO is deposited onto the LCD glass substrate and the remaining 70% is left on the shields of the sputtering chambers, in the process sludge and on the ITO target itself (Yang et al., 2013; Polinares, 2012).

The end-of-life recycling rate of indium is, instead, very close to zero (<1%) (UNEP, 2011).

2.4.4 FUTURE AVAILABILITY AND ECONOMIC ISSUES

Indium future availability is a much debated issue and no univocal conclusion has been reached so far.

No data are available for total indium reserves. In 2010 global zinc reserves were estimated at around 250 million t (USGS, 2011). Assuming there is an average indium content of 50 g indium per ton of zinc content, the calculated indium reserves are 12,400 t, as shown in Figure 9:

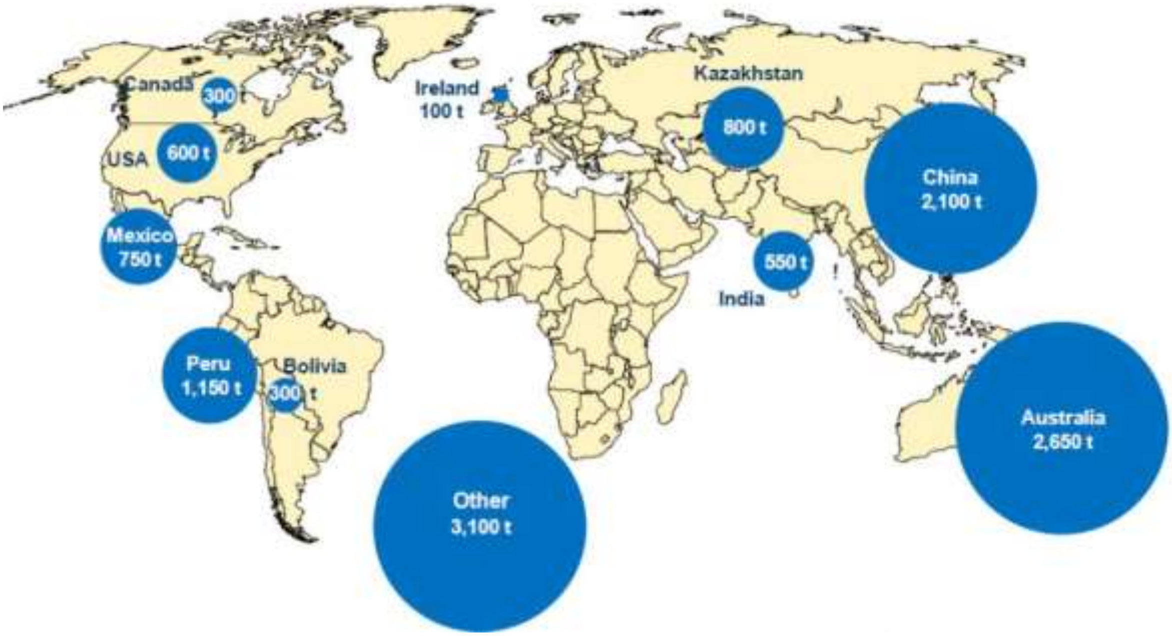


Figure 9. Estimated indium content in zinc reserves (Polinares, 2012)

Data refer to the resources that can be economically extracted or produced with available technologies at the time of determination.

According to Indium Corporation, world indium reserves identified in base metal mines are instead close to 50,000 t. This data includes mining reserves and residue reserves; moreover it takes into account the possible improvements in recoveries of virgin and reclaimed materials and ongoing exploration (Mikolajczak, 2010).

Indium global demand is continuously increasing: during 2011, U.S. imports for consumption of unwrought indium metal and indium powders totaled 146 tons, which corresponds to a 24% increase with respect to the previous year (USGS, 2013). High future demand is expected to occur due to the increase in thin film solar cells manufacturing (UK Energy Research Centre).

Moreover, indium availability is strongly affected by trade restrictions and economic protectionism of the producing countries, mainly China (Polinares, 2012).

Finally, it must be pointed out that indium substitution is possible in some applications only, such as antimony tin oxide coatings and carbon nanotube coatings (USGS, 2013).

All these factors are responsible for the high volatility of indium price, as shown in Figures 10-11:

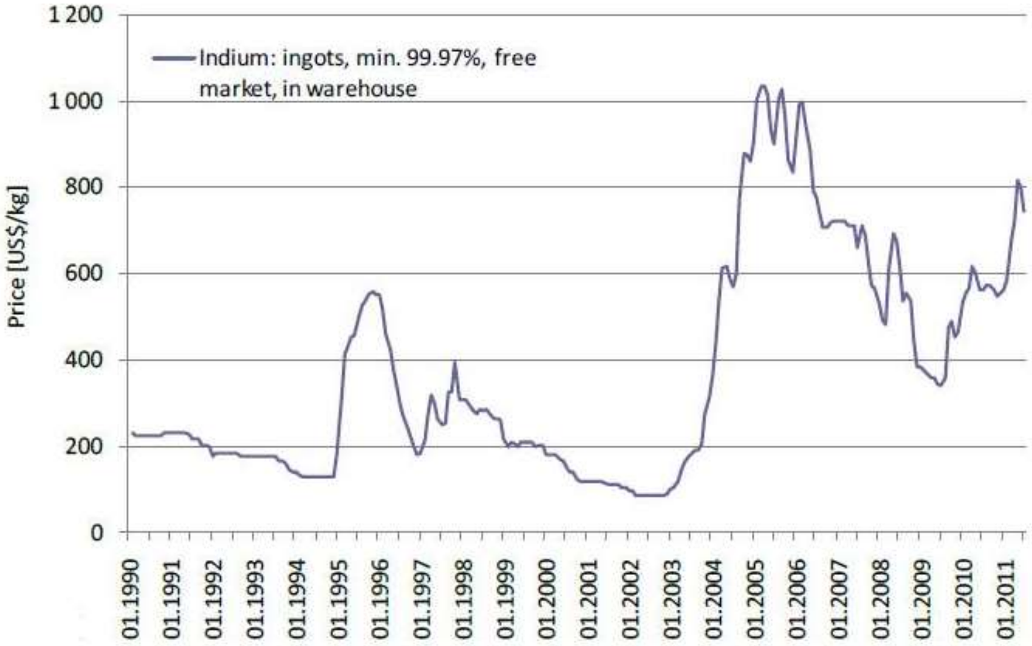


Figure 10. Indium monthly average price (Polinares, 2012)

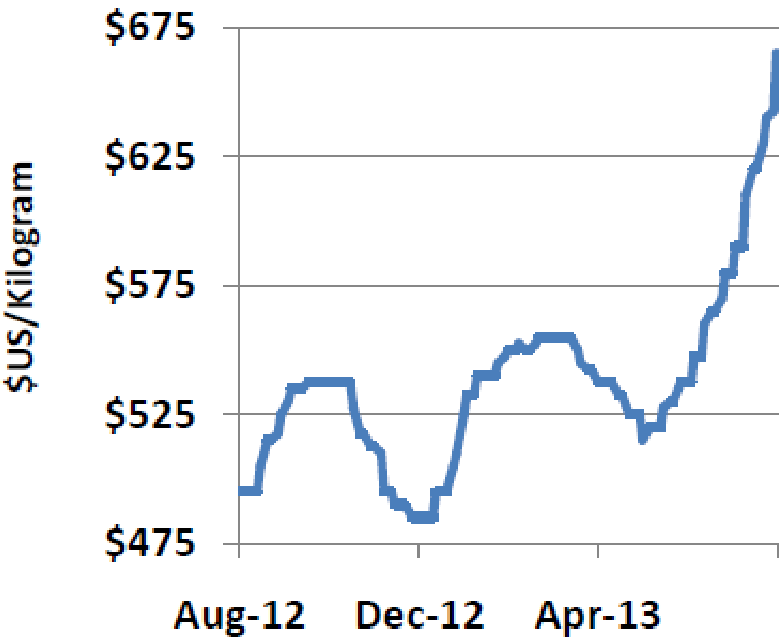


Figure 11. Indium prices of free market 99.99% purity indium ingots in U.S. Dollars per kilogram in Rotterdam warehouse. Displayed is the mid-point price for indium based on the high and low price range (Metals Bulletin, as posted on Bloomberg L.P.)

3. WASTE FLAT PANEL DISPLAYS MANAGEMENT

3.1 APPLIANCES PUT ON THE MARKET AND WASTE GENERATED

Among flat panel displays, the liquid crystal display technology currently holds the mainstream position and is widely used in notebook computers, desktop computer monitors and televisions (Li et al., 2009; Bucher et al., 2012).

In Table 9 the LCD appliances put on the market from 2000 to 2008 in Europe are reported:

Table 9. LCD appliances put on the market in Europe [1000 t] (Salhofer et al., 2011)

Year	**TV$_S$**	**Monitors**	**Notebooks**
2000	0.1	0	40
2001	0.3	10	13
2002	2	26	16
2003	12	78	22
2004	37	104	30
2005	111	135	40
2006	211	166	46
2007	270	187	56
2008	326	198	62

According to Bucher et al. (2012), the market for plasma TVs is significantly smaller than the market for LCDs appliances: sales in 2010 were only around 10% of the TV market in Germany, mainly because of the higher average price of PDP TVs, of its higher power consumption, along with the constant improvement in the image quality of LCD TVs.

The LCD devices with LED illumination are instead increasing over the past years. Notebooks already use white LEDs for the background illumination; the corresponding market share was around 92% worldwide in 2010, with an ongoing slightly upward trend (Young, 2011).

It has been estimated that a FPD PC monitor has a lifespan of 6.6 years (European Commission DG TREN, 2005), while a FPD TV of 10 years (Zangl et al., 2009).

Since FPD appliances have been on the market from several years, the amount of waste FPDs is rapidly increasing. Waste LCDs are indeed considered to be the fastest-growing waste stream in Europe (Dodson et al., 2012): as reported in Figure 11, it was estimated that approximately 600.000 tons of LCD devices are entering into their end-of-life stage for treatment in Europe by 2018 (Salhofer et al., 2011):

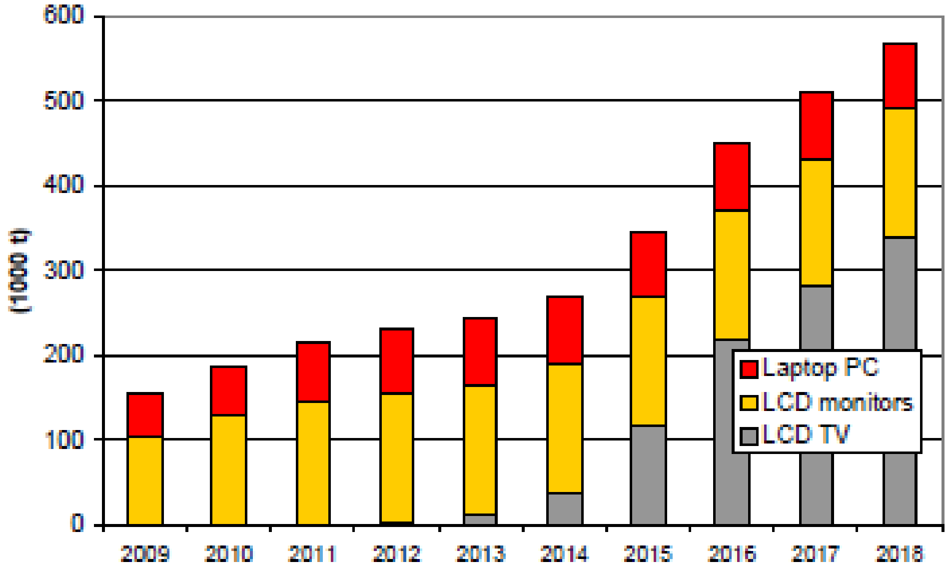


Figure 12. Waste LCDs in EU (Salhofer et al., 2011)

3.2 TREATMENT PRACTICES IN EUROPEAN COUNTRIES

The WEEE Directive 2012/19/EU of the European Parliament and of the Council on Waste Electrical and Electronic Equipment requires the disassembly of the liquid crystal displays with a surface greater than 100 cm^2 and all those back-lighted with gas discharge lamps (Directive 2012/19/EU). Once the backlight has been removed, an LCD becomes ‘safe’ and may be sent for incineration or landfilling (Matharu et al., 2008).

In EU flat screens are fed into a separate recycling process after collection (Buchert et al., 2012). The treatment process generally consists in a disassembly step aimed at removing the hazardous components (CCFLs) and the valuable ones (printed circuit boards, metallic fractions, plastic fractions etc.) for further treatment and recovery.

Instead of manual disassembly, the complete or partly disassembled display unit can be sent for mechanical pre-treatment where the devices are shredded in an airtight sealed shredder and the mercury eliminated from the process air. For example, at the STENA treatment plant in Germany (Criag Glass Recycling) the entire LCD screen is processed; the process allows to extract more than 88% mercury-free clean fractions which are separated into iron, other metals, plastics, printed circuit boards and glass with liquid crystals.

A further treatment option for waste FPDs is thermal treatment of the whole or partially disassembled display units (Böni and Widmer, 2011; Martens, 2011).

The main outputs obtained after manual disassembling of waste FPDs are:

- plastics fractions (sometimes subdivided according to the different polymers)
- metallic fractions
- PCBs
- CCFLs
- glass panels

The waste FPD components are sent to other treatment plants for further treatment and recovery, as explained in the following.

Plastic and metallic fractions are delivered to the relevant markets for materials recycling.

Due to the content of copper and precious metals, printed circuit boards (PCBs) are usually subjected to a melting process; the main destinations are Aurubis plant (Germany), Boliden plant (Belgium) and Umicore plant (Sweden).

The hazardous fraction constituted by cold cathode fluorescent lamps (CCFLs) is sent to general lamp recycling for mercury recovery; glass and metallic fractions are then sent to materials recycling and the fluorescent powder is usually landfilled.

The LCD panels are usually thermally recycled in waste incineration plants or in the Waelz kiln process for steel mill dust. The organic components (such as liquid crystals and the polarizing films) are incinerated and the glass along with the oxidized metals bound in an inert slag. Indium is lost through dissipation.

Some research projects focused on material recovery from waste FPDs are currently being developed at the European level.

RECYVAL-NANO project (NMP2-SE-2012-310312, December 2012-November 2016) is co-funded by the European Commission within the Seventh Framework Programme (2007-2013). It is aimed at developing innovative techniques for indium and rare earth recovery from waste FPDs. The recovery technique mainly involves a mechanical separation step followed by solvent extraction; the extracted solutions will be used as precursors in the direct production of advanced nanoparticles (such as ITO, Y_2O_3:Eu^{3+} and Nd-Fe-B). The main partners involved are COOLREC (Netherlands), expert in e-waste handling, recycling and logistics, and TECNAN (Spain), expert in industrial production of nanoparticles and nanodispersions (http://www.recyval-nano.eu/).

Recently a European project co-financed by Life+ Programme has been started, named High Technology Waste Treatment (HTWT) project and focused on the development of an integral waste management of LCD displays, plasma displays as well as photovoltaic panels. The aim of the project is the design and construction of an industrial prototype using induction technology, in order to test how to improve waste treatment by means of the first machine using induction energy (http://www.htwt.eu/).

3.3 THE ITALIAN CASE - A FOCUS ON LOMBARDIA REGION

In this Section a special focus on the current treatment practices for waste flat panel displays in Lombardia Region (Italy) is provided.

The results here presented were used in a more extensive research project aimed at evaluating the environmental performances of the current management system implemented in Lombardia Region in year 2011 (Biganzoli et al., 2014) and focused on two WEEE categories: R3 (TV and monitors) and R4 (small household appliances), according to the classification provided by the Italian Legislation (Decreto Ministeriale 25 Settembre 2007, n.185).

In order to perform the analysis, it was first necessary to assess the WEEE flows from the collecting platforms to the first delivery plants. This was done by means of the regional database O.R.SO. (Osservatorio Rifiuti Sovraregionale) and by directly contacting the storage plants/the platforms in case of missing information. The obtained results allowed the identification of the most important treatment plants that were thus selected for a field visit in order to collect primary data about the treatment process flow sheet and the main outputs; a number of secondary delivery plants were also contacted in order to gather information about the recovery process of the waste FPD components separated after primary treatment.

The plants selected for a field survey were:

- Stena Technoworld srl: Castenedolo (BS) and Angiari plant (VR)
- Relight srl: Rho plant (MI)

They are the most significant e-waste treatment plants in Italy, both in terms of amount of waste yearly processed and of cutting-edge technologies.

It was found that waste FPDs account for approximately 2.4% of the total R3 category (i.e. FPDs and CRTs); moreover, FPD TVs and FPD desktop PCs account for 90% and 10% of all waste FPDs, respectively.

As reported in Figure 13, treatment process consists of two main steps (Grosso et al., 2014):

- manual disassembling
- shredding of plastic components

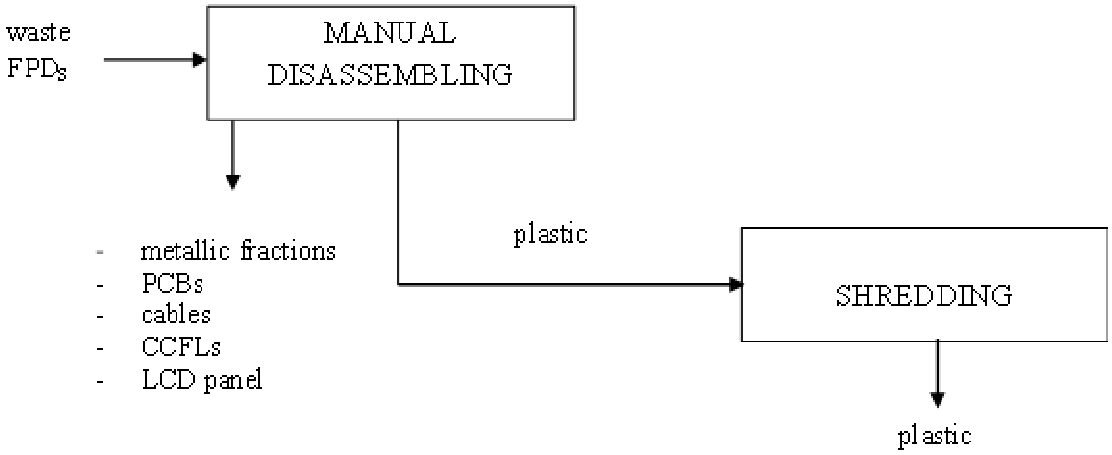


Figure 13. Waste FPDs primary treatment in Lombardia Region (Grosso et al., 2014)

Manual disassembling is aimed at removing the valuable components as well as the hazardous ones. Plastic casings are then shredded.

In Figure 14 the mass balance of the waste FPDs primary treatment is shown.

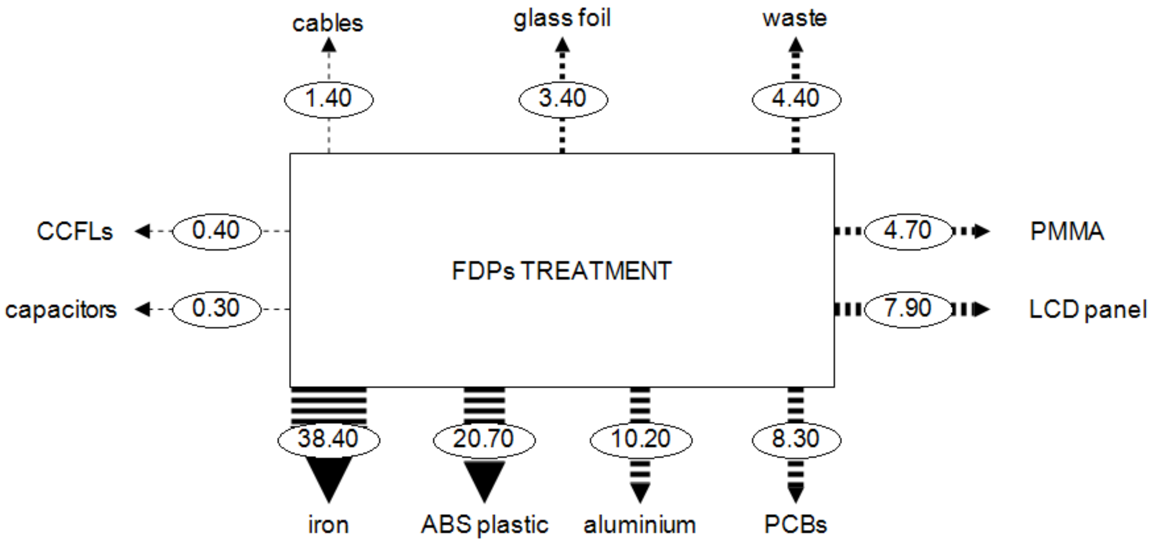


Figure 14. Mass balance of waste FPDs treatment in Lombardia Region (% w/w) (PMMA=polymethyl methacrylate; ABS=acrylonitrile butadiene styrene) (Biganzoli et al., 2014)

The destination of the waste FPDs components is discussed in the following.

Plastic treatment process generally consists in a sorting step followed by extrusion; it is performed both in Italy and abroad, depending on product's characteristics. The recovered product can be employed for the production of new ABS plastic. Further studies are required in order to establish the effectiveness of its recycling, with particular reference to the content of brominated flame retardants that in the last decades is gaining increasing attention among the scientific community.

The metallic fractions (mainly aluminium and iron) are classified as secondary raw materials and directly sent to smelters in Italy for final recovery.

Cables treatment consists in a shredding step followed by mechanical separation aimed at separating the plastic fraction from the metal-rich fraction; both of them are sent to other plants for further treatment and recovery. Cables treatment is performed both in Italy and abroad (China), depending on the request of the market.

Printed circuit boards (PCBs) treatment consists in a shredding step in hammer mills, followed by the separation of the different components (i.e. plastic and metallic fractions).
The metallic fraction is then recovered by means of pyrometallurgical processes for precious metal recovery (gold, silver and palladium). In some cases PCBs are not shredded, but directly fed into the furnace. Metal recovery is generally performed abroad; the main destinations are the Boliden plant (Sweden) and the Umicore plant (Belgium). In both plants integrated metallurgical processes are applied on both virgin and secondary streams. Treatment process is based on lead, copper and nickel metallurgy, which act as collectors for the precious metals. At the Umicore plant, antimony, indium and tellurium recovery is also performed. In the near future PCBs will be probably pretreated at the new PMR plant (Precious Metal Recovery plant, Stena Technoworld srl) located in Angiari (Veneto Region) and started up in 2013.

Cold cathode fluorescent lamps (CCFLs) are treated in other Italian treatment plants, specific for this WEEE category. They are crushed in a rotating drum and the different fractions are separated: glass, metallic and plastic components and fluorescent powder. The fluorescent powder is collected through air pollution control devices and sent to other plants for mercury recovery (through distillation); the residual waste is usually landfilled even if some research projects are now being focusing on rare earths recovery by hydrometallurgy (HydroWEEE Demo Project). Metallic fractions are finally separated from glass through magnetic and Eddy current separators.

PMMA (poly methyl methacrylate) fraction is sent to other treatment plants where chemical treatments are usually performed (de-polymerization and purification).

Capacitors are generally sent to hazardous waste incineration plants.

Finally, the LCD panels, which account for 7.9%, of the entire LCD display (Figure 14), are simply stored at the plant, because no recycling process is available yet. Some research projects are now being focused on indium recovery from indium tin oxide film, which is also the focus of this PhD thesis.

An estimate of potentially recoverable indium contained in waste FPDs stored in Lombardia Region e-waste treatment plants was also carried out, as explained in the following (Pizzagalli, 2014).

Data provided by O.R.S.O. database allowed to evaluate the amount of waste "TV and monitor" appliances sent to treatment in year 2011; waste FPDs were, thus, determined considering that they account for 2.4% of the R3 category. Regarding indium content in LCD displays, literature offers different values, mainly depending on their weight, thickness and surface area; this study refers to data of a 2011 report (Buchert et al., 2012), which provides information on the mean weight and indium content per device of a general stream of LCD waste (Table 10).

Table 10. Approximate calculation of indium content in LCD displays (adapted from Buchert et al., 2012)

	Mean weight of display	**Mean In content per device**
	[g]	**[mg]**
Notebooks	250	43.5
LCD monitors	300	52.2
LCD televisions	1800	36.3

Data collected allowed an estimate of indium content, both divided per type of device (FPD TVs and FPD desktop PCs) and total. Results are presented in Table 11, while a STAN model (subSTance flow ANalysis) of the whole process is shown in Figure 15.

Table 11. Estimated amounts of indium in waste FPD TVs and PCs sent to treatment (Lombardia Region, year 2011)

Waste “TV and monitor” appliances [kg]	20,068,612.00
waste FPDs [kg]	481,646.69
waste LCD panels [kg]	38,050
TV panels [kg]	34,245.08
PC panels [kg]	3,805.01
TV panels [♯]	19,025.04
PC panels [♯]	12,683.36
indium in TVs [kg]	0.69
indium in PCs [kg]	0.66
potentially recoverable indium [kg]	1.35
potentially recoverable indium per capita [kg/ab]	$1.35 \cdot 10^{-7}$

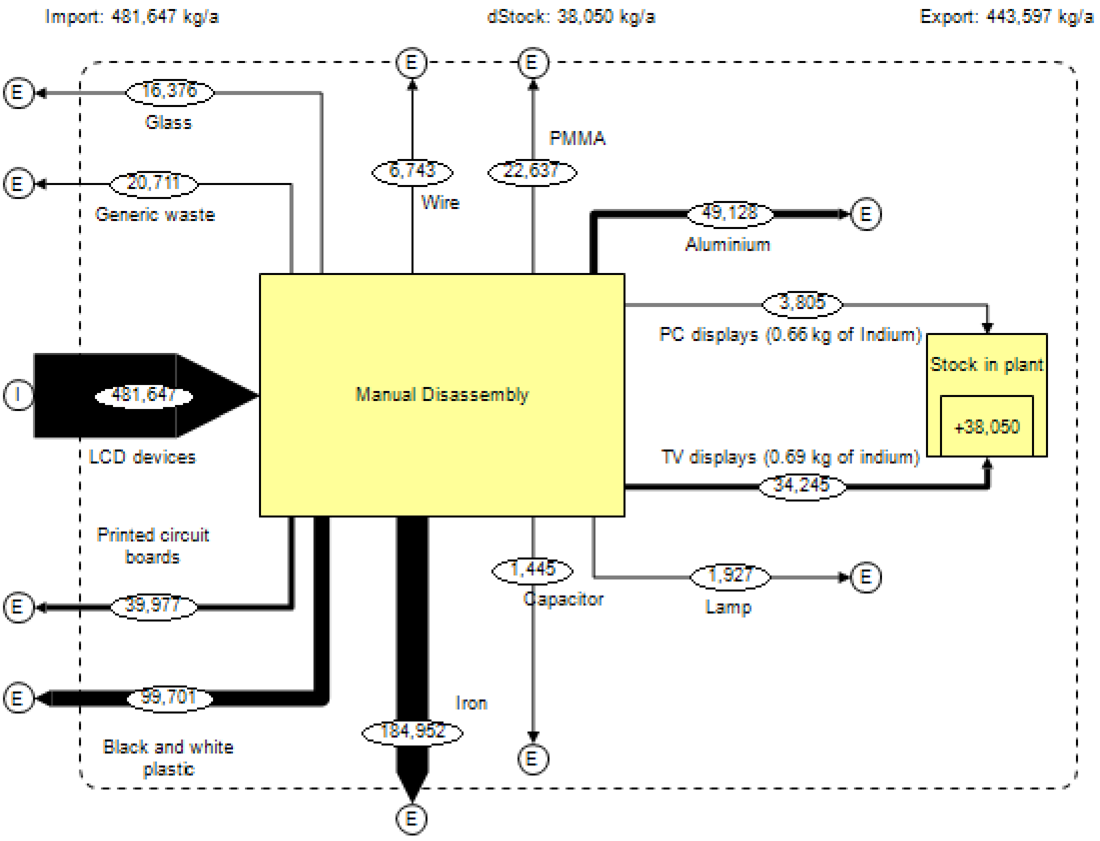


Figure 15. Material flow analysis of waste FPDs (Lombardia Region, year 2011)

It was found that potentially recoverable indium accounts for 1.35 kg (0.66 kg from waste PCs and 0.69 kg from waste TVs), which corresponds to approximately $1.35 \cdot 10^{-7}$ kg per capita.

3.4 MATERIAL RECOVERY FROM THE LCD PANEL - LITERATURE REVIEW

In the last decades a number of works have been focusing on material recovery from end-of-life LCDs. The main driver for waste LCDs treatment lies in indium recovery; to this aim hydrometallurgical techniques are usually employed, consisting in leaching followed by separation, that can be performed through different techniques (such as precipitation, cementation, solvent extraction, ion exchange, adsorption and electro-winning). Some pretreatments can be performed before the leaching aimed at removing the polarizing film and/or the liquid crystals, as explained in the following.

3.4.1 REMOVAL OF THE POLARIZING FILM

In most cases thermal treatment at high temperature is employed for the removal of the polarizing film from the glass substrate (Li et al., 2009; Lee et al. 2013; Ma et al., 2012), which implies high energy consumption and potential atmospheric emissions.

A density based separation method performed through gravity concentration was employed by Zhuang at al. (2012). The panel glass was first crushed by a hammer mill so to obtain a primary separation based on particle size; the samples were then sieved and treated through a saturated solution of K_2CO_3 in order to achieve further accumulation.

Ruan et al. (2012) employed liquid nitrogen to strip the polarizing film, but no information is given about the time required and the achieved removal efficiency.

3.4.2 REMOVAL OF THE LIQUID CRYSTALS

Ultrasound washing is often employed for the removal of the liquid crystals; several solvents can be used, such as distilled water, sodium dodecylbenzenesulfonate, isopropyl alcohol, acetone and surfactants (Li et al., 2009; Zhuang et al., 2012). Higher temperature generally led to an increase in the removal efficiency (Zhuang et al., 2012).

In Table 12 the operative parameters found in the available literature are reported:

Tabella 12. Removal of the liquid crystals - operative parameters

Operative parameter	**Ref.**	
	Li et al., 2009	Zhuang et al., 2012
time	10 min	45 min
temperature	-	60°C
frequency	40 kHz (P=40 W)	40 kHz (P=50 W)
solvent	isopropyl alcohol	isopropyl alcohol
solvent concentration	1:49 v/v%	16.7 vol.%
removal efficiency	85% w/w	100% w/w

The removal efficiency was estimated by measuring the maximum absorbance value under the best available conditions (ultrasound cleaning, isopropyl alcohol as solvent and the longest contact time).

3.4.3 SHREDDING

Shredding is usually carried out before leaching, in order to enhance the leaching efficiency. In some cases it is performed on the whole LCD panels (Dodiba et al., 2012), in other cases only on the glass substrate obtained after the removal of the polarizing film (Li et al., 2009; Ma et al., 2012; Lee et al., 2013).

Table 13 shows the operative conditions employed in the most significant studies.

Table 13. Shredding - operative parameters

Ref.	**Operative parameter**		
	apparatus	time	particle size
Li et al., 2009	shredding machine (HYP-250, Huanya)	-	5 mm
Ma et al., 2012	roll mill	-	<0.13 mm
Lee et al., 2013	planetary mill P100	1 min	7.5 µm

According to Lee et al. (2013), by increasing the milling time the average particle size of waste LCD panels firstly decreases and then increases. Such behaviour can be explained with the agglomeration of smaller particles among each other and it is responsible for the decrease of indium leaching efficiency.

According to Dodiba et al. (2012), electrical disintegration allows to disjoint the two glass substrates and therefore liberate or expose the ITO film, thus enabling a high leaching capacity for indium with respect to the conventional grinding.

3.4.4 LEACHING

Leaching is the first step of a hydrometallurgical technique and it is aimed at dissolving the elements of interest by contacting it with an adequate solvent.

A number of leaching agents can be employed for indium extraction from waste LCD panels, as reported in Table 14.

Indium dissolution kinetics in acidic media are quite slow, especially if nitric acid is employed as a lixiviant (Virolainen, 2011; Lee et al., 2013). A selectivity leaching of indium with respect to tin/iron can be obtained by employing: H_2SO_4 1M (Li et al., 2011); H_2SO_4 (0.01M and 0.1M), HNO_3 (0.1M and 1.0 M) (Virolainen et al., 2011) and H_2SO_4 1:1, v/v (Ruan et al., 2012).

It was also observed that leaching is often carried out by employing acid mixtures with inhomogeneous concentration values. Li et al. (2009) tested $HCl:H_2O=50:50$ v/v, $HCl:HNO_3:H_2O=45:5:50$ v/v and $HCl:H_2SO_4:H_2O=35:15:50$ v/v; Lee et al. (2013) employed the same acid mixtures listed above and also $HNO_3:H_2O$ 50:50 and $HCl:HNO_3:H_2O$ 25:25:50; Ruan et al. (2012) tested a number of acid systems such as concentrated HCl, concentrated $HCl\text{-}H_2O_2$ (4:1, v/v), concentrated HNO_3, aqua regia, H_2SO_4 (1:1, v/v) and $HCl\text{-}HNO_3\text{-}H_2O$ (1:0.1:1, v/v/v), in order to gather information about the dissolution character of the main elements, but the acid concentrations are not comparable between each other. Yang et al. (2013) and Virolainen et al. (2011) tested HCl, HNO_3 and H_2O_4 as leaching agents, by fixing the acid concentration in terms of molarity; in this case the comparison can be done only between HCl and HNO_3, since H_2SO_4 has a double hydrogen concentration.

Table 14. Leaching - operative parameters

Operative parameter	**Ref.**					
	Li et al., 2009	Virolainen et al., 2011	Ruan et al., 2012	Lee et al., 2013	Yang et al., 2013	Li et al., 2011
waste	waste LCDs	ITO powder	waste LCDs	waste LCDs	waste LCDs	ITO targets
leaching agent	HCl-HNO_3 mixture	HCl; H_2SO_4	H_2SO_4	HCl	HCl; H_2SO_4	H_2SO_4
concentration	$HCl:HNO_3:H_2O$ =45:5:50 %v/v	1 M	1:1, v/v	$HCl:H_2O$=40:50	1M	100 g/L
liquid/solid ratio	0.5 mL/g	1000 mL/g	1 mL/g	25 mL/g	10 mL/g	10 mL/g
temperature	60°C	-	160°C	25°C	20 ± 1°C	90°C
time	30 min	30 h	1 h	30 min	<8 h	2 h
leaching efficiency	92%	100%	91.5%	86%	~100%	99%

3.4.5 INDIUM RECOVERY FROM THE AQUEOUS PHASE

In this Section, indium recovery techniques from the aqueous phase are reported.

3.4.5.1 SOLVENT EXTRACTION

In most cases solvent extraction is used as a separation step, due to its characteristics of high selectivity and high recovery efficiency.

Solvent extraction (or liquid-liquid extraction) is a process for separating components in solution by their distribution between two immiscible liquid phases (Perry's Chemical Engineers' Handbook, 1997). It is carried out by contacting the metal-rich solution with a solution constituted by an organic extractant diluted in a diluent; in this way, organometallic complexes form, which are soluble in the organic phase and can be, thus, extracted in it. After separating the two phases, the organic one (that is rich in metal ions) is contacted with a "fresh" aqueous solution during the so-called "stripping" step: in this way the inverse reaction occurs and metal ions can be re-extracted.

Several extractants can be employed for indium extraction, such as D2EHPA[8] (Virolainen et al., 2011; Ruan et al., 2012; Yang et al., 2013), TBP[9] (Virolainen et al., 2011), Cyanex 272[10] and Cyanex 923[11] (Yang et al., 2013).

Solvent extraction tests on acid solutions obtained from indium tin oxide powder leaching were carried out by Virolainen et al. (2011) with the aim of verifying indium/tin selectivity. In the study carried out by Ruan et al. (2012) the focus is on indium/iron separation, since iron is the main impurity found in the aqueous phase obtained by dissolving waste LCDs in sulfuric acid; however, no information is given about the selectivity of the extraction technique. A more comprehensive study was carried out by Yang et al. (2013), since the extraction tests were carried out on simulated solutions containing indium as well as tin, iron, aluminium, copper and zinc and by comparing several extraction media.

The operative parameters found in the available literature are reported in Table 15.

---

[8] D2EHPA: Di-(2-ethylhexyl)phosphoric acid
[9] TBP: Tributyl phosphate
[10] Cyanex 272: bis(2,4,4-trimethylpentyl)phosphinic acid
[11] Cyanex 923: phosphine oxides mixture

Table 15. Solvent extraction - operative parameters

	Operative parameter	**Ref.**		
		Virolainen et al., 2011	Ruan et al., 2012	Yang et al., 2013
Solvent extraction	aqueous phase	H_2SO_4	H_2SO_4	H_2SO_4
	extractant	D2EHPA	D2EHPA	D2EHPA
	extractant concentration	1M	30%	0.1 M
	organic/aqueous volume ratio	1:8	1:5	
	time	3 h	5 min	-
Stripping	stripping agent	HCl	HCl	HCl
	stripping agent concentration	>1.5M	4M	1M
	organic/aqueous volume ratio	2:1	5:1	
	time	-	5 min	-
	recovery efficiency	94%	97%	>99%

3.4.5.2 PRECIPITATION AND CEMENTATION

Indium and tin are chemically very similar and separating one from the other in solution is not straightforward. Indium and tin oxides show the minimum solubility at pH around 7; moreover they both form complex with hydroxides to form various hydrated species at various pH (Han et al., 2002).

In the study carried out by Li et al. (2011), tin is separated from the leachate by sulphide precipitation; indium recovery is then performed through zinc cementation.

3.4.5.3 ION EXCHANGE

In the process proposed by Tsujiguchi (2102), indium solution is passed through a column packed with the anion-exchange resin; indium and tin are absorbed, whilst the impurities (such as aluminium) pass through the column without adsorption. The metal-rich solution, obtained by passing water though the column, is thus treated in order to recover indium. First sodium hydroxide is added to control the pH in the range of 1.5 to 2.5; in this way tin precipitates as hydroxide. By increasing the pH of the indium concentrated solution in the range of 4.5 to 5.5, high purity indium sludge is obtained.

3.4.6 METAL EXTRACTION WITH AQUEOUS BIPHASIC SYSTEMS (ABSs)

Solvent extraction has been widely used in the past as a concentration and separation technique; however, organic extractants are often employed, which are potentially hazardous for human health and the environment since they are responsible for VOCs emissions into the atmosphere.

Due to their characteristics of low cost, reduced flammability and reduced toxicity, aqueous-biphasic systems (ABSs) are now gradually emerging as an environmentally-sound alternative to the classical “oil-water” extraction systems (Rogers et al., 2005).

ABSs are formed when a water soluble polymer (e.g. PEG, polyethylene glycol) is mixed with a certain inorganic salt (such as $(NH_4)_2SO_4$, Na_2SO_4, Na_2CO_3, K_2HPO_4, KCl) at a suitable concentration (Ho-Butierrez et al., 1994; Wu et al., 1999; da Silva et al., 1997; Mishima et al., 1998). The formation of an aqueous two-phase system can be explained on the basis of the competition for hydration between the polymer and the salt phase (Cabezas, 1996). The addition of an inorganic salt increases the dehydration of the polymer chains, due to the salting-out effect and phase separation and two immiscible aqueous phases are obtained.

In such a system, metal ions are partitioned between the phases according to a certain distribution coefficient, defined as the solute concentration in the upper phase divided by the solute concentration in the lower phase (Fontana and Ricci, 2000).

Several water soluble polymers may be utilized to form aqueous two-phase systems, however polyethylene glycol is often used because it is non-toxic, non-flammable and non-volatile (Visser et al., 2000).

According to Roger et al. (2005), metal ion extraction in aqueous two-phase systems PEG-based can be classified into three categories:

- extraction in the PEG-rich phase alone, without an extracting agent;
- extraction of metal ions as chelates using water-soluble chelating extractants;
- extraction of metal ions as complexes with inorganic anions (such as Cl^-, Br^-, I^-).

A number of parameters affect metal ions partitioning in an ABS, such as the system characteristics (nature and concentration of the inorganic salt, molecular mass and concentration of the polymer), the hydration properties of the solute (Visser et al., 2009; Roger et al., 1996; Zaslavsky et al., 1991) as well as the temperature (Fontana and Ricci, 2000) and the type of extracting agents (Ammar et al., 2013; Bulgariu and Bulgariu, 2008).

In recent years, an increasing number of works are being focusing on metal extraction through aqueous biphasic systems. Ammar et al. (2011) studied the extraction of Zn (II) and Cu(II) ions using PEG 300-KCl salt aqueous two-phase systems, at room temperature and without using an extracting agent. In another work, Ammar et al. (2013) investigated the extraction behavior of Cd(II), Cu(II), Fe(II) and Zn(II) in an aqueous biphasic system composed of PEG and sodium sulfate in the presence of KI and KSCN as extractants; it was found that the extraction percentage increases by increasing the extractant concentration, the phase ratio and the initial concentration of the metal ions. Cd(II) extraction was investigated by Bulgariu et al. (2008) in PEG 1550-$(NH_4)_2SO_4$ system; Dzherayan (2006) studied the extraction of gallium from alkaline carbonate solutions with phenylfluorone in the system PEG–sodium carbonate–water; copper extraction through PEG 3,350-ammonium sulphate-water system was studied by Fontana and Ricci (2000) in the presence of 1,10 phenantroline as complexing agent.

4. MATERIALS AND METHODS

The experimental activity aimed at materials recovery from waste LCDs was carried out at the ENEA Research Centre, in Rome (Casaccia Research Centre, Eco-Innovation of production processes Laboratory, UTTAMB ESP).

The waste LCD panels were provided by STENA Technoworld srl (Castenedolo, BS), an e-waste treatment plant located in Northern Italy; moreover, some LCD monitors (not dismantled) were provided by a e-waste collecting platform.

4.1 MANUAL DISMANTLING AND CHARACTERIZATION OF THE WASTE LCD COMPONENTS

Two LCD monitors of different size and composition (Table 16) were manually disassembled in order to sort out the different components (Figure 16).

Table 16. Waste LCD monitors characteristics

	Size	**Weight**
	[in]	[kg]
LG Philips LCD	17.5	4.7
IBM ThinkVision	17.5	4.2

Each component was weighted in order to evaluate the percentage contribution; moreover, FTIR spectroscopy (Shimadzu IR Affinity-1) was employed in order to gather information about their chemical composition.

The LCD panel was then subjected to the recovery process represented in Figure 17.

			
Metallic fraction (Al, Fe)	plastic fraction	optical foils	light guide
			
printed circuit boards (PCBs)	cables	cold cathode fluorescent lamps (CCFLs)	LCD panel

Figure 16. Waste LCD components obtained after manual dismantling

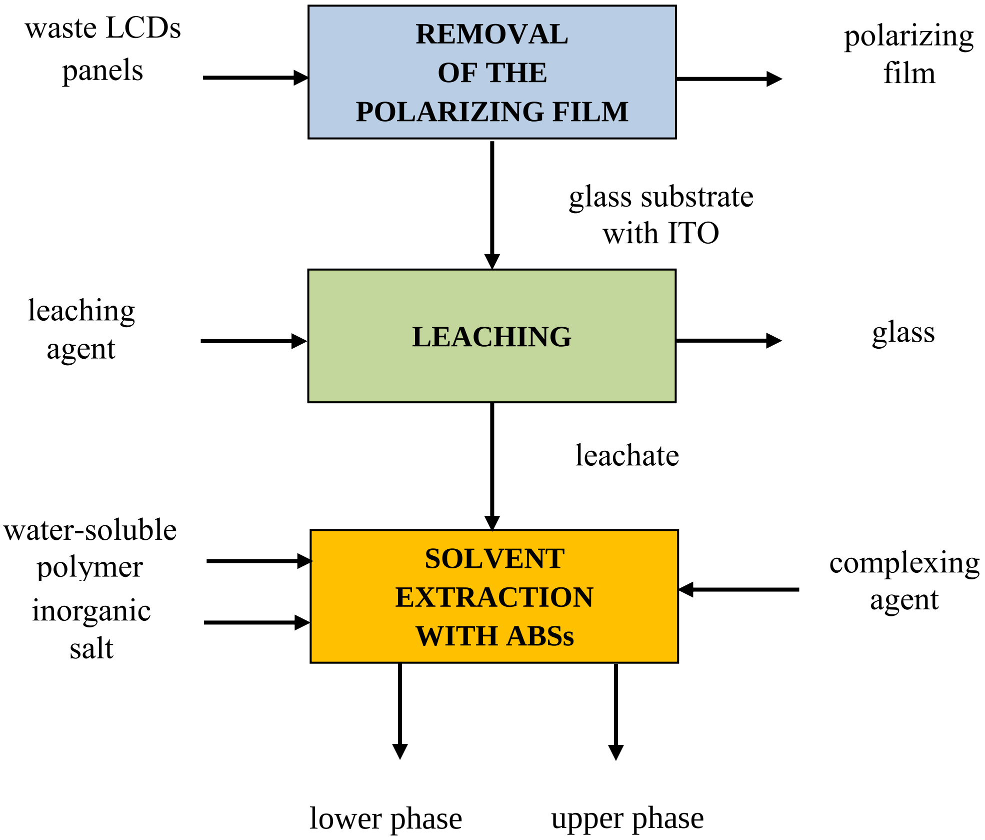


Figure 17. Waste LCDs recovery process flow-sheet

4.2 REMOVAL OF THE POLARIZING FILM

The first step of the process here proposed is aimed at removing the polarizing film from the glass substrate. The advantages are mainly related to the recovery of a product that can be recycled; moreover in this way a non-contaminated glass fraction can be obtained, thus facilitating the subsequent leaching step.

The external side of four LCD panels was analyzed by FTIR spectroscopy to determine its composition.

The removal of the polarizing film was studied through different techniques, which include thermal and chemical treatments. Each test was repeated on two different LCDs (in size and composition), previously cut in square pieces (5cm x 5cm).

The obtained product was then analyzed by FTIR spectroscopy and by stereomicroscope (Olympus SZX12), in order to gather information about the treatment performances.

4.2.1 CHEMICAL TREATMENTS

Chemical treatments were performed by soaking the waste LCDs with a number of organic solvents:

- acetone
- limonene,
- ethyl acetate
- isopropyl alcohol

All chemicals were used as received without any further purification.

Samples were mechanically pretreated (i.e. crushed with a mortar) in order to maximize the surfaces contact with the solvents. The experiments were then carried out in glass bekers on a mechanical shaker. The influence of the ultrasound treatment (f=35 kHz) was also tested.

The experiments were carried out at room temperature; regarding the liquid/solid ratio, it was set at 3 mL/g in order to guarantee a complete contact between the waste LCDs and the solvent.

4.2.2 THERMAL TREATMENTS

Thermal treatments at high temperature were carried out in a furnace by increasing the temperature by 20°C/h. A first test was performed in the range 100°C-160°C, a second one in the range 160°C-240°C.

Other tests were carried out by cooling the waste LCD panels at -196°C with liquid nitrogen.

4.3 CHARACTERIZATION OF THE GLASS SUSBTRATE

In this Section the procedure applied to determine indium and tin content in the glass substrate is described. The experiments were carried out on two LCD panels obtained after primary dismantling (see Table 16).

As shown in Figure 18, the glass panel was first cut in four pieces (size: ~7cm x 8cm, weight: ~24g) (blue line); one of them was cut again and three samples thus obtained were selected for the characterization step (red colored).

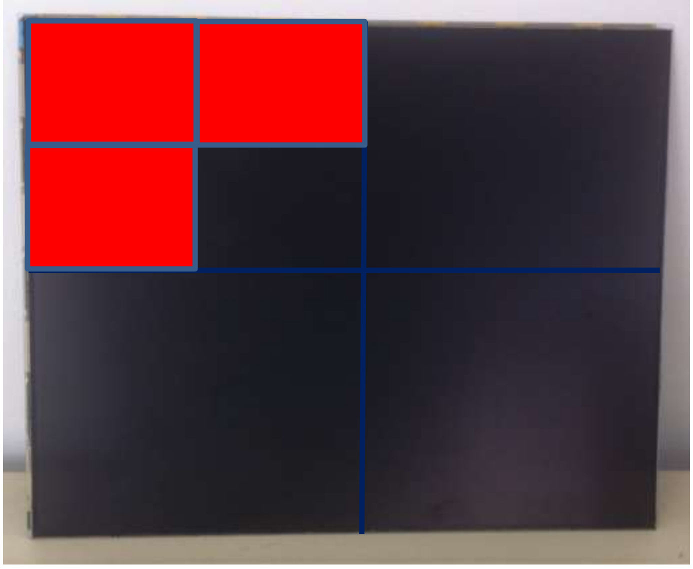


Figure 18. Samples preparation for the characterization step

The polarizing film was removed through the technique defined as optimal according to the results obtained in the previous step (Section 4.2). Scanning electron microscope (ZEISS EVO MA 15) was employed in order to gather information about possible variations in the glass composition before and after the removal of the film; both the TFT (thin-film transistor) and the color filter layer were analyzed.

The glass residue was then leached through aqua regia ($HCl:HNO_3$, 3:1 v/v) to determine indium and tin initial amount.

In order to establish the operative conditions, preliminary tests with aqua regia were carried out on a pure reagent, that is indium tin oxide powder (-325 mesh, ≥99.99% trace metals basis, Sigma Aldrich; 90% In_2O_3 and 10% SnO_2).

The operative parameters were the following:

- T=25°C
- t=8h; t=24h
- L/S=500 mL/g

Experiments were carried out in glass bekers on a magnetic stirrer. The aqueous phase was separated from the solid residue by vacuum filtration and analyzed by MP-AES (Microwave Plasma-Atomic Emission Spectrometer, Agilent 4100). Indium and tin leaching efficiency E(%) was determined according to Eq. (1):

$$E(\%) = \frac{M}{M_{IN}} \cdot 100 \qquad (1)$$

where:

- M is the amount of indium/tin dissolved (g);
- M_{IN} is the amount of indium/tin in the initial sample (g); it is a known value, since indium tin oxide composition is given.

Once the optimal conditions were established (mainly the contact time), the LCD samples were leached with aqua regia. The operative parameters were the following:

- T=25°C
- t=8h
- L/S=3 mL/g

In this case, experiments were carried out in glass bekers on a mechanical shaker. As in the case of indium tin oxide, the aqueous phase was separated from the solid residue through vacuum filtration and analyzed at the MP-AES.

The glass residue after the treatment was analyzed through scanning electron microscope in order to verify the presence of residual indium.

4.4 LEACHING

The second step of the recovery technique is the leaching. It is aimed at dissolving the valuable elements from the glass substrate and it is performed by bringing it into contact with an adequate solvent.

In order to define the best operative conditions, a number of leaching tests were first performed on indium tin oxide powder; once the optimal conditions were established, indium leaching from the glass substrate was carried out.

4.4.1 LEACHING OF INDIUM TIN OXIDE POWDER

A number of inorganic acids were tested as leaching agents:

- HCl
- HNO_3
- H_2SO_4
- HCl-HNO_3 3:1 v/v

Acid concentration was 6N in each experiment, while different values of the liquid/solid ratio were employed (20 mL/g, 100 mL/g and 500 mL/g).

Leaching tests were carried out up to 24 hours, at room temperature and by providing agitation; the supernatant was sampled every 2 hours and analyzed by the MP-AES in order to determine indium leaching efficiency, as reported in Eq. (1).

4.4.2 LEACHING OF THE GLASS SUBSTRATE

As shown in Figure 19, three samples selected from the same panels employed during the characterization step (blue colored) were treated in order to remove the polarizing film and then subjected to the leaching step.

It must be reminded that the ITO layer is only present on one of the two sides of the glass substrates; since particle size is not supposed to have an influence on the leaching efficiency, a shredding step was not performed before the leaching.

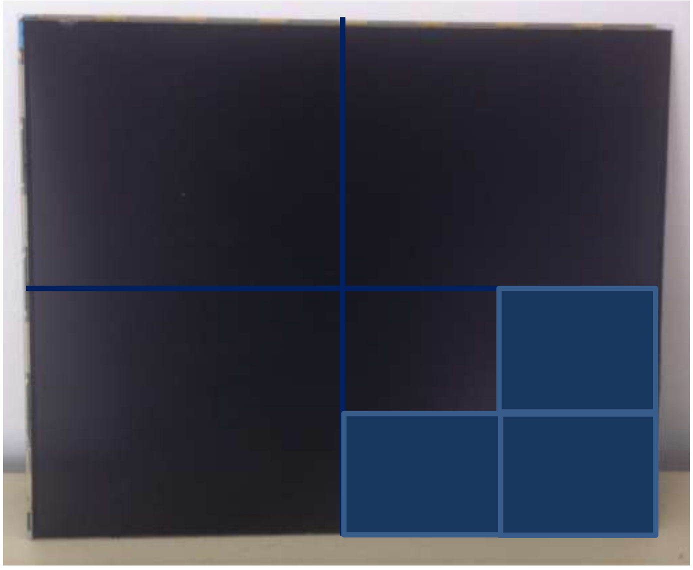


Figure 19. Samples preparation for the leaching step

Indium and tin leaching efficiency was calculated according to Eq. (1). In this case, M_{IN} is the initial amount of indium/tin determined in the previous step (Section 4.3). The presence of other ions in the leachate (mainly aluminum and chromium) was also investigated.

The glass residue was analyzed through scanning electron microscope, as in the case of aqua regia leaching.

4.5 INDIUM EXTRACTION WITH AQUEOUS BIPHASIC SYSTEMS (ABSs)

Indium extraction from the leachate was investigated through solvent extraction with aqueous biphasic systems.

The system considered is constituted by polyethylene-glycol (PEG), ammonium sulfate and water in the presence of a complexing agent.

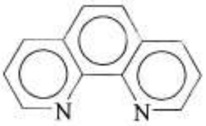
Solid glycol polyethylene (MW 3,350 and 10,000) and ammonium sulfate were analytical grade and used as received.

4.5.1 PRELIMINARY INVESTIGATION ON INDIUM CHELATES

The objective of the experimental tests here described is to gather information about indium behavior in the presence of a complexing agent, which is one of the parameters that strongly affect metal ions partitioning in an ABS (See Section 3.4.6); the influence of pH was also investigated.

Two complexing agents were selected, namely 1,10 phenantroline and ammonium thiocyanate; their chemical formula is reported in Table 17:

Table 17. Chemical formula of 1,10 phenantroline (a) and ammonium thiocyanate (b)

	NH_4SCN
(a)	(b)

Indium solutions were prepared by dissolving indium (III) nitrate hydrate in distilled water in a suitable concentration ($[In] = 1.2\cdot10^{-6}$ M). Other metal-rich solutions were prepared by dissolving indium salts and the complexing agent. Since no information is available from literature about indium extraction reaction stoichiometry with the selected complexing agents, a molar ratio of 5 was employed; in the following it will be referred to as *r*, as reported in Eq. (2):

$$r = \frac{\text{1,10 phenantroline moles}}{\text{In moles}} = \frac{\text{CNS}^{-}\text{moles}}{\text{In moles}} \tag{2}$$

Finally, other samples were prepared which only contain the complexing agent.

Each solution was prepared at different pH values, namely:

- pH~4.5
- pH~7.5
- pH~11.5

Samples were analyzed by UV-VIS spectrometer (Shimadzu UV-VIS Spectrophotometer UV-2550). Once the best operative conditions were defined (mainly complexing agent and pH), they were applied for the extraction tests, as explained in Section 4.5.2.

4.5.2 INDIUM EXTRACTION TESTS

The aqueous-biphasic system was prepared according to the phase diagram reported in Figure 20:

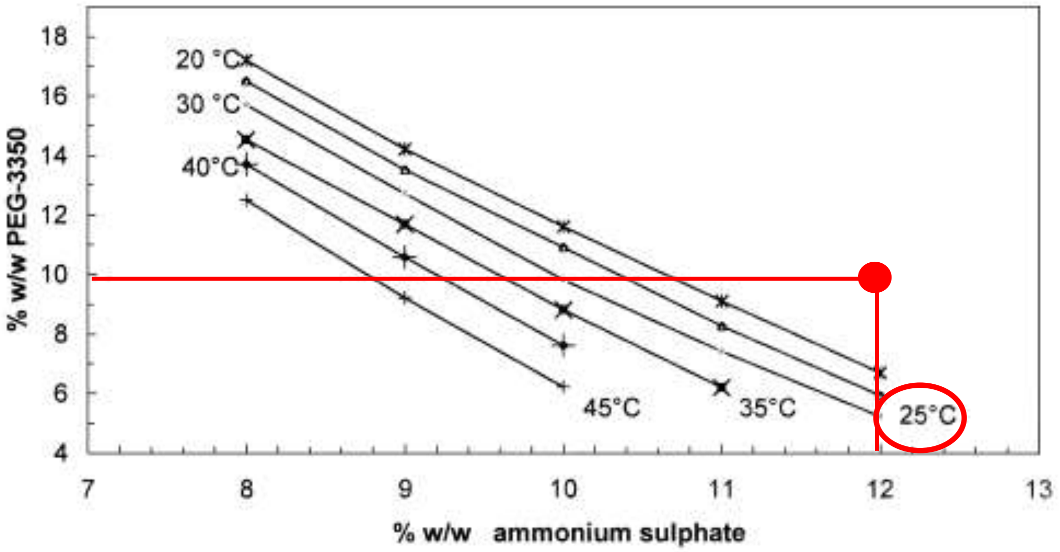


Figure 20. Phase diagram of PEG 3,350-ammonium sulfate-water system (Fontana and Ricci, 2000)

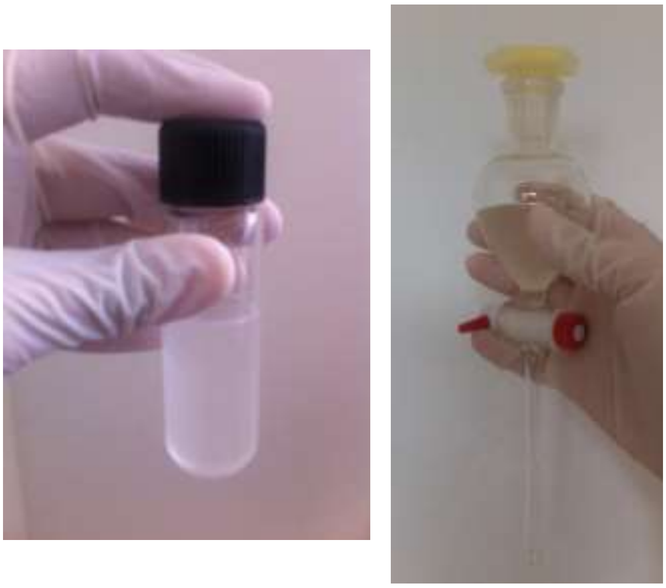
Given a temperature value, all compositions represented by points below the curved lines give a one-phase system; all compositions above the curves give a two-phase system.

Starting from an initial composition that allows the formation of the two phases at a fixed temperature (red point, i.e. [PEG]=10% w/w and $[(NH_4)_2SO_4]$=12% w/w), PEG and salt concentrations were varied in a certain range in order to evaluate the influence of system composition on indium partitioning.

Since PEG chemical properties may influence indium partitioning as well, two type of PEG were employed, i.e. PEG 3,350 and PEG 10,000.

Extraction tests were carried out by mixing the desired amounts of PEG and ammonium sulfate with the metal-rich solution in glass-capped tubes on a mechanical shaker (Figure 21).

The extraction time was fixed at 2h. Samples were then located in a thermostatic bath (T=25°C) and were allowed to settle for 2h; the two phases were then separated with a separating funnel and analyzed by atomic absorption spectrophotometry (AAS Shimadzu 6300) in order to evaluate indium partitioning between the lower and upper phase. Indium content in the initial solution was also determined, so to assess the mass balance.



(a) (b)

Figure 21. Extraction step (a), separation step (b)

The operative parameters were the followings:

- PEG 3,350; PEG 10,000
- complexing agent: 1,10 phenantroline
- $[In]=5\cdot 10^{-3}$ M
- r=5
- [PEG]=9-25% w/w
- $[(NH_4)_2SO_4]$=11-25% w/w
- pH_{eq}~5.5
- T=25°C
- $t_{extraction}$=2h
- $t_{settling}$=2h

All the experiments were performed in duplicate, in order to check the experimental technique and its precision.

5. RESULTS AND DISCUSSION

In Chapter 5 the results of the experimental activity are presented and discussed.

5.1 MANUAL DISMANTLING AND CHARACTERIZATION OF THE WASTE LCD COMPONENTS

Table 18 shows the results of the dismantling step performed on two LCD monitors (See Section 4.1).

Table 18. Waste LCD components separated after manual dismantling

Waste LCD components	**Amount [**% w/w**]**	
	LCD 1	LCD 2
Iron (Fe)	32.9	29.4
plastic fraction	20.5	17.5
light guide	19.8	21.8
LCD panel	8.3	9.5
aluminium (Al)	7.3	9.6
printed circuit boards (PCBs)	4.2	8.8
residual waste	2.4	0.7
optical foils	2.2	1.6
cables	1.8	0.5
cold cathode fluorescent lamps (CCFLs)	0.6	0.5

It was found that iron is the most significant fraction, accounting for approximately 30% w/w. The LCD glass panel accounts for 8-9% w/w, thus confirming data provided by the WEEE treatment plants.

As explained in Chapter 4, the waste LCD components were analyzed by FTIR spectroscopy. In Table 19 the composition of the optical foils is reported.

Table 19. Optical foils composition

	LCD 1	LCD 2
foil 1	PC[12]	epoxy resin and polyester
foil 2	PMMA[13] and acrylonitrile	acrylonitrile
foil 3	acrylonitrile and epoxy resin	PMMA and acrylonitrile
foil 4	PET[14]	polyester

Table 20 shows the composition of the external side of the polarizing films.

Table 20. Polarizing film composition

	Rear polarizing film	**Front polarizing film**
LCD 1	epoxy resin	epoxy resin
LCD 2	acetyl cellulose	epoxy resin
panel 1	acetyl cellulose	epoxy resin
panel 2	PBT[15]	epoxy resin

where:

- "*LCD*" refers to the LCD monitors manually dismantled;
- "*panel*" refers to the LCD glass panels provided by the e-waste treatment plant.

Light guide composition was determined by directly reading it on the monitor casing; it was found that it is constituted by poly(methyl methacrylate) (PMMA). Plastic casing composition is provided by the manufacturer as well; it is reported in Table 21:

Table 21. Plastic casing composition

	LCD 1	**LCD 2**
polymer	ABS[16]; PC+ABS; HIPS[17]	PC/ABS; PC+ABS
flame retardants	FR[18](17); FR (40)	FR (40)

---

[12] PC: polycarbonate
[13] PMMA: poly(methyl methacrylate)
[14] PET: polyethylene terephthalate
[15] PBT: polybutylene terephthalate
[16] ABS: acrylonitrile/butadiene/styrene
[17] HIPS: high impact polystyrene
[18] FR: flame retardant

5.2 REMOVAL OF THE POLARIZING FILM

In this Section, results of the first step of the recovery technique, i.e. the removal of the polarizing film, are reported.

5.2.1 CHEMICAL TREATMENTS

Among the organic solvents tested, acetone and ethyl acetate proved to be the most effective since 8h and 5h, respectively, were sufficient for removing the polarizing film in the absence of the ultrasound treatment; this result could be probably linked to a partial solubilization of the pressure sensitive adhesive.

Limonene and isopropyl alcohol treatment did not allow removing the film within 8h.

With the aid of the ultrasound treatment some improvements were obtained, since 4h and 2-3h were sufficient by employing acetone and ethyl acetate respectively; limonene and isopropyl alcohol treatment required 8h, then the film could be easily removed by soft brushing.

5.2.2 THERMAL TREATMENTS

Thermal treatment with liquid nitrogen was an effective option since only 10-20 minutes were required, according to the type of LCD considered. The amount of reagent added during the tests was ~0.025 L/g.

Thermal treatments at high temperature are ineffective since no detachment is achievable in the range T=100-220°C; in correspondence of T=240°C, carbonization occurs.

In Table 22 the time required to obtain a complete removal of the polarizing film from the glass substrate with the different techniques (both thermal and chemical) is reported:

Table 22. Removal of the polarizing film

Treatment	**Operative parameters**		**Time**
Thermal treatment	Liquid nitrogen		10-20 min
	Furnace, T=100-240°C, 20°C/h		not achievable at T<240°C
		Ultrasound assisted	
Chemical treatment	Limonene	-	not achievable within 8 h
		✓	8 h
	Isopropyl alcohol	-	not achievable within 8 h
		✓	8 h
	Acetone	-	8 h
		✓	4 h
	Ethyl acetate	-	5 h
		✓	2-3 h

The obtained product was analyzed by FTIR spectroscopy and stereomicroscopy in order to check its composition and chemical-physical properties.

Results are shown in Table 23-24 and in Figure 22-23.

Table 23. Outer side of the polarizing film after the treatments - FTIR spectroscopy analysis

		Panel 1	**Panel 2**
Liquid nitrogen	rear	acetyl cellulose	PBT
	front	epoxy resin	epoxy resin
Limonene	rear	acetyl cellulose	PBT
	front	epoxy resin	NN[19]
Acetone	rear	acetyl cellulose	epoxy resin
	front	acetyl cellulose	epoxy resin
Ethyl acetate	rear	acetyl cellulose	PBT
	front	epoxy resin	epoxy resin
Isopropyl alcohol	rear	acetyl cellulose	epoxy resin
	front	epoxy resin	NN

Table 24. Inner side of the polarizing film after the treatments - FTIR spectroscopy analysis

		Panel 1	**Panel 2**
Liquid nitrogen	rear	cellulose	acrylic adhesive
	front	NN	NN
Limonene	rear	acrylonitrile film	acrylic adhesive
	front	acrylic adhesive	acetyl cellulose
Acetone	rear	NN	acetyl cellulose
	front	epoxy resin	epoxy resin
Ethyl acetate	rear	acrylic adhesive	acrylic adhesive
	front	acrylic adhesive	diethyl adipate
Isopropyl alcohol	rear	acrylonitrile film	acrylic adhesive
	front	epoxy resin	acrylic adhesive

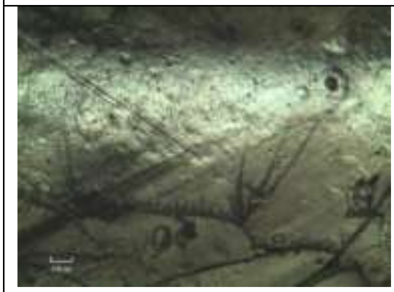
---

[19] NN: not detected

FTIR analysis revealed that the composition of the external side of the two polarizing films does not change after the treatment; this result can be explained with the chemical resistance of the PBT/epoxy resin/acetyl cellulose layer. However, as shown in Figure 22, the product appears strongly damaged if ethyl acetate is employed as solvent (on the front polarizer grooves are visible). Acetone treatment is similar to that of ethyl acetate. The polarizing film removed through liquid nitrogen does not show degradation, since only few scratches were observed. Limonene and isopropyl alcohol treatment did not led to substantial degradation as well, but some porosity appears.

Regarding the internal side of the product (Table 24 and Figure 23), the analysis confirmed the presence of the acrylic adhesive employed for assembling the polarizing film on the glass substrate.

Finally, Figure 24 shows the polarizing film stratification that was observed on the front polarizing film after the treatment with acetone.

Rear polarizing film	**Front polarizing film**
	
Liquid nitrogen	
	
Limonene	
	

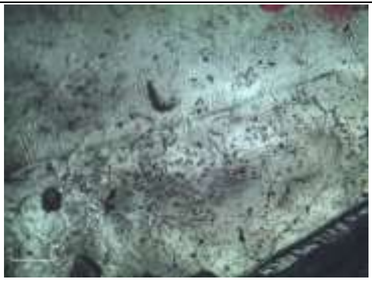
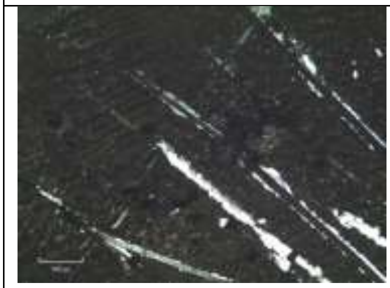
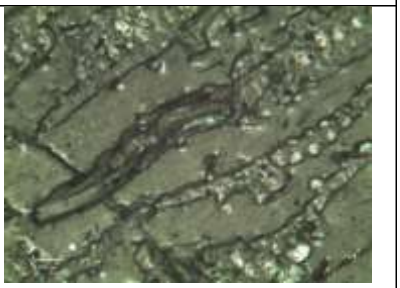
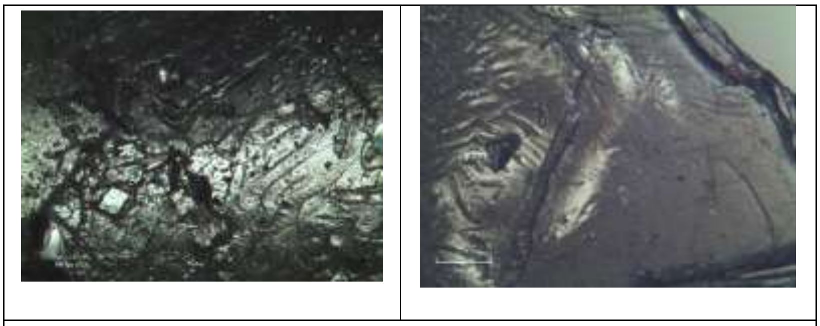
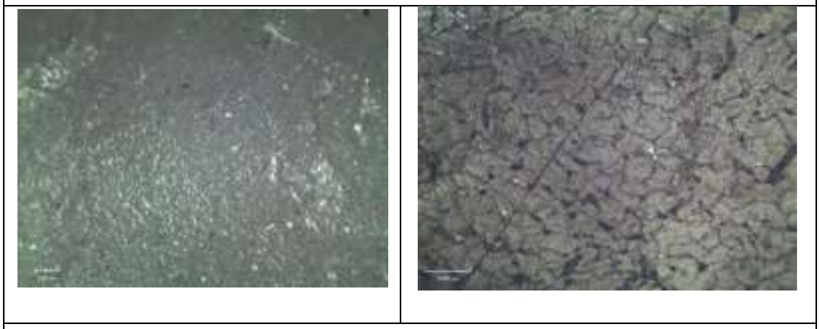
<table>
<tr><td colspan="2">Ethyl acetate</td></tr>
<tr><td></td><td></td></tr>
<tr><td colspan="2">Acetone</td></tr>
<tr><td></td><td></td></tr>
<tr><td colspan="2">Isopropyl alcohol</td></tr>
</table>

Figure 22. Outer side of the polarizing film after the treatments - stereomicroscope analysis

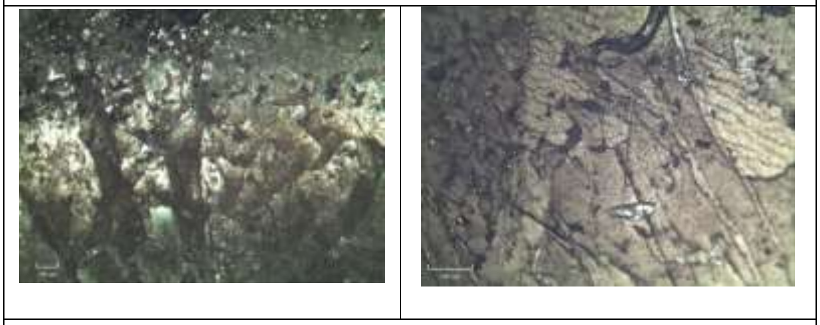
<table>
<tr><th>Rear polarizing film</th><th>Front polarizing film</th></tr>
<tr><td></td><td></td></tr>
<tr><td colspan="2">Liquid nitrogen</td></tr>
<tr><td></td><td></td></tr>
<tr><td colspan="2">Limonene</td></tr>
</table>



Ethyl acetate



Acetone



Isopropyl alcohol

Figure 23. Inner side of the polarizing film after the treatments - stereomicroscope analysis

Figure 24. Polarizing film stratification observed after chemical treatment with acetone – stereomicroscope analysis

It can be concluded that the best technique for the removal of the polarizing film is thermal treatment with liquid nitrogen, both in terms of time (10-20 minutes) and of final product quality, thus encouraging reuse possibilities as secondary raw material.

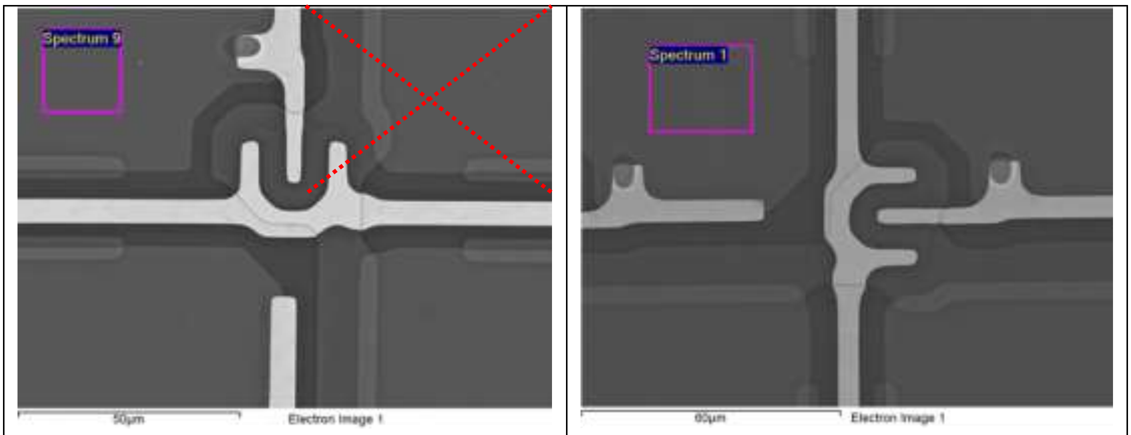
5.3 CHARACTERIZATION OF THE GLASS SUBSTRATE

As explained in Section 4.3, the polarizing film was removed from the glass substrate with the technique that gave the best results, which is thermal treatment with liquid nitrogen. As reported in Table 25, the glass substrate and the polarizing film account for 86% w/w and 14% w/w of the LCD panel, respectively.

Table 25. Glass and polarizing film content in the LCD panel

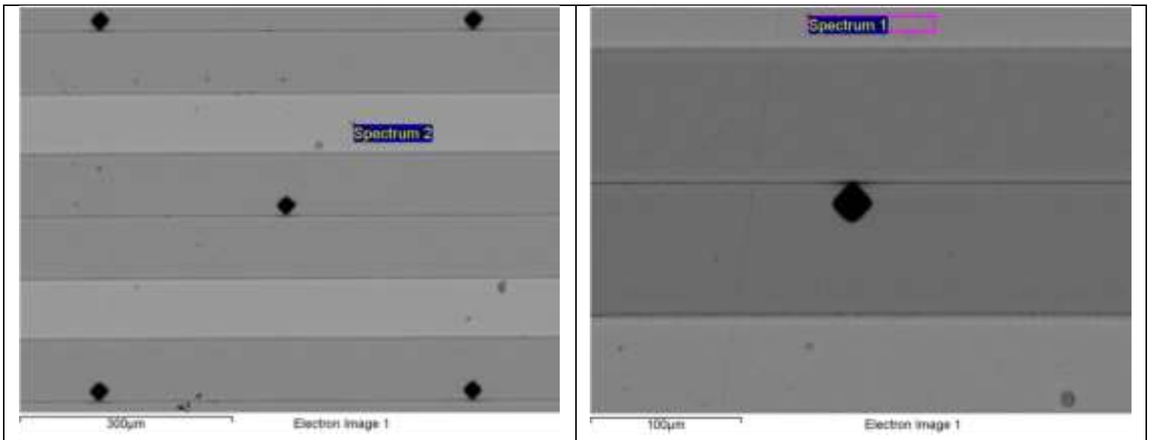
	Glass substrate	**Polarizing film**
	[%]	[%]
LCD 1	87	13
LCD 2	85	15
Average composition	86	14

In Figure 25-26, SEM analyses performed on the glass substrate before and after the treatment with liquid nitrogen are reported. .



(a) (b)

Figure 25. SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with liquid nitrogen – TFT layer



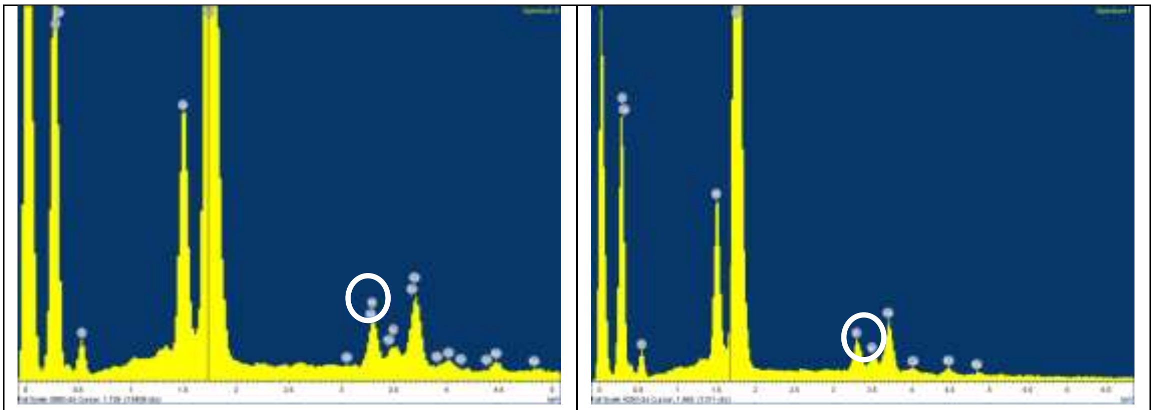
(a) (b)

Figure 26. SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with liquid nitrogen - color filter layer

Figure 25 refers to the TFT layer; it reveals the presence of pixel electrodes, constituted by indium tin oxide (red colored), as well as the gate electrode and the source/gate electrode constituted by refractory metals, such as molybdenum (lighter parts) (see Table 5).

Figure 26 refers to the color filer layer: in this case, indium is evenly deposited on the glass substrate as common electrode. The stratification that is clearly visible could be linked to the presence of the three color filters, i.e. red, green and blue.

In Figure 27-28, the corresponding EDS[20] spectra are reported; the circles (white colored) identify the X-ray peaks corresponding to indium element.



(a) (b)

Figure 27. EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with liquid nitrogen - TFT layer

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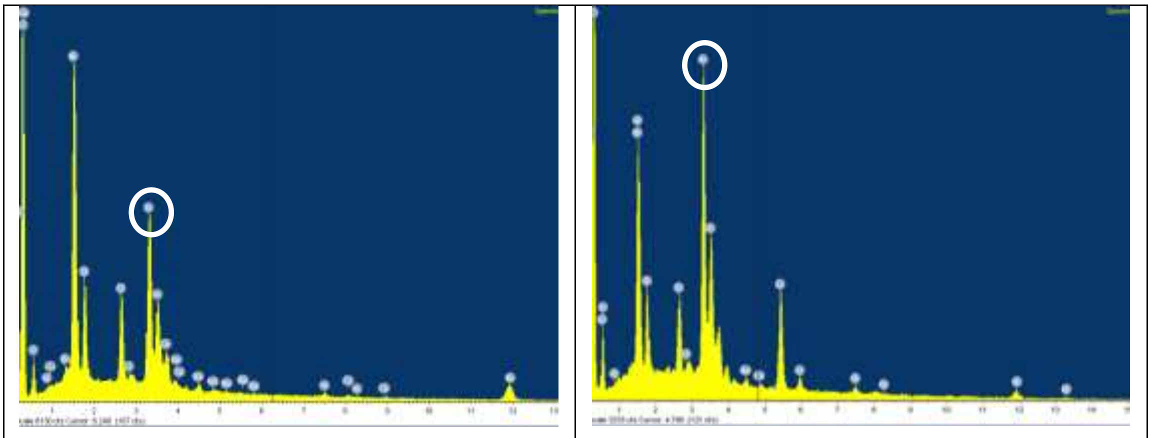
[20] Energy Dispersive Spectroscopy



(a) (b)

Figure 28. EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with liquid nitrogen - color filter layer

It was found that indium was not removed from the glass substrate after the treatment with liquid nitrogen, since the EDS spectrum still revealed its presence.

Indium peak intensity is more significant in the color filter layer spectrum with respect to the TFT layer, due to the higher amount of indium.

The glass substrate was then characterized in order to determine its indium and tin content.

As explained in Section 4.3, preliminary leaching tests with aqua regia were performed on indium tin oxide. Results are reported in Table 26.

Table 26. Indium and tin leaching efficiency with aqua regia (ITO powder, T=25°C, L/S=500 mL/g)

	In	**Sn**
	[%]	**[%]**
t=8h	95	51
t=24h	96	49

It was found that a complete dissolution of tin oxide cannot be achieved even in 24h; since the same leaching efficiency was achieved in 8h, the characterization of the LCD glass substrate was performed by setting 8h as the contact time.

Indium and tin content in the glass substrate is reported in Table 27; it is expressed as indium and tin mass with respect to the glass substrate (without the polarizing film):

Table 27. Indium and tin content in the glass substrate (aqua regia leaching, T=25°C, t=8h, L/S=3 mL/g)

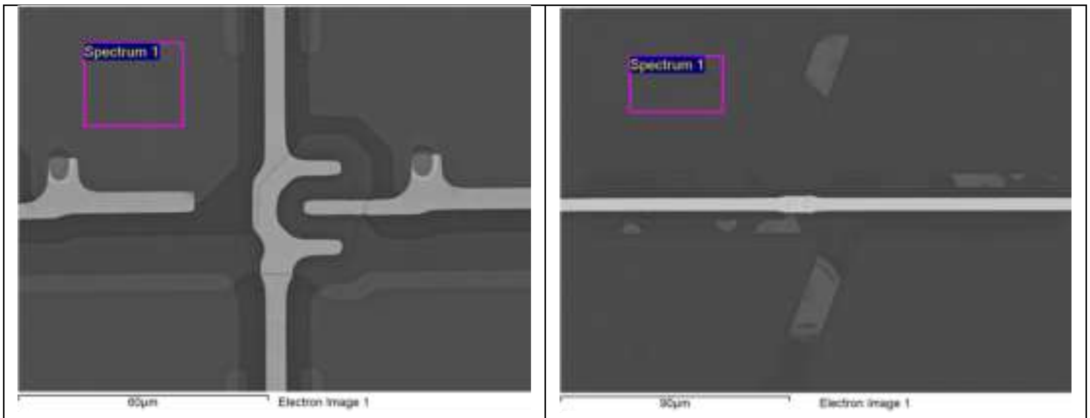
	In	**Sn**
	[%]	**[%]**
LCD 1	0.0270	0.0028
LCD 2	0.0259	0.0027

By assuming that the dissolved indium and tin are respectively 95% and 51% of the total amount (see Table 26), the estimated amount of indium and tin were calculated, which are reported in Table 28:

Table 28. Estimated indium and tin content in the glass substrate

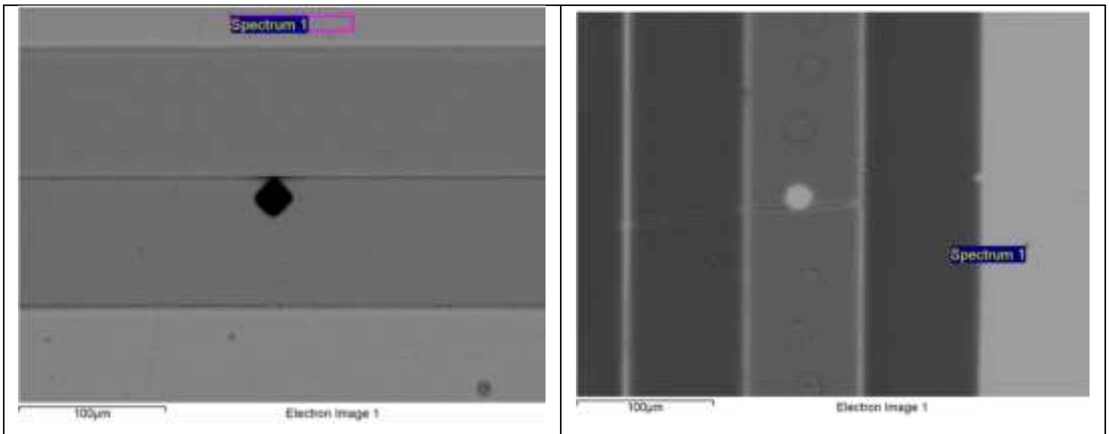
	In	**Sn**
	[%]	**[%]**
LCD 1	0.0285	0.0056
LCD 2	0.0272	0.0053

SEM analysis performed on the glass substrate after the characterization step (Figure 29-32) confirmed the complete dissolution of indium oxide: as shown in Figure 31-32, indium peaks were not detected anymore after the treatment with aqua regia (dashed line refers to the X-ray peaks corresponding to indium).



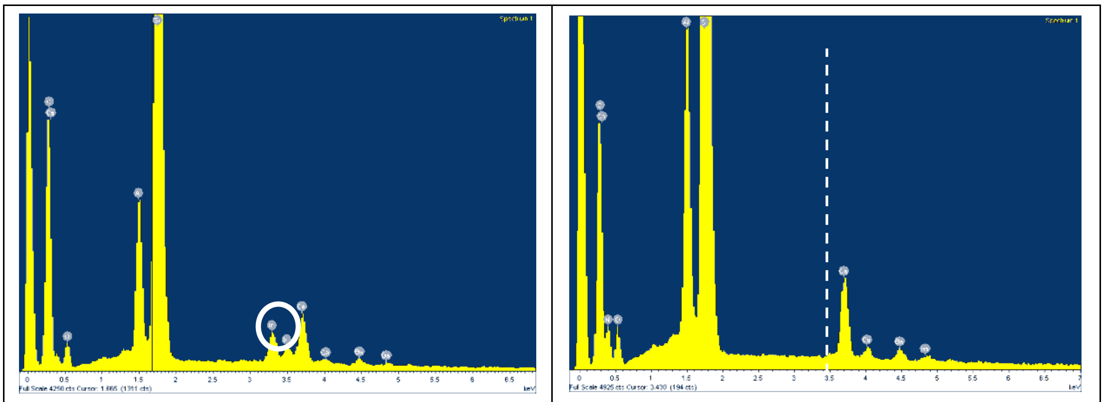
(a) (b)

Figure 29. SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with aqua regia - TFT layer



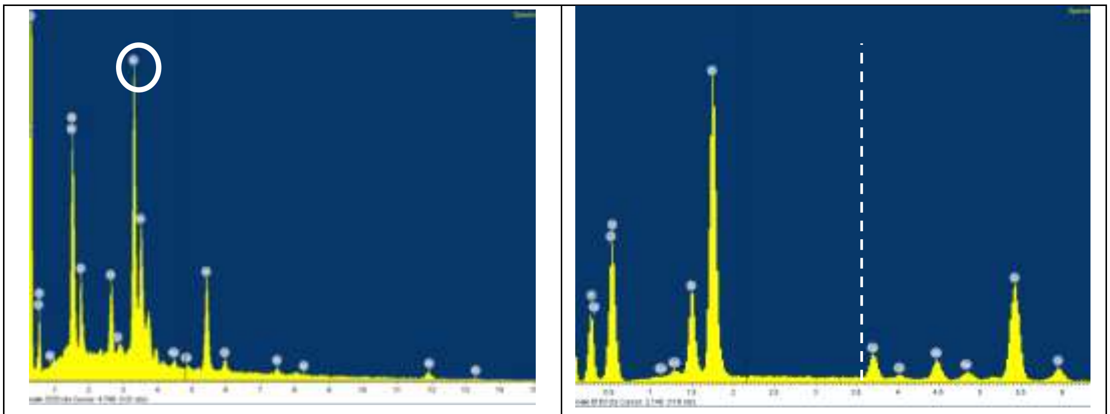
(a) (b)

Figure 30. SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with aqua regia - color filter layer



(a) (b)

Figure 31. EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with aqua regia - TFT layer



(a) (b)

Figure 32. EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with aqua regia - color filter layer

5.4 LEACHING

In Section 5.4.1 leaching tests carried out on indium tin oxide powder (-325 mesh, ≥99.99% trace metals basis, Sigma Aldrich) are presented; those referring to the glass substrate are described in Section 5.4.2.

5.4.1 LEACHING OF INDIUM TIN OXIDE POWDER

In Figures 33 indium leaching efficiency with HCl 6N is reported as a function of time and liquid/solid ratio.

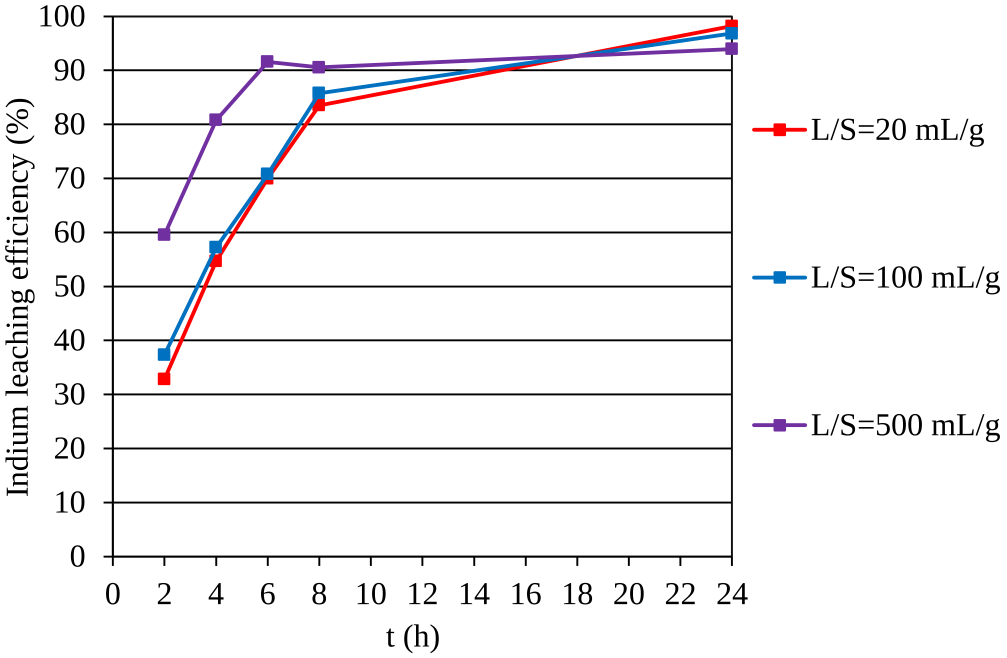


Figure 33. Indium leaching efficiency from indium tin oxide (HCl 6N, T=25°C)

In Figures 34-36 indium extraction kinetics with HNO_3, H_2SO_4 and the mixture HCl-HNO_3 6N are reported.

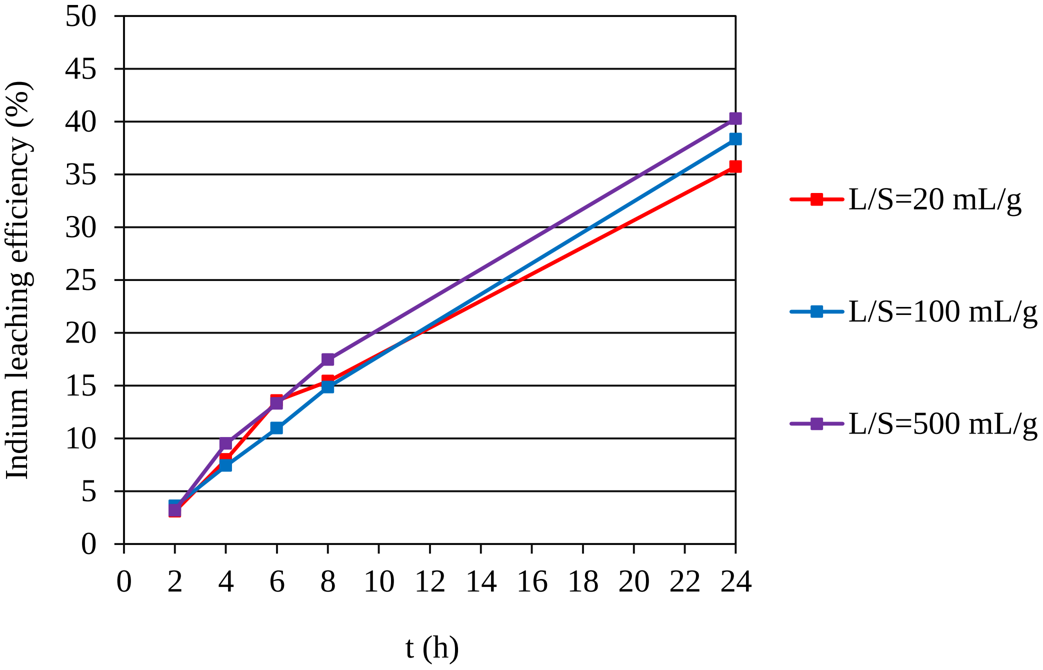


Figure 34. Indium leaching efficiency from indium tin oxide (HNO_3 6N, T=25°C)

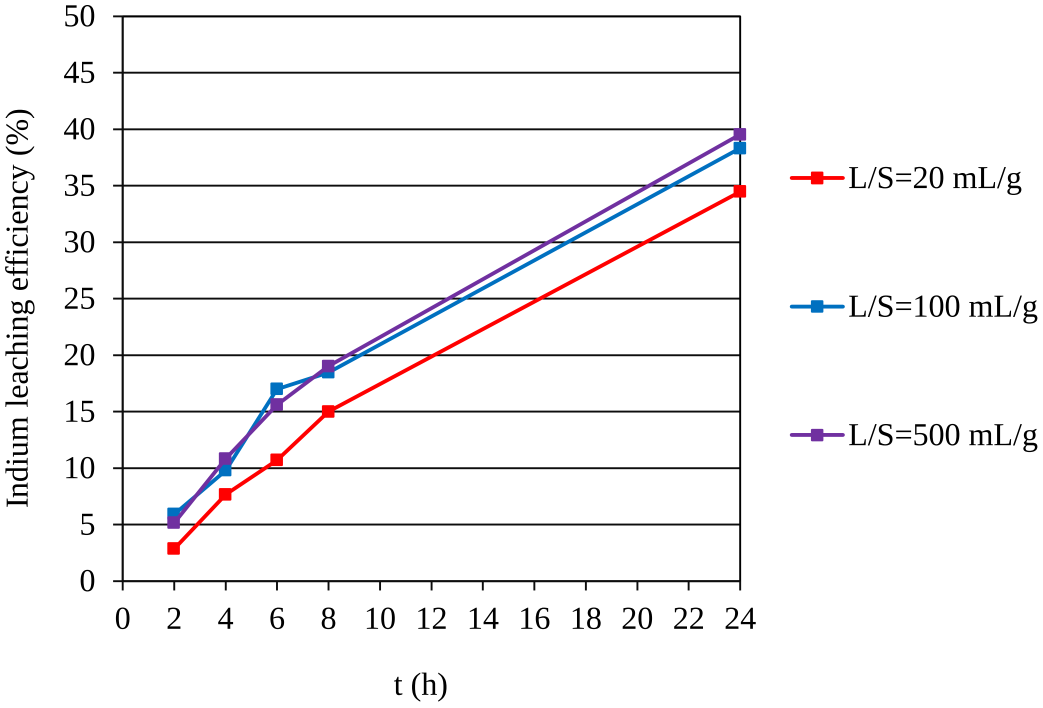


Figure 35. Indium leaching efficiency from indium tin oxide (H_2SO_4 6N, T=25°C)

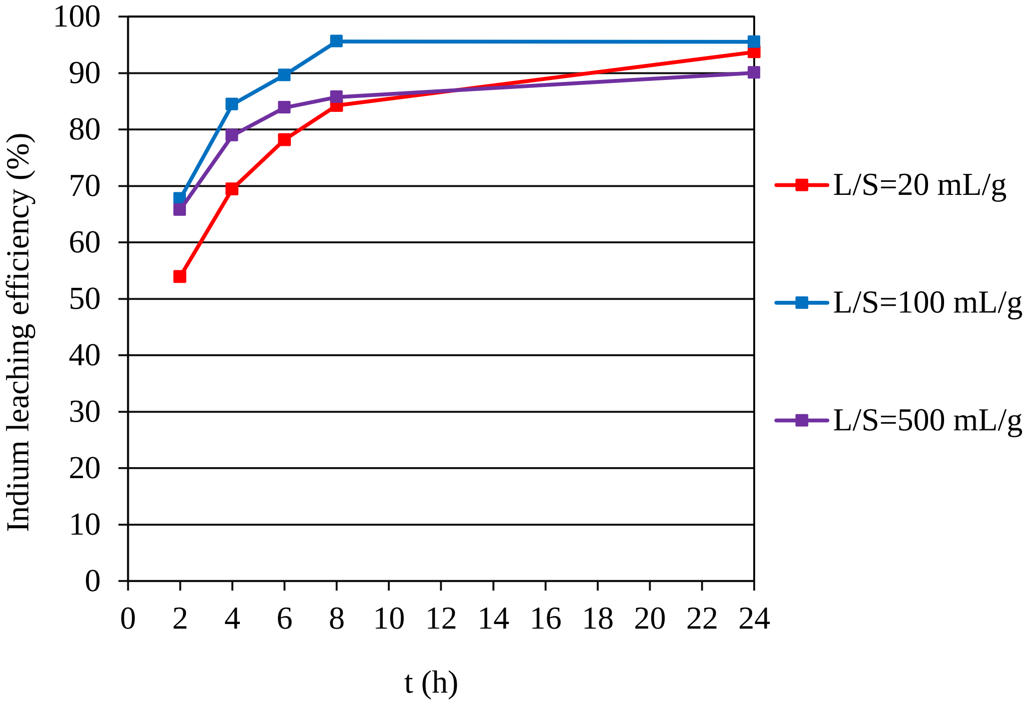


Figure 36. Indium leaching efficiency from indium tin oxide (HCl-HNO_3 6N, T=25°C)

All the leaching tests are also represented in Figure 37:

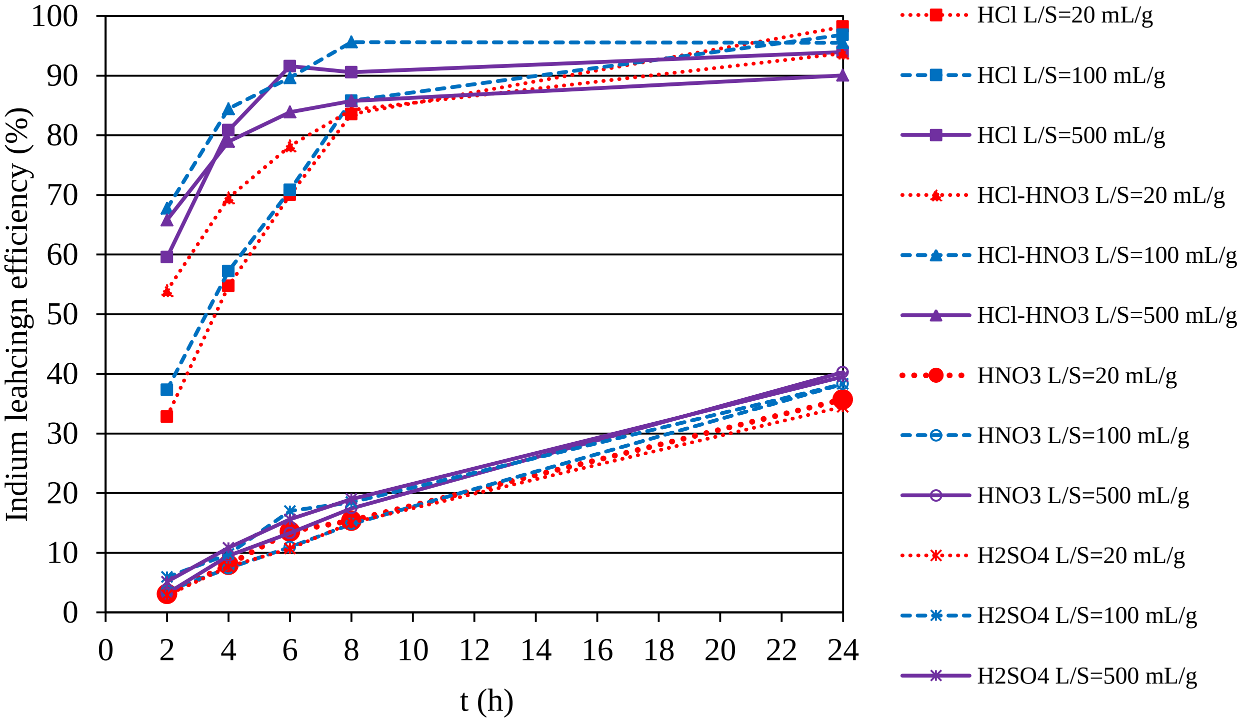


Figure 37. Indium leaching efficiency from indium tin oxide (T=25°C)

It was found that indium extraction kinetics are very slow if nitric acid and sulfuric acid are employed as leaching agents: as reported in Figure 37, only 40% indium was extracted in 24h.

The mixture hydrochloric acid / nitric acid showed a better behavior since approximately 95% indium was extracted in 8h by employing a liquid/solid ratio of 100 mL/g; however, by increasing the liquid/solid ratio up to 500 mL/g, a decrease in the leaching efficiency was observed.

Hydrochloric acid leaching is effective as well since, by employing a liquid/solid ratio of 20 mL/g or 100 mL/g, 85% indium was extracted in 8h; by increasing the liquid/solid ratio up to 500 mL/g, 6h are sufficient to obtain an extraction efficiency of approximately 90%.

Tin analysis was performed only at 24h; indium and tin extraction efficiency is reported in Table 29.

Table 29. Indium and tin leaching efficiency (ITO powder, T=25°C, t=24h)

Leaching agent	**Liquid/solid ratio**	**In**	**Sn**
		Leaching efficiency	
	[mL/g]	**[%]**	
HCl 6N	20	98	53
	100	96	59
	500	94	71
HNO_3 6N	20	36	12
	100	38	11
	500	40	10
H_2SO_4 6N	20	34	2
	100	38	13
	500	40	15
HCl-HNO_3 6N	20	94	54
	100	96	56
	500	90	60

5.4.2 LEACHING OF THE GLASS SUBSTRATE

The optimal conditions defined in Section 5.4.1 were applied for the leaching of the glass substrate obtained after the removal of the polarizing film.

Leaching tests were thus carried out by employing HCl 6N as a lixiviant, at room temperature and by fixing 6h as contact time; regarding the liquid/solid ratio, it was set at 3 mL/g in order to guarantee a complete contact between the solvent and the solid residue, which is now mainly constituted by glass.

Leachate analyses are reported in Table 30.

Table 30. Leachate composition (HCl 6N, T=25°C, t=6h, L/S=3 mL/g)

	LCD 1	**LCD 2**	**Average composition**
	[ppm]	**[ppm]**	**[ppm]**
In	87.54	83.78	~85.66
Sn	9.48	8.92	~9.20
Al	7.85	4.92	~6.39
Cr	2.34	-	~1.17

The presence of aluminum could be linked to a partial solubilization of the gate electrode as well as the gate insulator present on the TFT layer; chromium traces may be due to the solubilitation of the black matrix on the color filter layer.

In Figures 38-39 indium and tin leaching efficiency with the respect to the initial content (See Table 28) is reported.

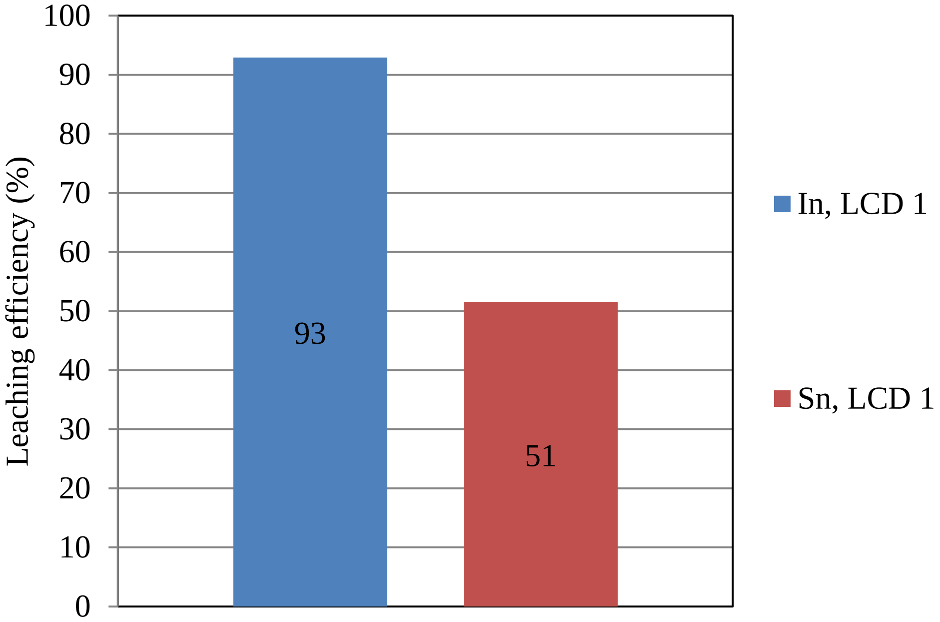


Figure 38. Leaching of the glass substrate - LCD 1 (HCl 6N, T=25°C, t=6h, L/S=3 mL/g)

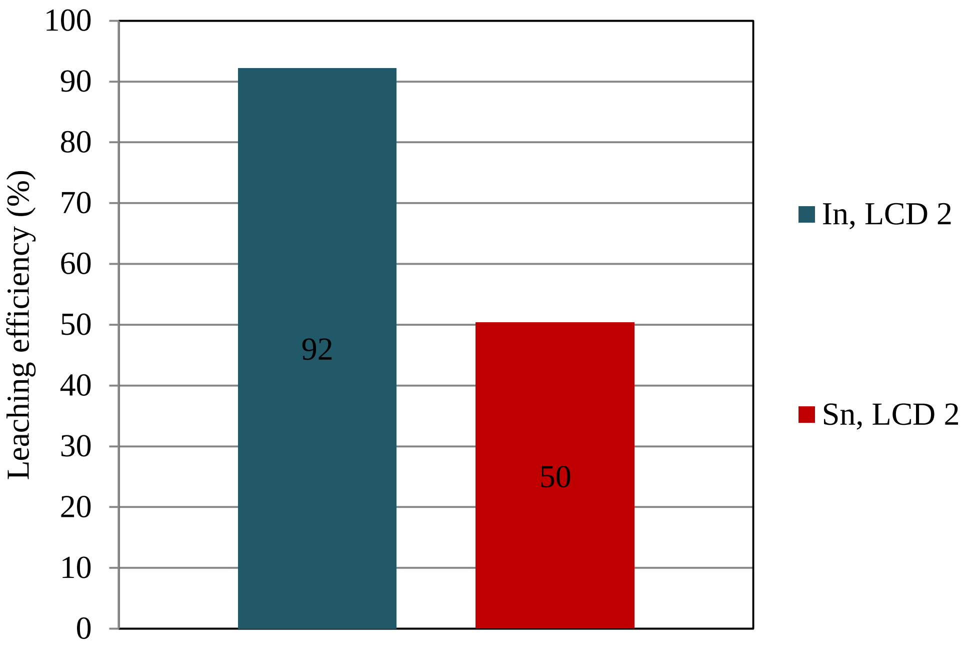
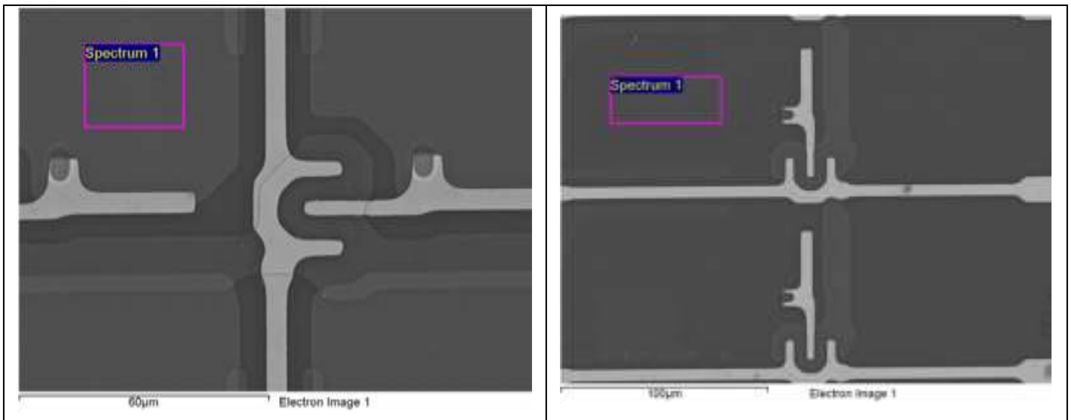


Figure 39. Leaching of the glass substrate - LCD 2 (HCl 6N, T=25°C, t=6h, L/S=3 mL/g)

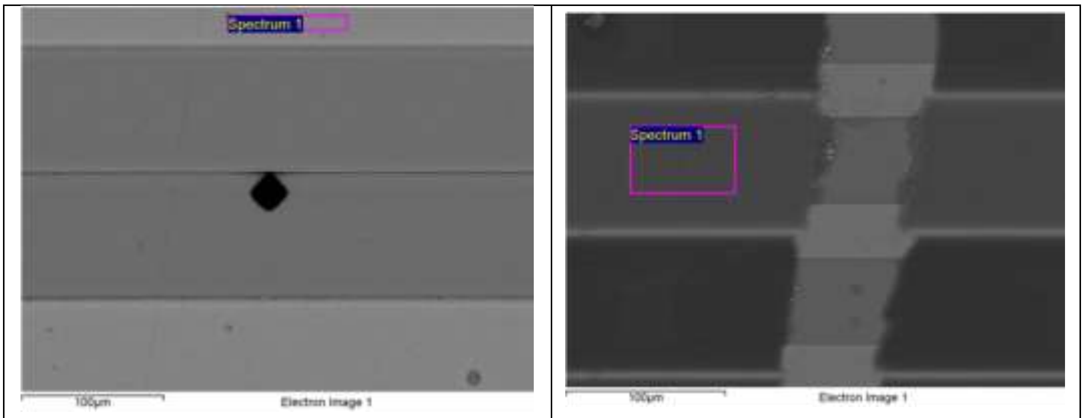
It was found that almost all indium oxide is solubilized by employing HCl 6N as a lixiviant.

SEM analysis were performed on the glass substrate obtained after the leaching with HCl 6N (Figures 40-43). As reported in Figures 42-43, indium is no more detected in the EDS spectrum.



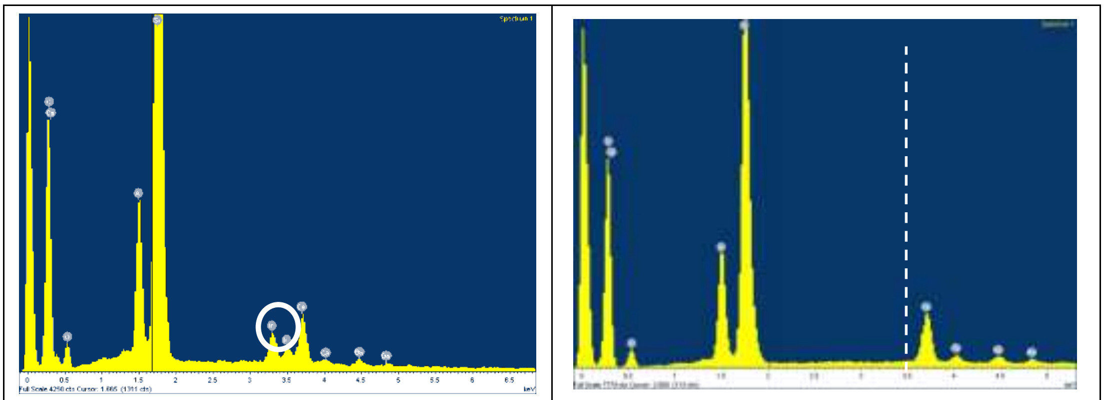
(a) (b)

Figure 40.SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with HCl 6N - TFT layer



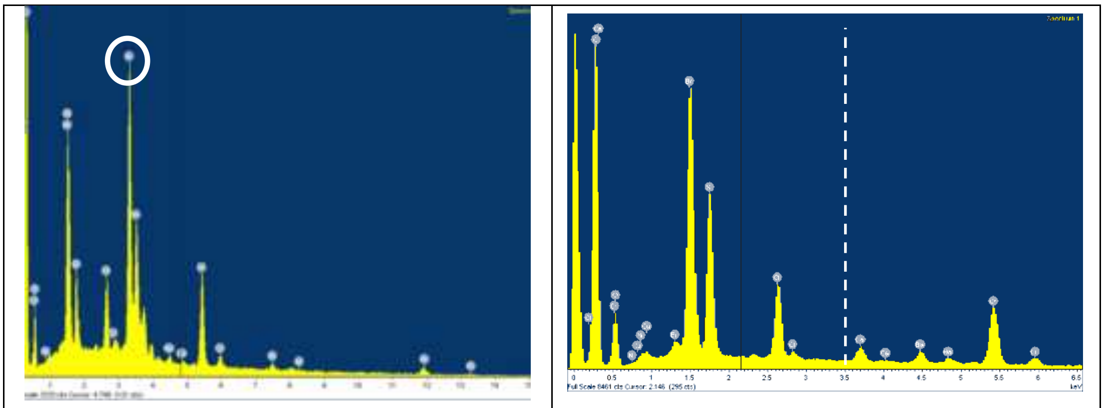
(a) (b)

Figure 41. SEM analysis of the LCD glass substrate before (a) and after (b) the treatment with HCl 6N - color filter layer



(a) (b)

Figure 42. EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with HCl 6N - TFT layer



(a) (b)

Figure 43.EDS spectrum of the LCD glass substrate before (a) and after (b) the treatment with HCl 6N - color filter layer

5.5 INDIUM EXTRACTION WITH AQUEOUS BIPHASIC SYSTEMS (ABSs)

In this Section, indium extraction tests with aqueous biphasic systems are reported. Section 5.5.1 is dedicated to the description of a preliminary study on indium chelates; in Sections 5.5.2-5.5.3 indium extraction tests results are reported.

5.5.1 PRELIMINARY INVESTIGATION ON INDIUM CHELATES

As explained in Section 4.5.1, two complexing agents were selected, ammonium thiocyanate and 1,10 phenantroline.

In Figures 44-46, UV spectra of indium solutions by employing ammonium thiocyanate as complexing agent are reported; they respectively refer to the three values of the pH (i.e., ~4.5, ~7.5 and ~11.5).

The analysis were restricted to the range λ=190-370 since preliminary tests carried out ranging from λ=190 to 800 did not provide significant information.

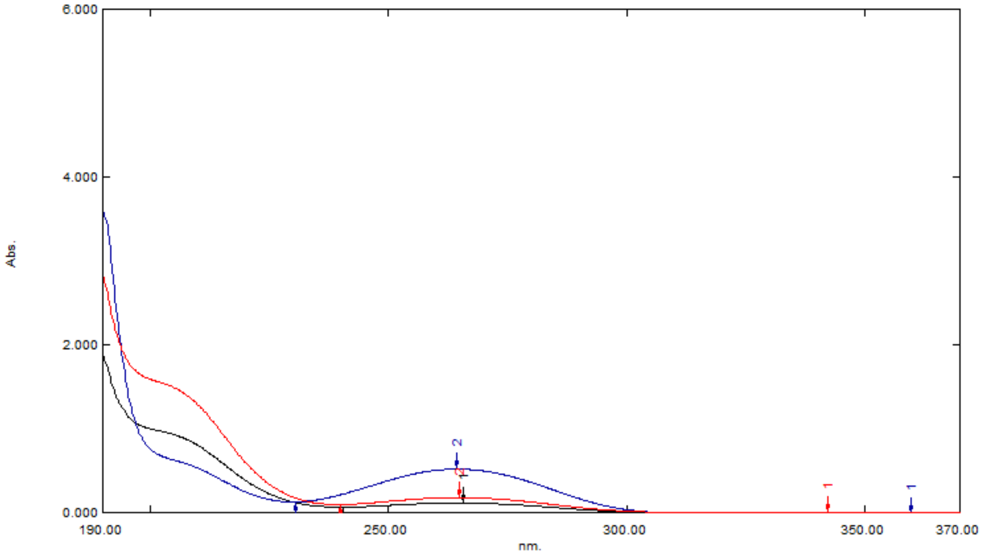


Figure 44. Thiocyanate solution $6 \cdot 10^{-6}$ M (black); indium solution $1.2 \cdot 10^{-6}$ M (blue); indium ($1.2 \cdot 10^{-6}$ M) - thiocyanate ($6 \cdot 10^{-6}$ M) solution (red); pH_{eq}~4.5

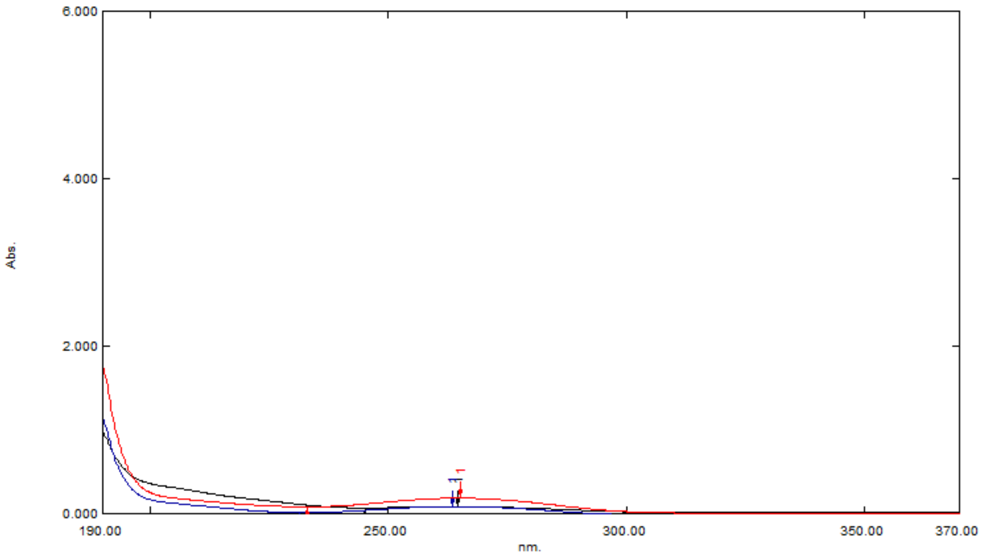


Figure 45. Thiocyanate solution 6·10^{-6} M (black); indium solution 1.2·10^{-6} M (blue); indium (1.2·10^{-6} M) – thiocyanate (6·10^{-6} M) solution (red); pHeq~7.5

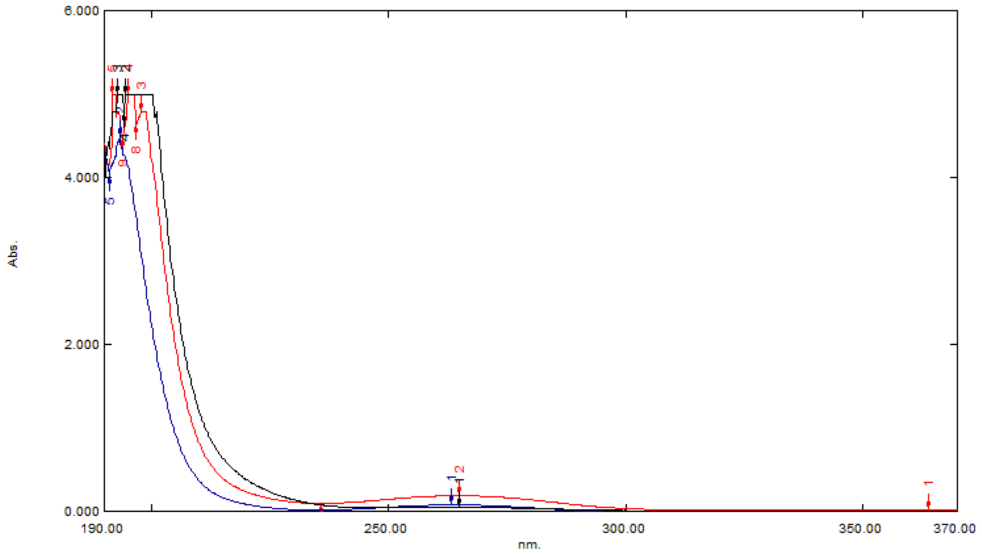


Figure 46. Thiocyanate solution 6·10^{-6} M (black); indium solution 1.2·10^{-6} M (blue); indium (1.2·10^{-6} M) - thiocyanate (6·10^{-6} M) solution (red); pH$_{eq}$~11.5

It was observed that thiocyanate spectra in the presence of indium ions are comparable with those referring to the thiocyanate solution in the absence of the metal ions, whatever the pH.

Other tests were performed by employing 1,10 phenantroline as complexing agent. In Figure 47-49, the corresponding UV spectra are reported for the three values of the equilibrium pH.

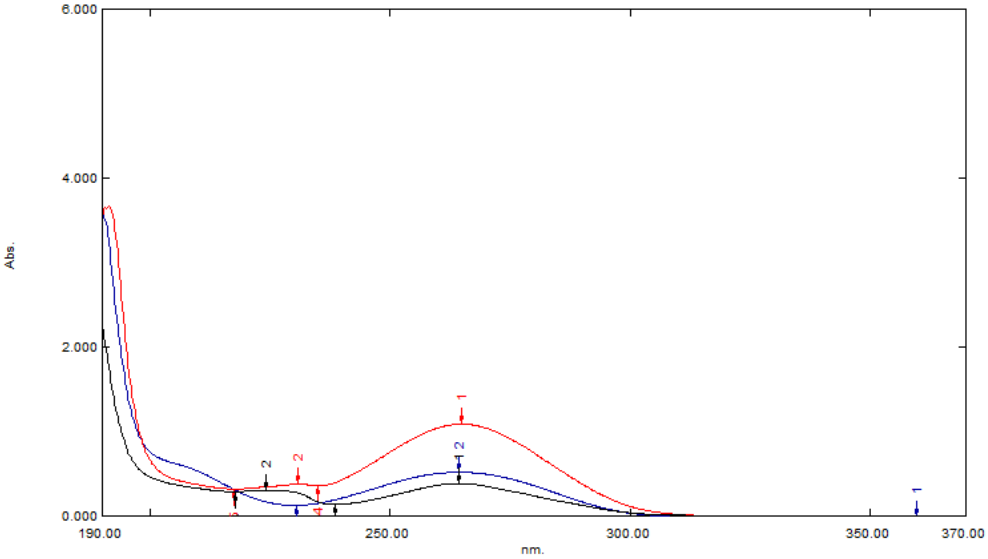


Figure 47. 1,10 phenantroline solution $6 \cdot 10^{-6}$ M (black); indium solution $1.2 \cdot 10^{-6}$ M (blue); indium ($1.2 \cdot 10^{-6}$ M) - phenantroline ($6 \cdot 10^{-6}$ M) solution (red); pH_{eq}~4.5

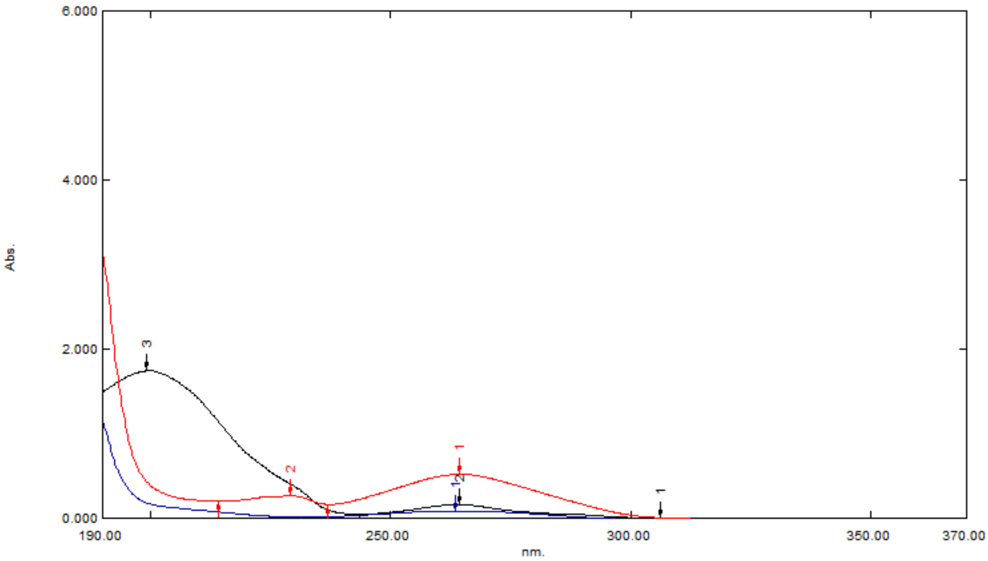


Figure 48. 1,10 phenantroline solution $6 \cdot 10^{-6}$ M (black); indium solution $1.2 \cdot 10^{-6}$ M (blue); indium ($1.2 \cdot 10^{-6}$ M) - phenantroline ($6 \cdot 10^{-6}$ M) solution (red); pH_{eq}~7.5

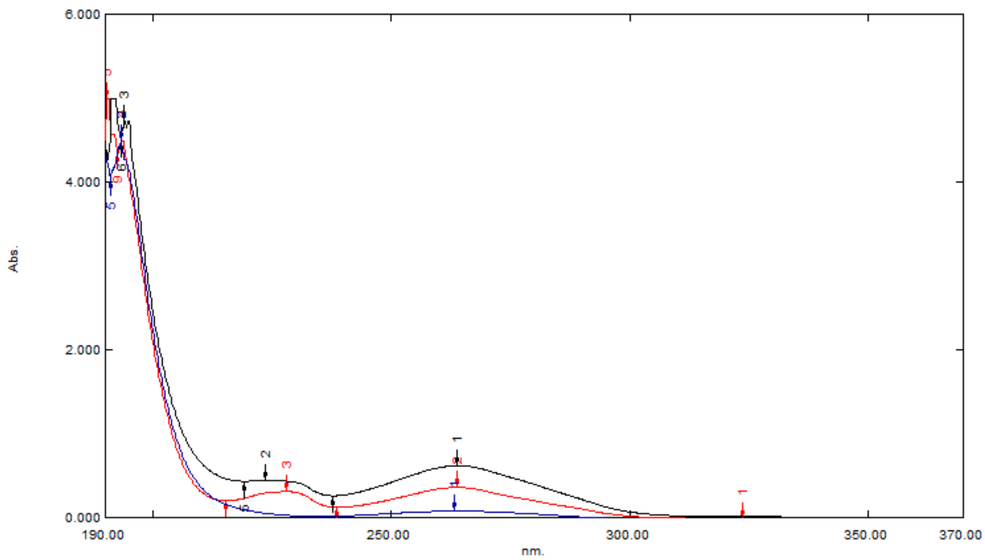


Figure 49. 1,10 phenantroline solution $6\cdot10^{-6}$ M (black); indium solution $1.2\cdot10^{-6}$ M (blue); indium ($1.2\cdot10^{-6}$ M) - phenantroline ($6\cdot10^{-6}$ M) solution; pH_{eq}~11.5

It was found that if 1,10 phenantroline is employed as complexing agent, a slight difference between the spectra was observed for a pH value of ~7.5 in the range λ=190-250, thus suggesting the formation of metal complexes.

Data collected allowed defining the operative conditions for the extraction tests of indium ions through ABSs, namely:

- 1,10 phenantroline as complexing agent
- pH~7.5

5.5.2 INDIUM EXTRACTION TESTS

Preliminary extraction tests were carried out by employing 1,10 phenantroline as complexing agent; the pH of the metal-rich solution was ~7.5. However, after few hours a precipitate was observed, probably linked to the low stability of indium complexes; for this reason, the extraction tests were then performed at a lower pH, namely ~5.5.

In Figure 50-51 indium extraction efficiency in the lower and the upper phase by employing PEG 3,350 is reported as a function of PEG concentration and ammonium sulfate concentration, respectively.

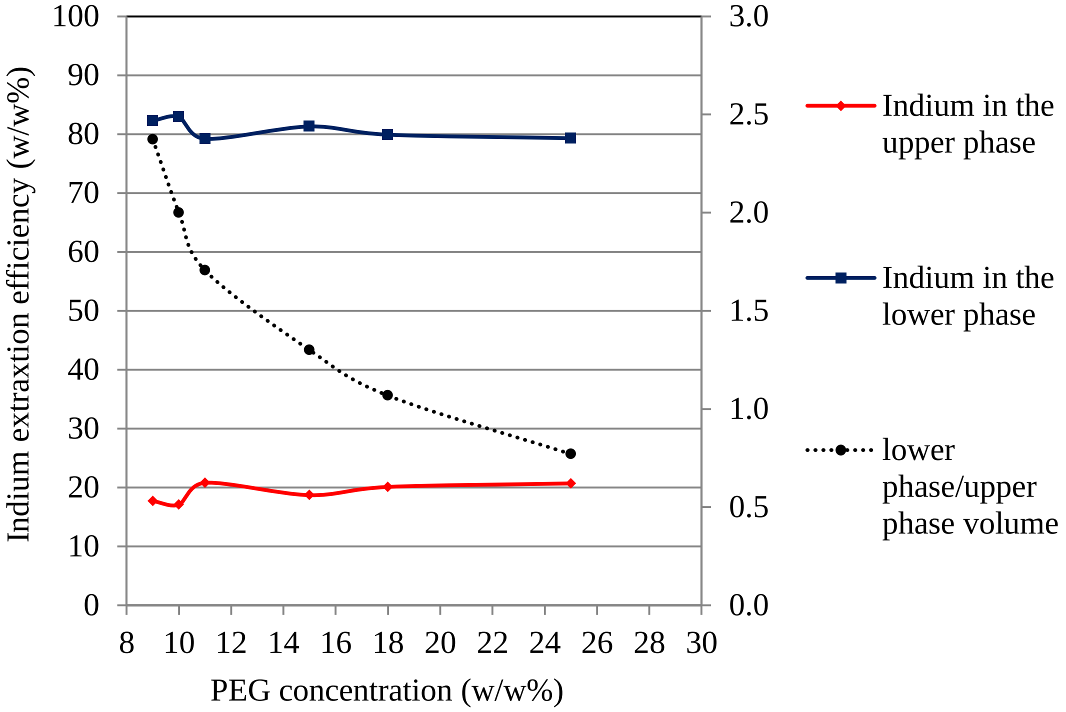


Figure 50. Indium extraction efficiency as a function of PEG concentration ([$(NH_4)_2SO_4$]$_{ABS}$=12% w/w; pH_{eq}~5.5; PEG 3,350)

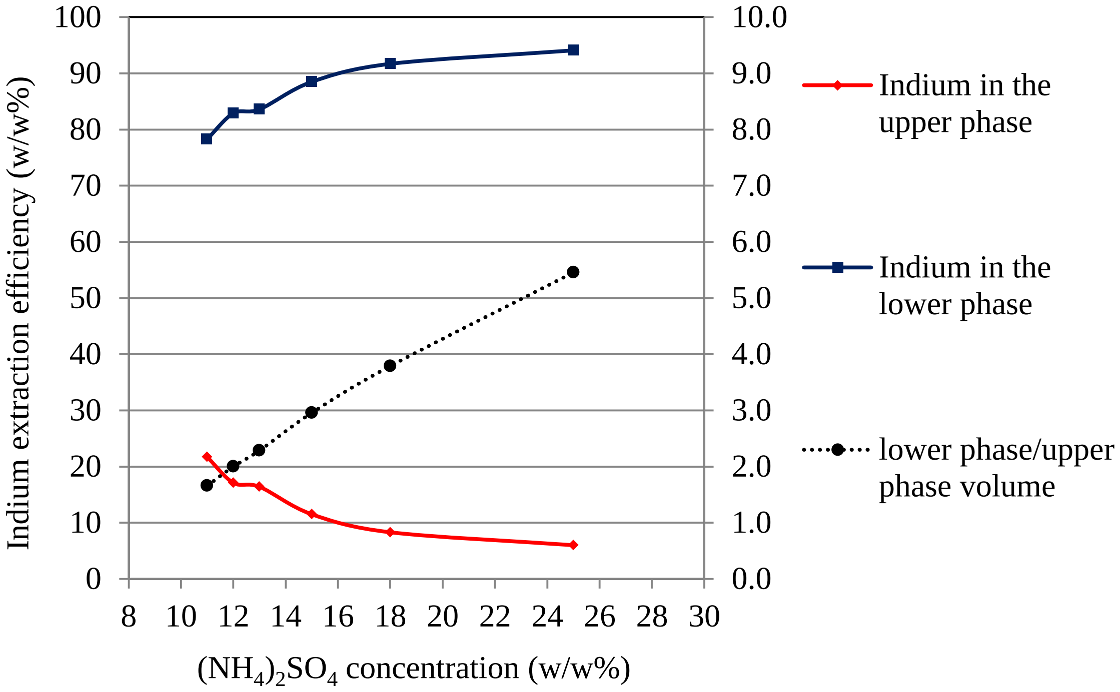


Figure 51. Indium extraction efficiency as a function of $(NH_4)_2SO_4$ concentration ([PEG]$_{ABS}$=10% w/w; pH_{eq}~5.5; PEG 3,350)

It was found that indium repartition between the lower and the upper phase is quite independent from system composition, since 80-90% indium is extracted in the lower phase and 10-20% in the upper phase.

As reported in Figure 50, by increasing PEG concentration the ratio between the lower and the upper phase decreases; since the percentage of indium extracted in the lower phase is invariable, that leads to a concentration of the species of interest.

When PEG concentration reaches 25% w/w, the system starts to show some turbidity; for this reason it would be better to set PEG concentration below this value.

The opposite behavior was registered by increasing salt concentration, since the volume ratio between the phases increases, thus determining a decrease in indium concentration in the lower phase.

In Figures 52-53, indium extraction tests with PEG 10,000 are reported as a function of PEG concentration and salt concentration, respectively.

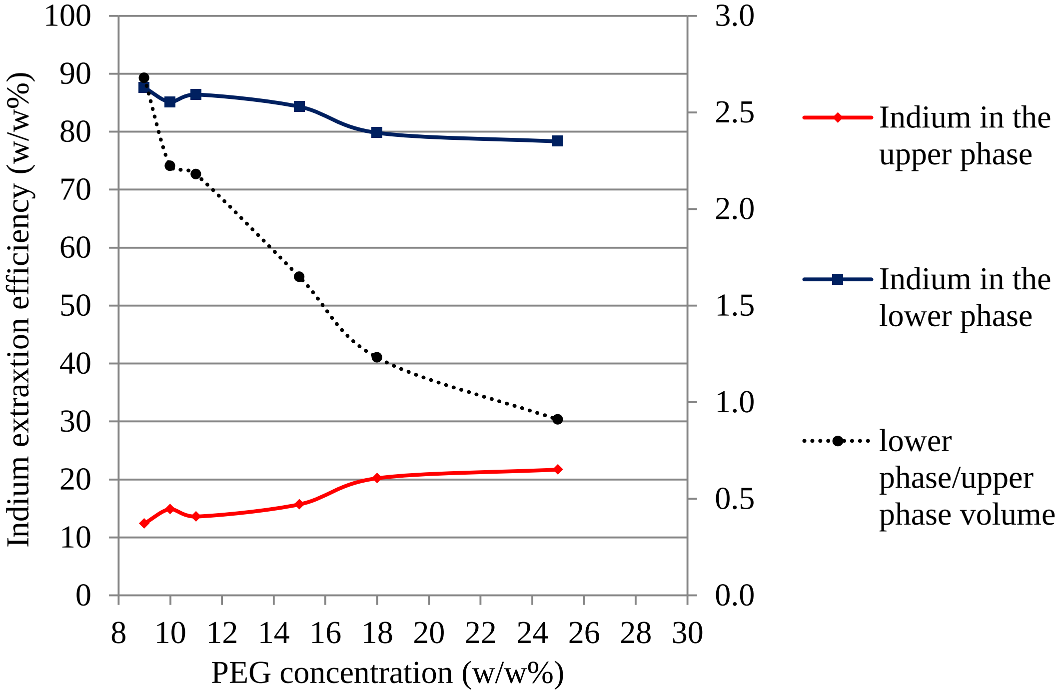


Figure 52. Indium extraction efficiency as a function of PEG concentration ($[(NH_4)_2SO_4)]_{ABS}$=12% w/w; pH_{eq}~5.5; PEG 10,000)

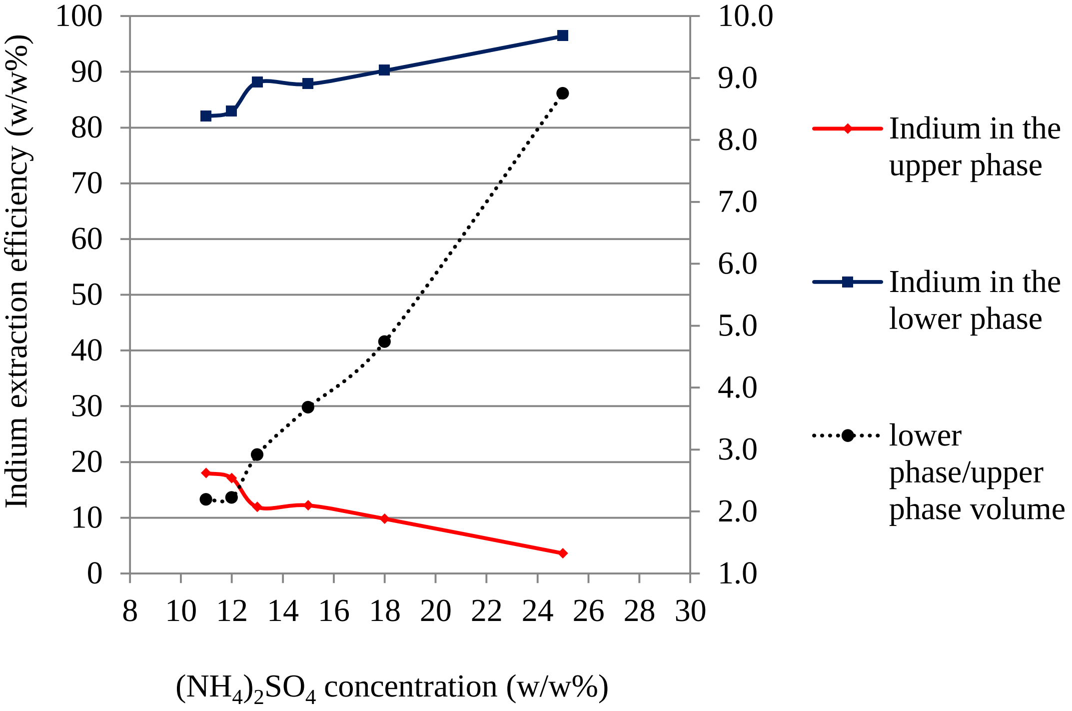


Figure 53. Indium extraction efficiency as a function of $(NH_4)_2SO_4$ concentration ($[PEG]_{ABS}$=10% w/w; pH_{eq}~5.5; PEG 10,000)

It was found that indium partitioning between the two phases is, again, quite independent from system composition.

In Figures 54-55 the extraction results obtained with the two PEG tested are reported:

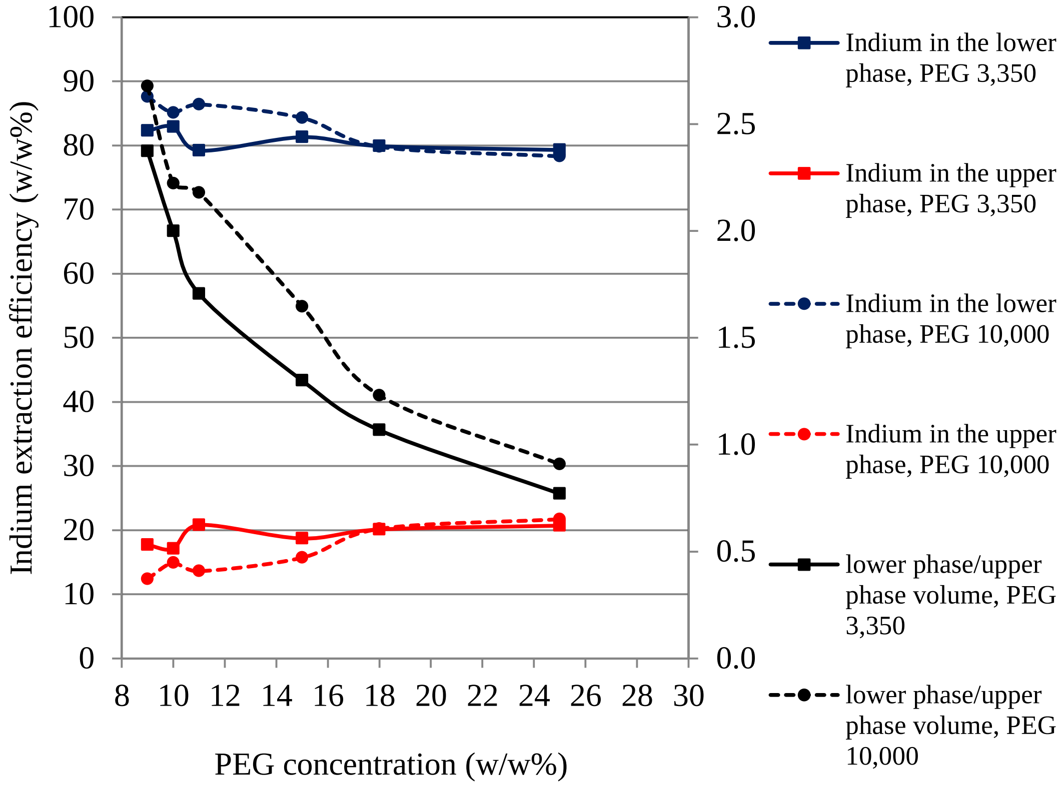


Figure 54. Indium extraction efficiency as a function of PEG concentration ($[(NH_4)_2SO_4]_{ABS}$=12% w/w; pHeq~5.5)

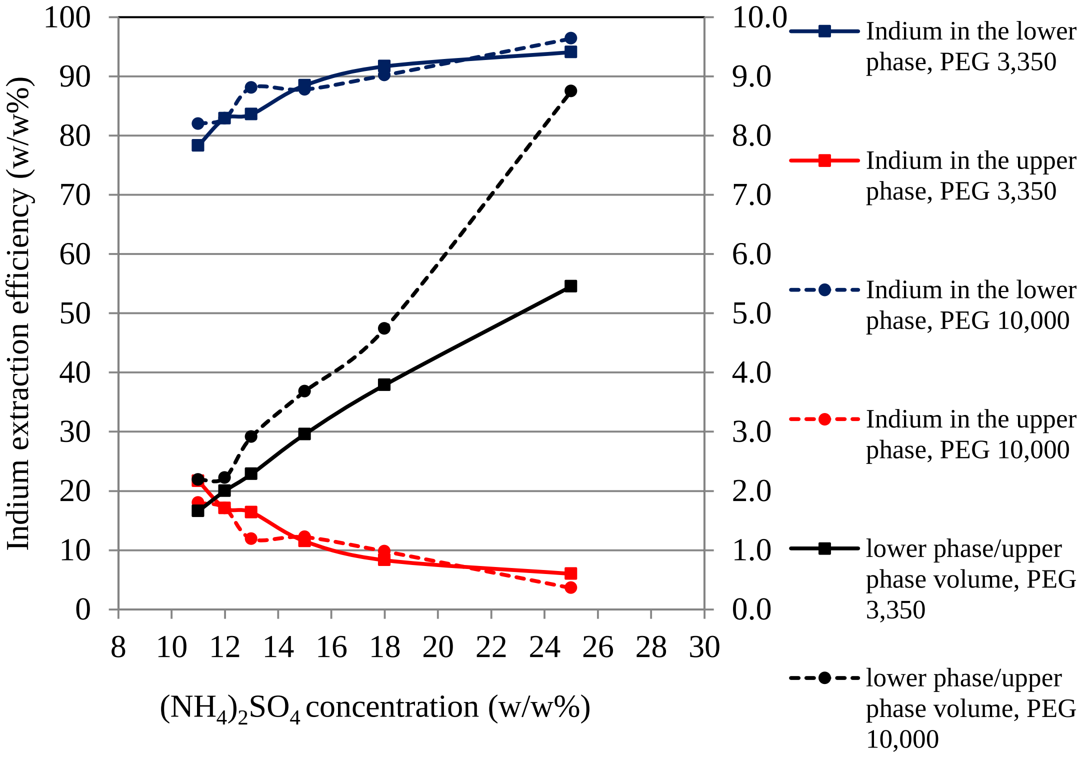


Figure 55. Indium extraction efficiency as a function of $(NH_4)_2SO_4$ concentration ($[PEG]_{ABS}$=10% w/w; pH_{eq}~5.5)

Experimental data showed that indium extraction is quite similar by employing PEG 3,350 as well as PEG 10,000; however the volume ratio decrease is more significant if PEG 3,350 is employed. The optimal conditions for the extraction step can be, thus, defined as follows:

- PEG 3,350
- [PEG]=18%
- $[NH_4]_2SO_4$=12%

In these conditions, the ratio between the lower and upper phase volume is ~1.1.

5.6 MATERIALS RECOVERY FROM WASTE LCDs – A MASS BALANCE

In Tables 31-33 the input/output flows referring to the three steps of the recovery process are reported; the overall mass balance is reported in Table 34. The process flow-sheet is shown in Figure 56.

STEP 1: REMOVAL OF THE POLARIZING FILM

Table 31. Removal of the polarizing film - mass balance

IN	LCD panel	1 kg
	Liquid nitrogen	25 L
OUT	Glass substrate with ITO	0.860 kg
	Polarizing film	0.140 kg

STEP 2: LEACHING

Table 32. Leaching - mass balance

IN	Glass substrate with ITO	0.860 kg
	HCl 6N	2.58 L
OUT	Glass substrate	0.860 kg
	Leachate	2.58 L [In]=85 ppm;

		[Sn]=9 ppm; [Al]=6 ppm; [Cr]=1 ppm

STEP 3: SOLVENT EXTRACTION WITH AQUEOUS BIPHASIC SYSTEMS (ABSs)

Table 33. Solvent extraction through ABSs - mass balance

IN	Leachate	2.58 L [In]=85 ppm
	1,10 phenantroline	~1.7 g
	PEG 3,350	0.66 kg
	$(NH_4)_2SO_4$	0.44 kg
OUT	Lower phase	1.35 L [In]=130 ppm
	Upper phase	1.23 L [In]=36 ppm

Table 34. Waste LCDs recovery process – mass balance

IN	LCD panel	1 kg
	liquid nitrogen	25 L
	HCl 6N	2.58 L
	PEG 3,350	0.66 kg
	$(NH_4)_2SO_4$	0.44 kg
	1,10 phenantroline	$1.7 \cdot 10^{-3}$ kg
OUT	Polarizing film	0.140 kg
	Glass substrate	0.860 kg
	Lower phase	V=1.35 L; [In]=130 ppm
	Upper phase	V=1.23 L; [In]=36 ppm

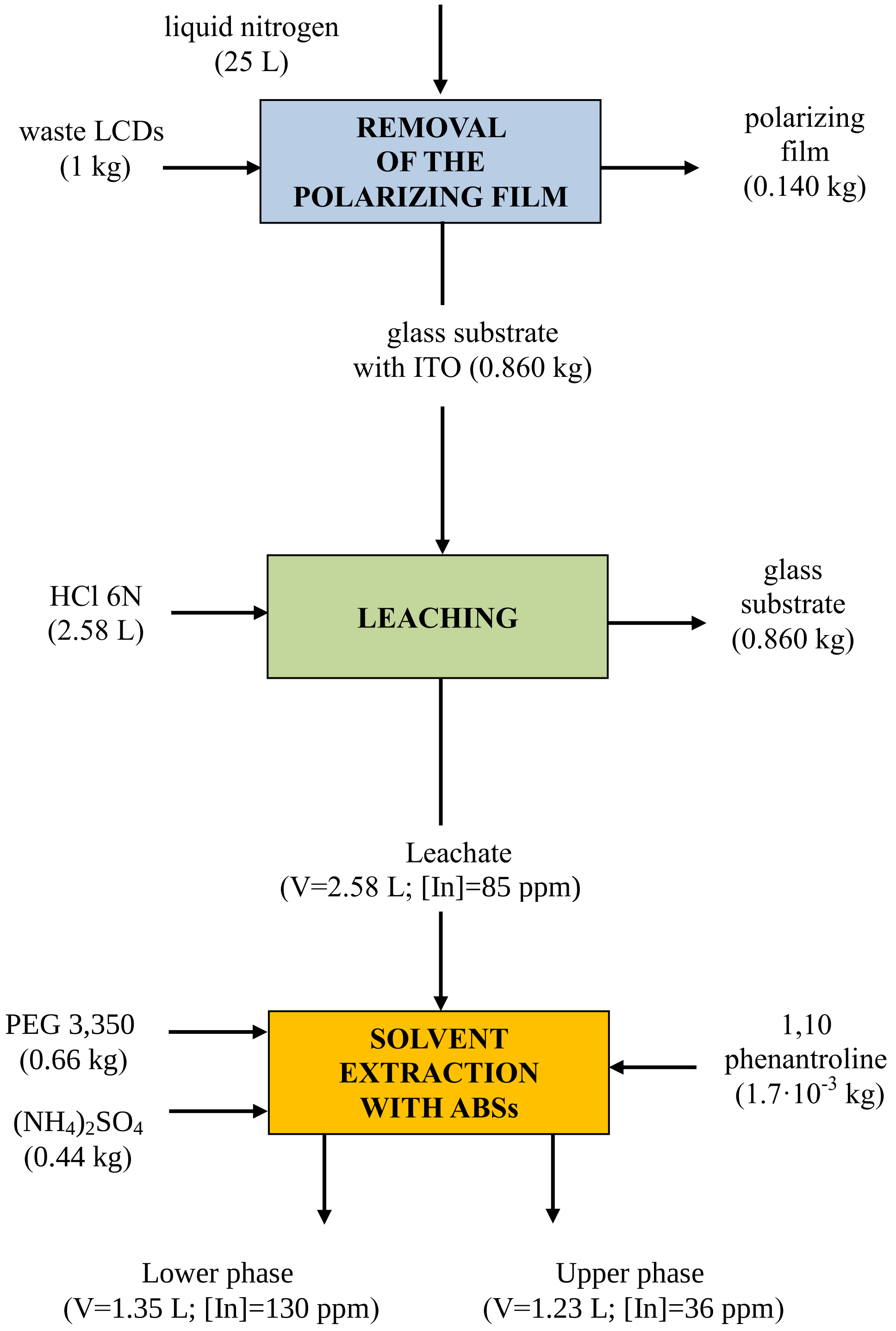


Figure 56. Waste LCDs recovery process - mass balance

As reported in Section 5.4.2., by employing HCl 6N as leaching agent (T=25°C, t=6h, L/S=3 mL/g) indium leaching efficiency is equal to ~90%. Since 80% indium is extracted in the lower phase of the considered aqueous biphasic system ([PEG]=18%, $[NH_4]_2SO_4$=12%), it can be concluded that the overall recovery efficiency of the proposed process is equal to 72% w/w.

6. CONCLUSIONS

In the present work a hydrometallurgical technique for the recovery of valuable materials from waste liquid crystal displays (LCDs) is proposed.

The recovery process can be divided in three main steps:

1. Removal of the polarizing film from the glass substrate;
2. Leaching of the glass substrate;
3. Indium recovery through solvent extraction with aqueous-biphasic systems (ABSs)

It was found that liquid nitrogen is an effective agent for the removal of the polarizing film, since only 20 minutes are required; moreover, the obtained product does not show substantial degradation.

Regarding the leaching step, HCl 6N allows solubilizing 90% indium in a relatively short time (t=6h) at room temperature.

Indium recovery from the aqueous phase was then investigated through solvent extraction by means of aqueous biphasic system (ABSs). This system is constituted by PEG-$(NH_4)_2SO_4$-water. It was found that indium partitioning is quite independent from system composition, since approximately 80-90% is extracted in the lower phase and 10-20% in the upper phase.

By increasing PEG concentration, the volume ratio between the lower and the upper phase decreases thus increasing the concentration of indium ions in the lower phase. Indium extraction is quite similar by employing PEG 3,350 as well as PEG 10,000; however, the volume ratio decrease is more significant if PEG 3,350 is employed.

When [PEG]=18% w/w, the volume ratio is equal to 1.1 and indium concentration in the lower phase is 1.5 times the initial one.

6.1 FURTHER RESEARCH

Most of the works focused on metal extraction through aqueous biphasic systems are studied at room temperature; however possible improvements could be reached at different temperatures: a possible development of the research project could be focused on the evaluation of indium partitioning in the ABS PEG 3,350-$(NH_4)_2SO_4$-water as a function of temperature.

The extraction tests described in this work should be then performed on the leachate (i.e. the aqueous phase coming from the leaching with HCl 6N), in order to verify the selectivity of the recovery technique compared to other ions (mainly tin).

Moreover, techno-economic evaluations should be carried out in order to verify the possibility to apply the proposed process in a full-scale treatment plant.

REFERENCES

Ammar, S. H., Abdul-Nabi, W. A.-W., Rasheed, M. K. (2011). Extraction of Zn (II) and Cu (II) Ions Using PEG (300)-KCl Salt Aqueous Two-Phase Systems. Al-Khwarizmi Engineering Journal, Vol. 7, n. 2, 68-74.

Ammar, S. H., Mohammed, S. B., Kareem, Y. S. (2013). Extraction of Cd, Cu, Fe and Zn metal ions mixture using PEG-inorganic salt aqueous two phase systems in the presence of iodide (KI) and Thiocyanate (KSCN) ions as Extractants. Journal of Babylon University. 21 (2), 470-476.

Becker, W., Simon-Hettich, B. (2003). Toxicological and Ecotoxicological Investigations of Crystals and Disposal of LCDs.

Biganzoli, L., Falbo, A., Forte, F., Rigamonti, L., Grosso, M. (2014). LCA of the WEEE management system in Lombardia. 4th International Conference on industrial and hazardous waste management. September 2nd-5th 2014, Chania, Crete.

Bogdanski, G. (2009). Development and analysis of treatment options for implementing recycling concepts for liquid crystal displays (LCD) for a company in the waste electrical and electronic recycling sector.

Boni, H., Widmer, R. (2011). Disposal of Flat Panel Display Monitors in Switzerland. EMPA St. Gallen.

Buchert, M., Manhart, A., Bleher, D., Pingel, D. (2012). Recycling critical raw materials from waste electronic equipment.

Bulgariu, L. and Bulgariu, D. (2008). Cd(II) extraction in PEG (1550)-$(NH_4)_2SO_4$ aqueous two-phase systems using halide extractants. J. Serb. Chem. Soc. 73 (3). 341-350 (2008).

Cabezas, H., (1996). Theory of phase formation in aqueous two phase systems J. Chromatoger. 3-30.

Chelmsford City Council. (2014). Small Waste Electronic & Electrical Equipment (WEEE). Retrieved from http://www.chelmsford.gov.uk/weee

Corning Display Technologies. EAGLE XG Glass Substrates. Available: http://www.corning.com/AdvancedGlass/EAGLEXGSlim.aspx.

Cottam, L., Sheldon, R.P. (1965), Solubility of Polyethylene Terephthalate, Nature. DOI:10.1038/2051005a0.

da Silva, L. H. M., Coimbra, J. S. R., da A.Meirelles, A. J. (1997). Equilibrium phase behavior of poly (ethylene glycol)+potassium phosphate+water two-phase systems at various pH and temperatures. J. Chem. Eng. Data 42. 398.

Decreto Ministeriale 25 Settembre 2007, n.185

den Boer, W. (2005). Active Matrix Liquid Crystal Displays: Fundamentals and Applications. Oxford, UK: Newnes.

Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on Waste Electrical and Electronic Equipment (WEEE).

Dodbiba, G., Nagai, H., Wang, L. P., Okaya, K., Fujita, T. (2012). Leaching of indium from obsolete liquid crystal displays: Comparing grinding with electrical disintegration in context of LCA. Waste Management 32, 1937-1944.

Dodson, J. R., Hunt, A. J., Parker, H. L., Yang, Y., Clark. J. H. (2012). Elemental sustainability: Towards the recovery of scarce metals. Chemical Engineering and Processing 51, 69-78.

Dzherayan, T. G., Shkinev, V. M., Reznik, A. M., Mitronov, A. N., Karandashev, V. K. (2006). Extraction–Photometric Determination of Gallium with Phenylfluorone in Alkaline Carbonate Solutions in the Presence of Polyethylene Glycol. Journal of Analytical Chemistry. Vol. 61, n. 6, 566–570.

ERECON Conference draft. Strengthening the European rare Earths Supply-Chain (2014).

European Commission (2010). Report on critical raw materials for the EU. Report of the Ad hoc Working Group on defining critical raw materials.

European Commission (2014). Report on critical raw materials for the EU. Report of the Ad hoc Working Group on defining critical raw materials.

European Commission DG TREN. (2005). Preparatory studies for Eco-design Requirements of EuPs. Lot 3: Personal Computers (desktops and laptops) and Computer Monitors. Final Report (Task 1-8).

Fang, D. W., Liu, X. Z., Yang, J. Z., Xiong, Y., Zang, S.-L. (2008). Thermodynamics of Solvent Extraction of Indium with EHEHPA. JPEDAV 29, 217-221.

Felix, N. (2000). Indium and Indium Compounds. Ullmann's Encyclopedia of Industrial Chemistry.

Fontana, D. and Ricci, G. (2000). Poly(ethylene glycol)-based aqueous biphasic systems: effect of temperature on phase equilibria and on partitioning of 1,10-phenanthroline–copper(II) sulphate complex. Journal of Chromatography B, 743, 231–234.

FEM and IUTA (2011). Metallurgical recovery of indium, gallium and germanium from electronic waste and development of suitable pre-treatment methods for the recycling industry. Project report, Schwäbisch Gmünd & Duisburg.

Franke, C., Kernbaum, S., Seliger, G. (2006). Remanufacturing of Flat Screen Monitors, in Innovation in Life Cycle Engineering and Sustainable Development. Brissaud, D., Tichkiewitch, S., Zwonlinski, P. Ed. Dordrecht: Springer, 139-152.

Fraunhofer IZM (2007). EuP Preparatory Studies “Televisions” (Lot 5), Final Report on Task 1 “Definition”.

Graedel, T.E., Barr, R., Chandler C., Chase T., Choi, J., Christoffersen, L., Friedlander, E., Henly, C., Jun, C., Nassar, N. T., Schechner, D., Warren, S, Yang, M.-y, Zhu, C. (2012). Methodology of Metal Criticality Determination. Environ. Sci. Technol. DOI: 10.1021/es203534z.

Grosso, M., Rigamonti, L., Biganzoli, L., Falbo, A., Forte, F. (2014). Valutazione di sostenibilità ambientale della gestione di una particolare categoria di rifiuto speciale in Lombardia: il caso dei RAEE. Relazione Finlombarda SpA.

Gupta, B., Deep, A., Malik, P. (2004). Liquid–liquid extraction and recovery of indium using Cyanex 923. Analytica Chimica Acta 513, 463-471.

Haig, S., Morrish, L., Morton, R. (2011). Market flows of WEEE materials.

Han, K. N., Kondoju, S., Park, K., Kang, H.-m. (2002). Recovery of Indium from Indium/Tin Oxides Scrap by Chemical Preipitation. Geosystem Eng. Vol. 5, n. 4, 93-98.

Hasegawa, H., Rahman, I. M. M., Egawa, Y., Sawai, H., Begum, Z. A., Maki, T., Mizutani, S. (2013). Recovery of indium from end-of-life liquid-crystal display panels using aminopolycarboxylate chelants with the aid of mechanochemical treatment. Microchemical Journal 106, 289-294.

Ho-Gutierrez, V., Cheluget, E. L., Vera, J. H., Weber, M. E. (1994). Liquid-Liquid Equilibrium of Aqueous Mixtures of Poly(ethylene glycol) with Na_2SO_4 or NaCl. J. Chem. Eng. Data 39, 245.

Hsieh, S.-J., Chenb, C.-C., Say, W. C. (2009). Process for recovery of indium from ITO scraps and metallurgic microstructures. Materials Science and Engineering B 158, 82-87.

Huisman, J. (2013). WEEE recast: from 4kg to 65%: the compliance consequences.

ISI. Fraunhofer Institute for Systems and Innovation Research ISI & Institute for Futures Studies and Technology Assessment. (2009). Raw materials for future technologies: the effect of the raw material needs of specific sectors on future demand.

Jin, X., Bai, Y. P., Shao, L., Yang, B. H., Tang, Y. P. (2009). Properties of solvent-borne acrylic pressure-sensitive adhesives synthesized by a simple approach. Express Polymer Letters, vol. 3, n. 12, 841-820.

Juchneski, N. CF, Scherer, J., Grochau I. H, Veit, H. M. (2013). Disassembly and characterization of liquid crystal screens. Waste Management & Research. Vol. 31. n. 6, 549-558.

Lee, H.-C., Seo, J.-Y., Choi, Y.-W., Lee, D.-W. (2004). The growth of indium-tin-oxide thin films on glass substrates using DC reactive magnetron sputtering. Vacuum 72, 269-276.

Lee, C.-H., Jeong, M.-K., Kilicaslan, M. F., Lee, J.-H., Hong, H.-S., Hong, S.-J. (2013). Recovery of indium from used LCD panel by a time efficient and environmentally sound method assisted HEBM. Waste Management. Vol. 33, n. 3, 730–734.

Lee, S.-J. & Cooper, J. (2008). Estimating Regional Material Flows for LCDs. Proceeding of the International Symposium on Electronics and the Environment ISEE.

Li, J., Gao, S., Duan, H., Liu, L. (2009). Recovery of valuable materials from waste liquid crystal display panel. Waste Management 29, 2033-2039.

Li, Y., Liu, Z., Li, Q., Liu, Z., Zeng, L. (2011). Recovery of indium from used indium–tin oxide (ITO) targets. Hydrometallurgy 105, 207-212.

Luo, F. (1997). Thin-Film-Transistor-Addressed Liquid Crystal Displays in Microlitography, Micromachining and Microfabrication, P. Rai-Choudhury, Ed. Bellingham: SPIE and IEE.

Kameda, T., Park, K. –S., Sato, W., Grause, G., Yoshioka T. (2009) Recovery of indium from In_2O_3 and liquid crystal display powder using dehydrochlorination of poly (vinyl chloride). The 5th ISFR, Chengdu, China.

Katayama, M. TFT-LCD Technology, Thin Solid Films, vol. 341, 140-147.

Kurdesau, F., Khripunov, G., da Cunha, A. F., Kaelin, M., Tiwari, A. N. (2006). Comparative study of ITO layers deposited by DC and RF magnetron sputtering at room temperature. Journal of Non-Crystalline Solids 352, 1466-1470.

Kuo, Y., Okajima, K., Takeichi, M. (1999). Plasma processing in the fabrication of amorphous silicon thin-film transistor arrays, IBM J. Res. Develop., vol. 43, n. 1.2, 73-88.

Ma, E., Lu, R. Xu, Z. (2012). An efficient rough vacuum-chlorinated separation method for the recovery of indium from waste liquid crystal display panels. Green Chem.. 14, 3395-3401.

Martens, H. (2011). Recycling technology – a textbook of theory and practice, Heidelberg.

Martin, R.. (2007). Use of liquid-crystal displays and processes for the recycling thereof. American patent, n. US2007/0193414 A1.

Matharu, A.S., Wu, Y. in: R. E. Hester, R. M. Harrison (Eds.). Electronic Waste Management: Issues in Environmental Science and Technology, RSC Publishing, Cambridge. UK, 2008.

Mikolajczak, C. (2010). Availability of Indium and Gallium. Indium Corporation Tech Paper.

Mishima, K., Matsuyama, K., Ezowa, M., Taruta, Y., Takarabe, S., Nagatani, M. J. (1998). Interfacial Tension of Aqueous Two-Phase Systems Containing Polyethylene Glycol and Hydrogenphosphate Chromatogr. B. 711, 313.

Nam, I., Ha, K., Lee, K., Kim, L. J., Lee, C., Kim, M.S., Chang, T. (2012). Effect of chemical structure of acrylic pressure-sensitive adhesives for polarizing film on light leakage phenomenon in TFT-LCDs. Polymers Advanced Technologies, vol. 23, n.8, 1181-1186.

O’Mara, W. (1993). Liquid Crystal Flat Panel Displays: Manufacturing Science & Technologies, New York, NY: Van Nostrand Reinhold.

Paiva, A. P. (2001). Recovery of indium from aqueous solutions by solvent extraction. Separation Science and Technology. Vol. 36, n. 7, 1395-1419.

Park, Ju-O., Lee, J.-H., Kim, J.-J., Cho, S.-H., Cho, Y. K. (2005). Crystallization of indium tin oxide thin films prepared by RF-magnetron sputtering without external heating. Thin Solid Films 474, 127– 132.

Park, J.-C. (2011). The Recovery of indium Metal from ITO-scrap using Hydrothermal Reaction in Alkaline Solution. Bull. Korean Chem. Soc. Vol. 32, n. 10, 3796-3798.

Passamani, A. (2011). Strato su strato: funzione e materiali del cuore ottico e sensibile di un pannello Liquid Crystal Display di modo Twisted Nematics. Corso di Chimica per l'Elettronica. Bertani, R.

Perry’s Chemical Engineer’ Handbook (1997). McGraw Hill, Seventh Edition.

Pizzagalli, G. (2014). Urban mining: the recovery of critical metals from waste electrical and electronic equipment (WEEE). The case of indium. Master of Science Thesis, Politecnico di Milano.

Polinares. EU Policy on Natural Resources. (2012). Fact Sheet: Indium.

Reich, F. and Richter, T. H. (1863). J. Prakt. Chem. 89, 441.

Rogers, R. D., Bond, A. H., Bauer, C. B., Zhang, J., Griffin, S. T. (1996). J. Chromatogr. B 680, 221.

Rogers, R. D., Chen, J., Spear, S. K., Huddleston, J.G. (2005). Polyethylene glycol and solutions of polyethylene glycol as green reaction media. Green. Chem., 7, 64-82.

Roskill (1987). The Economics of Indium 1987, 4th ed., Roskill Information Services Ltd., London.

Ruan, J., Guo, Y., Qiao, Q. (2012). Recovery of indium scrap TFT-LCDs by solvent extraction. Procedia Environmental Sciences 16, 545-551.

Salhofer, S., Spitzbart, M., Maurer, K. (2011). Recycling of LCD Screens in Europe - State of the Art and Challenges, Glocalized Solutions for Sustainability in Manufacturing, 454-458.

Slattery, J. A. (2000). Indium and Indium Compounds. Kirk-Othmer Encyclopedia of Chemical Technology.

Socolof, M. L., Overly, J. G., Geibig, J. R. (2003). Environmental life-cycle impacts of CRT and LCD desktop computer displays. Journal of Cleaner Production 13, 1281-1294.

Socolof, M. L., Overly, J. G., Geibig, J. R. (2001). Desktop Computer Displays: A Life-Cycle Assessment – Vol. 1, University of Tennessee Center for Clean Products and Clean Technologies.

Tsai, H.-S. & Tsai T.-H. (2012). Extraction Equilibrium of Indium(III) from Nitric Acid Solutions by Di(2-ethylhexyl)phosphoric Acid Dissolved in Kerosene. Molecules 17, 408-419.

Tsujiguchi, M. (2012). Indium Recovery and Recycling from an LCD Panel. Design for Innovative Value Towards a Sustainable Society, 743-754.

Tsukada, T. (1996). TFT/LCD: Liquid Crystal Displays Addressed by Thin-Film Transistors. Amsterdam: Gordon and Breach Publishers.

UK Energy Research Center. Indium Fact Sheet.

UNEP (2011). Recycling Rates of Metals. A Status Report.

United Nations University. (2008). Review of Directive 2002/96 on Waste Electrical and Electronic Equipment (WEEE). Final Report.

USGS (2004). Mineral Commodity Profile. Indium.

USGS (2011). 2011 Minerals Yearbook U.S. Department of the Interior U.S. Geological Survey. Indium Advance Release.

USGS (2012). Mineral Commodity Summaries.

USGS (2013). Mineral Commodity Summaries.

Villavecchia, V. (1977). Nuovo dizionario di merceologia e chimica applicata, Vol. 2.

Virolainen, S., Ibana, D., Paatero, E. (2011). Recovery of indium from indium tin oxide by solvent extraction. Hydrometallurgy 107, 56-61.

Visser, A. E., Griffin, S. T., Ingenito, C. C., Hartman, D. H., Huddeston, J. G., Rogers, R. D.. (2000). Aqueous biphasic systems as a novel environmentally benign separation technology for metal ion removal. Metal Sep. Technol. Beyond, 119.

Yang, J., Retegan, T., Ekberg, C. (2013). Indium recovery from discarded LCD panel glass by solvent extraction. Hydrometallurgy, vol. 137, 68-77.

Yen, T. and Tso, P. (2004). An Effective Fabrication Method for Producing Color Filters for Liquid Crystal Displays. Japanese Journal of Applied Physics, vol. 43, n. 7A, 4229-4233.

Young, R. (2011). Global Manufacturing Trends: What Can We Learn from the HB LED Market Explosion?. Solid-State Lighting Manufacturing R&D Workshop, Boston, MA, 2011-04-12.

Zaslavsky, B. Y., Borovskaya, A. A., Gulaeva, Nelli D., Miheeva, L.M. (1991). Partitioning in aqueous two-phase systems as a method of estimation of the relative hydrophobicity of solutes. J. Chem. Soc., Faraday Trans., 87, 137-140.

Zangl, S., Brommer, E., Grießhammer, R., Gröger, J. (2009). PROSA television sets. Oeko-Institut e.V., Freiburg.

Zhuang, X., He, W., Li, G., Huang, J., Ye, Y. (2012). Material separation from waste liquid crystal displays using combined physical methods. Pol. J. Environ. Stud. Vol. 21, n. 6, 1921-1927.

Wang, H.-Y. (2009) A study of the effects of LCD glass sand on the properties of concrete. Waste Management 29, 335-341.

Wang, X., Lu, X., Zhang, S. (2013). Study on the waste liquid crystal display treatment: Focus on the resource. Journal of Hazardous Materials 244–245, 342–347.

Watanabe, K., Kitamura, K., Fujishiro, K., Teramoto, T. (1996). High performance topcoats and color filter photoresist derived from cardo-type resins. Soc. Inform. Display Digest, vol. 27, 530-533.

Wu, Y. T., Zhu, Z. Q., Liu, D. Q., Li, M. (1999). Modeling of liquid–liquid equilibrium of polyethylene glycol-salt aqueous two-phase systems-the effect of partial dissociation of the salt. Fluid Phase Equilibr. 154, 109.

Web Sites:
http://www.htwt.eu/

http://www.metalbulletin.com/

http://www.recyval-nano.eu/