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Innovative and sustainable strategies of urban mining

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The important thing is not to stop questioning.

Einstein

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Summary

The management of the huge quantity of waste from electric and electronic equipment (WEEE) produced in recent years represents a critical issue for the modern society. Frequently, the high economic costs, connected with the treatment of these flows, cause their exportation towards poor countries where illegal processes are often applied. The negative environmental and health effects due to the improperly management are combined with the loss of contained valuable materials. Indeed, several fractions, with different recovery potential, like: plastic, glass, steel and metals can be identified.

The present work focused on the recovery of metals from electric and electronic waste with particular attention to indium from end-of-life liquid crystal displays (LCD).

The research activity has addressed the following specific questions:

1) Which are the best conditions to apply for an indium extraction process from end-of-life LCD with high efficiency?
2) How the solution from extraction can be treated for the indium recovery? Is the process suitable for the implementation in a real plant with the minimum environmental impact?
3) Considering the current strategies of end-of-life LCD management, which is the best option, from an environmental point of view? How the optimized innovative process can be improved in order to increase its sustainability?
4) How an environmental approach could be implemented to evaluate the sustainability of different processes for the treatment of several WEEE?
5) Considering the necessity of the application of metals recovery from WEEE in a real plant, which are the risks for the workers and the environment?

To answer to these questions, the research activities were organized in five work-packages. The first experimental section allowed the optimization of an acid leaching characterized by an innovative cross-current design that considerably decreased the environmental and the economic impacts. The high obtained efficiency, almost a complete indium extraction, pushed the research towards the second phase of experimental activity with the aim to develop the recovery phase. The results revealed the effectiveness of the cementation with zinc powder carried out at acid conditions with a final recovery efficiency higher than 90%. Considering the success on the lab scale, the whole process was studied from an environmental point of view comparing the emissions of the innovative treatment with those produced by the current management strategies (disposal in landfilling sites, incineration and traditional recycling). A life cycle assessment (LCA) of the different scenarios proved the significant advantage of recycling options compared to landfilling and incineration. Moreover, the traditional recycling resulted to be the most favorable, due for both the relevant water consumption of the innovative treatment and to the low indium content in the LCD. However, the assessment highlighted that a simple water recirculation system, combined with a physical pretreatment for indium upgrading in the waste, could make the innovative option the best choice. The simple design of the optimized process could allow its implementation in a mobile plant, that has been realized within the European project, HydroWEEE. The plant mobility permits the treatment in the site of recyclers, avoiding the impacts due to the waste transport, that contributes to the 30-40% of the currently applied treatments. Furthermore, this advantage is combined with the possibility to treat several WEEE for the recovery of different metals. This aspect represents a strong point for European recyclers, typically small and medium enterprises, that have relatively small quantity of several typologies of WEEE to be treated. The sustainability of this approach that combines processes with simple designs in the same plant was proved by a LCA study. The assessment highlighted the relevant advantage of recycling compared to the disposal in landfilling sites. The positive effect of material recovery was also proved in the comparison with the primary production, with a final benefit variable between 20 and 80%. Last, but not least, the risk for workers was also assessed, considering the real mobile plant where the innovative recycling processes have been demonstrated.

Innovative and sustainable strategies of urban mining

DOCTORATE DISSERTATION

Dissertation outline

1. Overview

The modern economic growth and the constantly evolving market have caused the production of enormous quantity of waste. The management of these flows represents a critical issue to address, taking into account the main available strategies of recovery, recycling, treatment for energy recovery and disposal (Di Maria et al., 2013). Nevertheless, considering the significant content of valuable materials in municipal waste, the recycling represents the best option of waste management in Europe (Bing et al., 2016). For this reason, the old linear management method, in which every product became a waste at the end of its life, evolved in a circular approach following the principle "resource-product-regenerated resource" (Li et al. 2010). In this context, the strategy of "urban mining", in which municipal waste is converted in a resource, was developed. The name of this approach includes the term "urban" to define the scraps origin and the term "mining" since the end-of-life products become the substitute of the traditional ores (Krook and Baas, 2013). This kind of waste management allows to combine environmental protection, resources conservation and economic advantages. Talking about urban waste, all fractions are included, as plastic, paper, glass etc.; nevertheless, considering their content of valuable materials, end-of-life electronic equipment represent the most interesting target. It is important to stress that recycling cannot entirely replace traditional activities of primary resource supply, because the demand is higher than the recycling rates (Krook et al., 2011). Nevertheless, urban mining represents a positive perspective for Europe to reduce its dependence on the raw materials supply from other countries.

2. Electronic waste

Considering the modern scenario, a sensitive problem is that connected with a particular kind of waste, resulting from end-of-life electric and electronic equipment (EEE). The field of EEE is constantly evolving especially for the information and communication devices, like computers and mobile phones (Lu et al., 2015; Maragkos et al., 2013).The increase in the production of this technological equipment is combined with a lifespan that is becoming very short with the final production of large quantities of waste (Yang et al., 2008). The typical composition of this kind of scrap, best defined as waste electrical and electronic equipment (WEEE), includes five categories of materials: ferrous metals, non-ferrous metals, glass, plastics and other materials (Widmer et al., 2005). Each fraction has a different potential recovery that can be realized by three main steps: collection, pre-processing and end-processing (Maragkos et al. 2013). The high economical cost connected with WEEE management because of the content of hazardous components often encourages some companies to export WEEE from developed to developing countries, with negative consequences on social, economic and environmental spheres (Kolias et al., 2014). Indeed, in these poor countries, waste recycling activities are entrusted to the informal sector, that includes a range of legal and publicly accepted businesses, although unregistered, which often adopt illegal or clandestine processes (Song and Li, 2015). The result is the practice of inadequate conditions for the environment and the workers (Song and Li, 2015; Williams et al., 2008).

The most applied practices in the past included the disposal of WEEE in landfilling sites or the incineration; however, these management options require high attention levels due to the toxicity of the contained substances that can cause several effects on different environmental compartments, if the waste is not properly pretreated (Bereketli et al., 2011; Spalvins et al., 2008). In order to reduce these negative effects, recycling strategies should be used with the final target to make the waste a source of secondary raw materials. In this way, a double positive effect is achieved: the decrease of waste amount to dispose of in landfilling sites and the reduction of dependency from other countries for the primary resources supply. The relevance of the WEEE recycling issue is also confirmed by several worldwide research activities underway.

The waste stream composed of end-of-life LCDs, included in the WEEE category, is the main interest of the present study. Currently liquid crystal displays (LCDs) are largely used because they have replaced the old technology of cathode ray tube (CRT) in different applications as PC monitors, laptops, tablet, mobile phones, televisions. Compared to CRT monitors, the small weight and volume, and the cost that is becoming cheaper, favor the wide diffusion of LCDs. In addition, the lower power consumption and heat emissions make LCDs more convenient also from an ecological point of view (Lee et al., 2006). Nevertheless, their short lifespan of about 3-8 years (Ma and Xu, 2013), is causing the production of an estimated quantity of 17 million of personal computer that become a waste every year (Yamane et al., 2011). According with the RoHS Directive 2011/65/EU, there is a risk connected with end-of-life LCDs due the content of lead, mercury, cadmium, chromium (Lim and Schoenung, 2010; Salhofer and Tesar, 2011). The relevance of this issue is confirmed by the same Directive, which established some restrictions of the use of hazardous substances in EEE with a view to protect the human health and the environment, simplifying the environmentally sound recovery and the final disposal of WEEE. Indeed, these elements, combined with brominated flame retardants could have effects on the environment and human health (Binnemans et al., 2013; Cui and Forssberg, 2003; Tsydenova and Bengtsson, 2011). In addition, LCDs contain a potential carcinogenic compound, arsenic, usually added to glass in oxide form in order to improve the optical clarity of the glass panel (Atkarskaya and Bykov, 2003; Savvilotidou et al., 2014). The risk connected with this element is due to an improper disposal or to a possible dispersion in the shredding process during waste pretreatment (Salhofer and Tesar, 2011).

Therefore, the possibility to develop efficient and sustainable processes would favor a proper management with a consequent reduction of toxic metals and hazardous materials dispersions. Nevertheless, in order to make the recovery processes applicable, they should be an attractive and competitive option.

3. Critical raw materials

The valuable materials contained in WEEE include a series of elements, recently defined by European Commission as “critical raw materials”. More specifically, the raw materials criticality is defined as follows: “To qualify as critical a raw material it must face high risks with regard to access to it, i.e. high supply risks or high environmental risks, and be of high economic importance. In such a case, the likelihood that impediments to access occur is relatively high and impacts for the whole EU economy would be relatively significant” (European Commission, 2010). The list of critical raw materials (CRMs) for Europe is periodically reviewed. The most recent one (2014) includes seventeen materials (antimony, beryllium, borates, chromium, cobalt, coking coal, fluorspar, gallium, germanium, indium, magnesite, magnesium, natural graphite, niobium, phosphate rock, silicon metal, tungsten) and three groups of elements (platinum group metals, heavy rare earths, light rare earths).

The present study focuses mainly on one of these materials, indium, a metal located at the IIIA column in the periodic table and evenly distributed in the earth's crust (Virolainen et al., 2011). Indium has no ores of its own at all and it is mainly produced as by-product of zinc and lead from sphalerite and chalcopyrite sources, where it is present with concentrations of about 1-100 ppm (Alfantazi and Moskalyk, 2003; Zhang et al., 2015).

China is the largest producer of indium, followed by Korea, Japan and Canada, with an estimated world refinery production in 2013 of 770 metric tons (USGS, 2014). According to the European Commission, almost 90% of indium is used in electronics, mainly for the production of liquid crystal displays (LCDs) screens, a sector with a quick development (European Commission, 2014; Lin et al., 2009; Yuan and Shi, 2009). In particular, approximately 84% of the worldwide indium consumption is used for their production, where it is present in concentration from 100 to 400 ppm, comparable with that in ores (Gotze and Rotter, 2012; Hasegawa et al., 2013; Her-Yung, 2009; Lee et al., 2013; Ma and Xu, 2013). Indium is used in oxide form combined with tin, to form a film called ITO (indium tin oxide), an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection (Li et al., 2011). More in details, this material has a typical composition of 90% In_2O_3 and 10% SnO_2 by weight (Leung et al., 2013). Considering the concentration and the availability of end-of-life LCDs (Ma and Xu, 2013), obsolete displays are a valuable alternative resource for indium secondary production in a perspective of a circular economy where a waste becomes a resource (Ma and Xu, 2013; Menikpura et al., 2014; Park, 2009).

4. The FP7 European projects HydroWEEE and HydroWEEE Demo

Present study is part of an European project, named HydroWEEE Demo (01.10.2012 – 30.09.2016), that represents the progression of the previous project, HydroWEEE (01.03.2009 – 28.02.2012). More in details, this is the first FP7-Research for small and medium enterprises (SMEs) dealt with the recovery of rare and precious metals from WEEE by hydrometallurgical processes. The overall target is the building of 2 industrial scale, real-life demonstration plants (one stationary and one mobile) to test the performance and prove the viability of different recovery processes from an integrated point of view (technical, economical, operational, social). The assessment of the risks (including health) and the benefits to the society and the environment is included, in order to remove the barriers for a wide market uptake. More in details, the mobile plant was built with the aim to extract metals like indium, yttrium, cobalt, gold, silver, copper, in a high purity, from LCDs, lamps, cathode ray tubes (CRTs), Li-batteries (LIB) and printed circuit boards (PCB), respectively. By making this plant mobile (in a container) several SMEs can benefit from the same plant at different times and places, limiting the necessary quantities of waste as well as investments. The improvement of simple processes allows the treatment of the several fractions in the same mobile plant in batches, reducing the minimum quantity per fraction per recycler even more. The application of these treatments, will make the SMEs much more competitive than today and reverse the general trend to bigger, multinational companies in the waste management sector. In addition, the mobile plant use will have a positive effect on the environmental impact. Indeed, on the one hand it will increase substantially the resource-efficiency in Europe by an economical recycling of more precious and rare materials which are currently lost. On the other hand, the plant will be transported to the recyclers locations instead of shipping large quantities of materials through whole Europe as it is done today.

More in details, in the first part of research project (HydroWEEE project) a mobile pilot plant with a reactor size of 1 m^3 has been built for treatments development and optimization. However, in order to really demonstrate the stability, financial credibility and resource-efficiency of the innovative processes an industrial stationary plant and a full-scale mobile plant (4.5 m^3 reactor) are developed in the second part (HydroWEEE Demo project). The first industrial stationary plant is located at Relight site in Milan and the industrial mobile plant is in Romania (at Greentronics site), for the moment. Several partners participate to the project, each one with a different role. In particular, Università Politecnica of Marche is the research partner for LCDs and environmental assessments.

5. Aim and objectives of the research activity during the Doctorate

Since the strategy of urban mining is considered a valid alternative to conventional primary raw materials supply, techniques for metals recovery from WEEE were investigated, with particular attention to indium from LCDs. Several studies focused on this issue, nevertheless they involve complex treatments with high costs and long duration, that make them still far from a possible scale-up (Ruan et al., 2012; Wang et al., 2013; Yang et al., 2013). In addition, the application of extreme conditions of temperature and pressure and the use of reagents with high toxicity level make, in some cases, their environmental impact really high. Consequently, the research activity had as general goal the development of an environmentally sustainable process for the recovery of indium from end-of-life LCDs, combining the high efficiency with minimum reagents toxicity and low energy consumptions. Specific targets were:

- The identification of the best conditions for a complete indium extraction from end-of-life LCDs;
- The development of an indium recovery process from the extraction solution;
- The environmental assessment of different strategies of end-of-life LCDs management;

Moreover, another important goal was the application of the same sustainable approach to other WEEE involved in the HydroWEEE project (CRT, LIB, PCB and lamps). Therefore, all treatments, optimized for the mobile plant, were assessed on an environmental point of view with a final comparison with end-of-life LCD process. The risks assessment of the mobile plant, built within the European project, was the final objective, in order to make possible the processes application on a real scale.

Each one of the following chapters addresses one work-package and can be read independently, since the scientific background and the specific materials and methods are described chapter by chapter.

Chapter 1 describes a hydrometallurgical process, carried out in acidic conditions, for the indium extraction. The high efficiency, higher than 90%, was combined with a cross-current design that allows to decrease the total consumptions. In order to make the results representative, the experiments used samples from different suppliers, previously characterized. Starting from the satisfying results of extraction process, chapter 2 describes a high efficiency recovery treatment carried out by zinc powder. An analysis of environmental impacts closes both the chapters, including also a cost assessment for the extraction phase. After the optimization of the operative conditions, we performed a life cycle assessment (LCA) with the aim to identify the main steps to improve to increase the process sustainability. As, described in chapter 3, the LCA highlighted the environmental load due to the treatment of wastewater produced during the whole process. Therefore, an experimental activity was planned to realize a system of water recirculation with the final decrease of impacts. In addition, a sensitivity analysis proved how the increase of indium concentration in the waste could improve the process sustainability. The developed treatment, thanks to its simple design, is suitable to be implemented in the mobile plant built within the European project HydroWEEE. Chapter 4 studies the environmental impacts of the five HydroWEEE treatments (LCD, CRT, LIB, PCB and lamps), showing the double advantage compared to the disposal in landfilling sites and the primary production of raw materials. Furthermore, the LCA allowed the quantification of the benefit connected with the plant mobility. Chapter 5 concludes the study with a risk assessment of the HydroWEEE plant.

6. Products

List of peer-reviewed papers from the research activities within the Doctorate:

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Chapter 1

INDIUM EXTRACTION FROM END-OF-LIFE LCD PANELS

Abstract

Indium is a critical element mainly produced as a by-product of zinc mining, and it is largely used in the production process of liquid crystal display (LCD) panels. End-of-life LCDs represent a possible source of indium in the field of urban mining. In the present work, a cross-current leaching to mobilize indium from end-of-life LCD panels was applied for the first time. A series of treatments was carried out to leach indium. The best leaching conditions for indium were 2 M sulfuric acid at 80°C for 10 min, which allowed us to completely mobilize indium. Taking into account the low content of indium in end-of-life LCDs, of about 150 ppm, a single step of leaching is not cost-effective. Six steps of cross-current leaching were tested: in the first step indium leaching was complete, whereas in the second step it was in the range of 85-90%, and with 6 steps it was about 50-55%. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Then, the process scale-up was hypothesized including a cross-current leaching up to 10 steps, followed by cementation with zinc to recover indium. In this simulation, the process of indium recovery was advantageous from an economic and environmental point of view. Indeed, cross-current leaching allowed to concentrate indium, save reagents, and reduce the emission of CO_2 (on the basis of the assessment, with 10 steps about 90 kg CO_2-Eq.of emissions could be avoided) thanks to the recovery of indium. This new strategy represents a useful approach for secondary production of indium from waste LCD panels.

Content

1. Introduction

In the recent years, several physical and chemical treatments have been tested to recover indium from LCD panels, as reported in Table 1.1. The process of indium mobilization is generally carried out by means of strong acids under different reaction conditions. Table 1.1

also reports details regarding possible treatments to recover indium after its mobilization (e.g., precipitation, cementation, extraction with solvents or surfactants).

The aim of the present study is to apply a process for indium leaching from end-of-life LCD panels. Different operative conditions were investigated to identify the best conditions for indium mobilization. The approach consists of maximizing indium leaching efficiency and minimizing the concentration of co-mobilized metals in the leach liquor. Furthermore, a single step of leaching is not feasible considering the low concentration of indium in waste LCD. Therefore, a cross-current configuration was investigated for leaching, following the design described by Rousseau, 1987. According to this approach, a multistage mobilization is carried out: in the first step a quantity of waste LCD is leached, and in the next steps the same leach liquor is used to treat other LCDs. To the best of our knowledge, for the first time this approach is applied to end-of-life LCD panels to mobilize indium. A large scale simulation for indium recovery is also presented, along with an evaluation of process costs and CO_2 saving thanks to the new proposed approach of cross-current leaching applied to LCDs.

Table1.1 State of the art of processes for the recovery of indium from waste LCD panels. For the studies with many experimental conditions investigated, the table reports only the best operative conditions.

LCD panel pre-treatment		Leaching conditions				Acid consumption[a] (kg acid/kg LCD)	Post-treatment for indium recovery	Reference
	Organics removal	Acid	Time (h)	T (°C)	Pulp density (kg/L)			
Shredding/milling, washing with deionized water	no	2 M H_2SO_4 3-step cross-current	0.17	80	0.1	0.7	n.i [b]	This work
Thermal shock at 220°C , shredding and ultrasonic cleaning	no	5.4 M HCl and 0.8 M NO_3	0.5	60	2	0.27 (HCl) and 0.04 (HNO_3)	n.i.[b]	Li et al., 2009
Hot isostatic pressing (HIP) treatment, manual breaking and pulverization	yes	1 M H_2SO_4	2	90	0.1	1	Cementation	Li et al., 2011
Grinding and incineration at 500°C	yes	6 M HCl	2	n.a.[c]	0.036	17	n.i.[b]	Dodbiba et al., 2012
Electrical disintegration	no	6 M HCl	2	n.a.[c]	0.5	1.2	n.i [b]	Dodbiba et al., 2012
Freezing with liquid N_2, stripping of the polarizing film, grinding <1 mm	no	9 M H_2SO_4	1	160	1	0.9	Extraction with D2EHPA, stripping with HCl	Ruan et al., 2012
Crushing and thermal shock. Ultrasonic cleaning and milling	yes	6 M HCl	0.5	r.t.[d]	0.04	15	n.i.[b]	Lee et al., 2013
Shredding	no	<1 M H_2SO_4 or >1 M HCl	8	n.a.[c]	0.1	<1 (H_2SO_4) or >1 (HCl)	Solvent extraction and stripping	Yang et al., 2013
Pyrolysis at 450°C	yes	0.6 M H_2SO_4	0.7	65.6	0.5	0.1	Purification	Wang et al., 2013
Shredding	no	5 M HCl	2	75	0.5	1	n.i [b]	Swain et al., 2016

[a] 98% H_2SO_4, 37% HCl, 70% HNO_3 , [b] Not investigated, [c] Not available, [d] Room temperature

2. Materials and methods

2.1 Characterization of LCD fragments

End-of-life LCD panels ground by a 4-shaft shredder were provided by companies that collect and treat WEEE (Fig. 1.1a). In order to identify metal distribution in fragments of different size, further grinding and sieving were carried out. The ground panels contained pieces of several centimeters in length, and a blade grinding operation carried out by means of a Retsch knife mill, allowed us to obtain particles that could pass through a sieve of 10 mm (Fig. 1.1b). Before blade grinding big plastic and glass fragments, representing about 10% of the total amount of shredded LCDs, were removed. Their characterization revealed no significant indium content. Then 2 fractions were obtained: the coarse fraction, containing fragments between 1.25 mm and 10 mm in size (Fig. 1.1c), and the fine fraction, smaller than 1.25 mm (Fig. 1.1d). Once removed gross fragments of plastic and glass, the fine material was 40% and the coarse fraction was 60%. In the present study, leaching on the whole stocks were carried out, to obtain a high concentration of indium in the leachate solution.

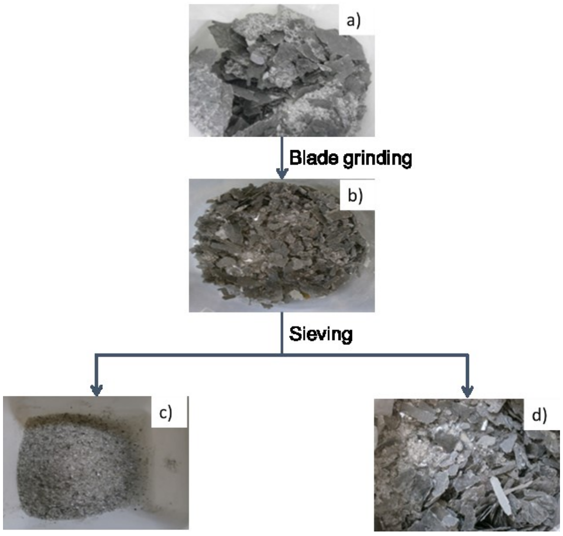

Fig. 1.1. Different size of ground LCDs. a) as provided by a company, after shredding, b) after blade grinding and sieving at 10 mm c) sieved fragments between 1.25 mm and 10 mm in size d) sieved fragments smaller than 1.25 mm.

2.2 Leaching treatments

Before each leaching treatment, a quantity of ground LCD panels was washed using deionized water (pulp density, 0.2 kg/L) for 30 min on a magnetic stirrer at room temperature. This pretreatment was necessary to physically remove the organic compounds of the LCDs (rod-shaped molecules containing benzene ring; Ma and Xu, 2013), as checked in preliminary tests. In the present study different leaching conditions were investigated for a total of 10 replicated treatments. Table 1.2 shows the experimental conditions for each leaching treatment. The considered variables were: acid concentration, leaching temperature and time and number of steps in the cross-current leaching. All leaching treatments were performed treating the ground LCDs, washed and filtered, in a solution of H_2SO_4 on an agitation system. A sample was collected every 10 min.

Table 1.2. Leaching conditions in the treatments of indium leaching.

Treatment	H_2SO_4(M)	Temperature (°C)	Volume (mL)	Pulp density (kg/L)	Mixing system	Leaching steps	Leaching time (min)
1	2	80	100	0.10	Magnetic stirrer	1	180
2	2	80	100	0.10	Dubnoff bath	1	180
3	2	25	400	0.15	Magnetic stirrer	1	20
4	2	80	400	0.15	Magnetic stirrer	1	20
5	1	80	100	0.10	Dubnoff bath	1	180
6	2	80	100	0.10	Dubnoff bath	1	180
7	2	80	500	0.20	Magnetic stirrer	1	10
8	2	80	500	0.20	Magnetic stirrer	1	30
9	2	80	500	0.20	Magnetic stirrer	1	60
10	2	80	100	0.20	Magnetic stirrer	6	10 (each step)

Data in literature reports process time between 30 min and 8 h (Table 1.1), therefore in the present study times smaller than 10 min are not taken into account. At the end of leaching, the solid was filtered and the remaining leach liquor was collected for chemical analyses. The treatment of cross-current leaching (number 10 in Table 1.2) needs further explanation. The filtered leach liquor, produced in a first leaching step, was collected and used it to treat a second amount of LCD fragments, adding a small amount of fresh H_2SO_4 to restore the volume lost for the high temperature (Fig. 1.2). Six leaching steps were carried out.

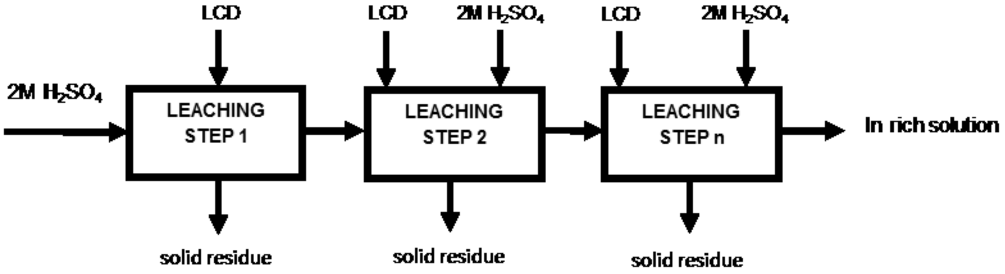

Fig. 1.2. Scheme of the cross-current leaching proposed for indium mobilization from end-of-life LCD panels. The sulfuric acid addition following the first step aims to refresh the solution volume.

2.3 Chemical analyses

The metal content was determined in the ground LCD panels after microwave-assisted acid digestion of the solid samples by means of inductively coupled plasma (ICP) analysis (using Agilent ICP-MS 7500, Agilent technologies; EPA, 1996; EPA, 2007). Before the chemical digestion, each sample was finely ground to avoid any error in chemical determinations. Chemical analyses determined the content of indium, aluminium, calcium, cerium, gallium, iron, manganese, molybdenum and tin. As a whole, the chemical characterization was performed on three different stocks supplied by different companies in different periods of time. Further analyses were carried out to determine the concentration of indium and tin in the following 5 size intervals: 0 - 0.125 - 0.25 - 0.50 - 1.25 and >1.25.

The concentration of metals in the aqueous phase was determined by inductively coupled plasma-atomic emission spectrometry in accordance with EPA (2001). Before the analysis, liquid samples were centrifuged and diluted by 2-fold with a solution of H_2SO_4 (pH 2) to avoid precipitation of metals.

Leaching efficiency (M) was calculated according to Eq. 1:

$$M = M_L / M_s * 100$$

(Eq. 1)

where M_L is the amount of metal in the leach liquor and M_s is the amount of metal in the solid sample.

A sample resulting from leaching with 2 M H_2SO_4 for 20 min at 80°C with 10% LCD was analyzed by X-ray fluorescence (XRF; Spectro Xepos) for a qualitative analysis of the composition of the solution.

2.4 Evaluation of costs and CO_2 emissions

The possible economic income was determined by the sale of indium produced in a simulated process at industrial scale, and the CO_2 emissions as well. In the simulation for the large scale process, the plant is of 5 m^3 in volume and works with a pulp density of 0.2 kg/L. The hypothetical extensive process includes cross-current leaching (based on the results achieved in the present study), pH adjustment with sodium hydroxide and cementation with zinc powder to recover indium (not investigated in the present study, based on literature data and on the research group expertise as well). The process costs were estimated for 1 kg LCD treated. They included raw materials, waste disposal, energy and man power, estimated for a wide range of leaching steps of the cross-current leaching, from 1 to 10, as predicted by Eq. 2, followed by cementation.

An empirical model was fitted (Eq. 2) using the experimental data of indium leaching: to the experimental data of indium leaching:

$$M_{CC} = M_{max} / (a+b*N) \qquad \text{(Eq. 2)}$$

where M_{CC} is the mobilization efficiency at different number of steps in the cross-current leaching, M_{max} is the maximum mobilization efficiency of indium, a and b are adjustable parameters and N is the number of steps in the cross-current leaching.

The costs of the reagents were set as follows: an average cost of 0.2 \$/kg for sulfuric acid, 0.19 \$/kg for sodium hydroxide and 0.37 \$/kg for zinc (www.alibaba.com).

The indium income was estimated based both on the amount of indium recovered in the hypothesized 10-step leaching treatment, and indium price. The considered indium quotations took into account the maximum (about 800 \$/kg) and the minimum (about 500 \$/kg) values in the last 3 years (www.metalprices.com).

The same hypothesized process was used for indium recovery also for the evaluation of the environmental impact of the process in the category of global warming (expressed as CO_2-Eq.). The software GaBi 5 (PE International) was used to quantify the CO_2 emissions according to the CML2001 - Nov. 09 problem-oriented method of the Institute of Environmental Sciences, Leiden University, Leiden, The Netherlands (previously the Centrum voor Milieukunde Leiden; hence CML) (Guinée et al., 2001a, 2001b). The production processes of the chemicals and energy used for the evaluation were taken from the GaBi database, integrated with EcoInvent 2.2.

3. Results and discussion

3.1 Characterization of ground end-of-life LCD panels

Experimental data concerning panel characterization are extremely relevant for the evaluation of the sustainability of indium mobilization from waste LCD panels. Indeed the composition of such waste is not homogeneous due to different production processes and data are poorly available in the scientific literature. Table 1.3 reports the metal content in the 3 stocks analyzed in this work (particle size up to 10 mm), along with the few data present in the literature. The different stock compositions of ground LCD panels showed a variability in an acceptable range of about 20%, in accordance with literature data. Such observed variability in the composition was probably due to the origin of ground LCD panels (e.g. different brand on the panels).

Table 1.3. Metal content in LCD panels (ppm, unless specified otherwise), as outcome of own determinations and comparison with literature data.

Metal	This work Stock 1	This work Stock 2	This work Stock 3	Wang, 2009	FEM and IUTA, 2011	Götze and Rotter, 2012	Hasegawa et al., 2013	Lee et al., 2013	Ma and Xu, 2013	Fontana et al., 2015
In	53 ± 6	130 ± 30	110 ± 20	102	174	195	380-410	260.7	219	290
Al (%)	3.3 ± 0.7	5 ± 2	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ca	n.a.[a]	29000 ± 6000	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ce	n.a.[a]	n.a.[a]	18 ± 1	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Fe	3100 ± 600	600 ± 400	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Ga	n.a.[a]	<10	<10	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Mn	53 ± 7	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Mo	14 ± 3	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]
Sn	260 ± 30	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	n.a.[a]	33	n.a.[a]

In addition, the content of other elements of commercial interest was evaluated through a qualitative X-ray fluorescence analysis. Arsenic, strontium, zirconium were observed with remarkable peaks in the emission spectrum (Fig. 1.3). The presence of arsenic, found at a concentration of 2 mg/L in the leach liquor, requires the application of an appropriate wastewater treatment (Beolchini et al., 2006; Beolchini et al., 2007).

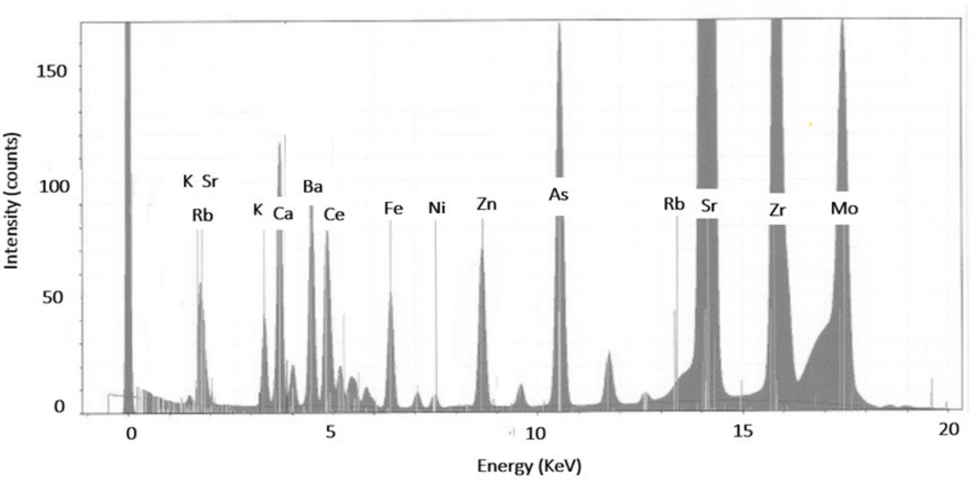

Fig. 1.3. Emission spectrum of the XRF analysis on a leached LCD sample (indium is not visible for peak overlap with other elements).

3.2 Distribution of indium in LCD fragments with different size

In order to understand whether indium was mainly present in a specific fraction of ground LCDs or equally distributed, the content of indium and tin was analyzed in several size intervals in the fraction smaller than 10 mm. The study of the distribution of indium was worthy of investigation, also considering the high variability in the choice of the fraction used in the literature. Indeed, it is reported that the range of size of LCD treated is wide, from scrap size of around 5 mm and 2-3 mm, to dimension smaller than 1 mm and 0.16 mm (Kato et al., 2013; Lee et al., 2013; Ma and Xu, 2013; Ruan et al., 2012). Fig. 1.4 reports the granulometric distribution of the <10 mm sample, along with indium and tin concentration in the different fractions. Indium concentration decreased as the size of the fragment increased. In the smallest fraction (< 0.125 mm), that was only 10% of the total mass, the highest concentration of indium was observed (about 400 mg/kg). It is known that leaching efficiency increases with the reduction of particle size (Olanipekun, 1999; Shin et al. 2005).

However, in the present study, both the fine and the coarse fractions resulting from blade grinding operations were used, to leach the highest amount of indium. In the perspective of a possible industrial application, the choice to treat end-of-life LCD panels with particle size up to 10 mm allows a considerable energy saving avoiding the mechanical pretreatment finalized to particle size reduction.

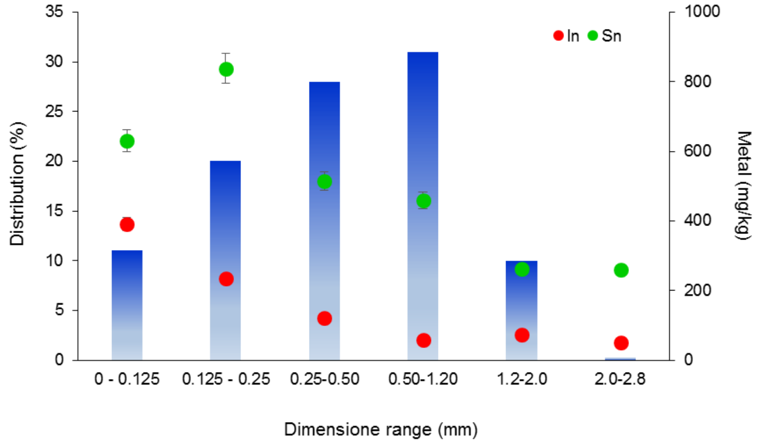

Fig. 1.4 Granulometric distribution of ground LCD panels (columns), indium and tin concentration (symbols).

3.3 Indium leaching from end-of-life LCD panels

Indium was mobilized from LCD panels using sulfuric acid in all the leaching treatments described in the present study. Differently from other acids currently used for this purpose (e.g. HCl and HNO_3), H_2SO_4 has many advantages (Dodbiba et al., 2012; Wang et al., 2013). One of these is that arsenic, in the form of highly toxic As_2O_3 in the LCDs, has a low dissolution concentration when H_2SO_4 is present (Ruan et al., 2012). However, the concentration of arsenic remaining in the solid residue was below the Italian regulatory limits for disposal. In addition, sulfuric is less expensive than the others, has a higher leaching efficiency and a limited environmental impact (Wang et al., 2013). The following part describes the results of the treatments.

3.4 Effect of temperature

Room temperature, which is about 25°C, compared to 80°C has the advantage that does not require any energy for its achievement. The observed extent of indium mobilization was significantly higher at 80°C. Indeed, at 25°C the efficiency of indium leaching was lower by 20% after 20 min, whereas at 80°C it was almost complete after 10 min. At 80°C leaching of metals requires a shorter time and therefore treatment scale-up to larger plants may lead to an increase of leaching cycles.

3.5 Effect of acid concentration

The results of the treatments aimed to identify the best concentration of H_2SO_4 showed that indium was almost completely mobilized both at 1 M and at 2 M. In the perspective of reagent saving, 1 M H_2SO_4 should be preferred. Some authors, using systems with ITO powder rather than LCD fragments, found that the selectivity of the acid was higher when H_2SO_4 had the lowest concentration (Virolainen et al., 2011). For example, they observed that with 0.1 M H_2SO_4 all the indium was leached, and tin was not leached, whereas with 1 M H_2SO_4 both indium and tin where completely mobilized. Nevertheless, in our systems with ground LCD panels containing indium, a higher concentration of H_2SO_4 (2 M) should be used in the perspective of a multistage cross-current leaching. Moreover, 2 M H_2SO_4 can guarantee the presence of more acidic conditions than 1 M acid, and as observed by other authors the rate of leaching increases with the increase of the acidity of the solution (Li et al., 2011).

3.6 Effect of leaching time

Some considerations about the time required for leaching were done based on the state of the art and by evaluating different mixing systems. On the one hand, literature data reports a wide range of leaching time at operative conditions different from those reported in the present study, from 30 min to 8 h (Lee et al., 2013; Li et al., 2009; Yang et al., 2013). On the other hand, with an equal efficiency of indium mobilization, with the Dubnoff bath, which determines a mild mixing, a longer time of leaching is required compared to magnetic stirrer, which produces a vigorous agitation. In the final perspective of scaling up the leaching process, the magnetic stirrer better simulates the mixing system used at industrial scale. Therefore, most of the treatments were carried out with the magnetic stirrer.

The treatments addressed to indium leaching showed different mobilization efficiencies and selectivity. The leaching time was a key variable to improve the selectivity of indium mobilization (Fig. 1.5a). Indeed, by increasing the time of leaching, a significant increase of the concentration of iron, aluminum and calcium was observed in the leach liquor. Conversely, a longer contact time of the LCD fragments with sulfuric acid did not determine important variations in indium, tin, manganese and molybdenum concentrations, which reached the maximum value within the first 10 minutes of treatment.

Fig. 1.5b confirms the complete mobilization of indium and shows the correlation between mobilization efficiencies of molybdenum, iron and tin and time. Indeed, these impurities doubled their leaching efficiencies up to 55% after 60 min. The structure of LCD could explain this different behavior of the considered elements. Under the glass substrate, there is a layer of ITO, and underneath a layer containing manganese (Rack and Holloway, 1998). Therefore, the elements indium, tin and manganese are more accessible to acid attack. Ten min of leaching are the best observed option to obtain a leach liquor containing indium in presence of other co-mobilized metals in traces. In this way, metals associated to the inner parts are leached to a minor extent.

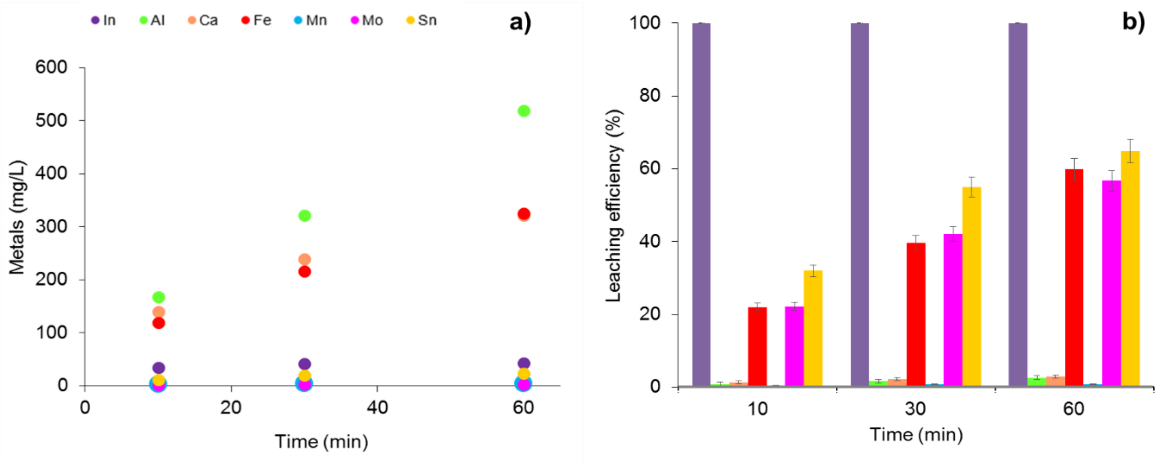

Fig. 1.5. a) Concentration of the considered elements in the leach liquor after 10, 30 and 60 min of contact of ground LCD panels with sulfuric acid (treatments 7-8-9 in Table 1.1). b) Leaching efficiencies of the considered elements after 10, 30 and 60 min of contact time.

For a better comprehension of the effect of time on the quality of the leached indium, Fig. 1.6 shows the percentage of each metal calculated in the 7-element system Al-Ca-Fe-In-Mn-Mo-Sn at time 10, 30 and 60 min. The highest percentage of indium, 7.3%, was observed after 10 min from the start of the leaching operation (Fig. 1.6a). As the leaching time increased, indium percentage in the metals system decreased (Fig. 1.6a-b). Therefore, for the purpose of the present study, the shortest leaching time (10 min) was favorable for the highest percentage of indium mobilized. The percentage of the co-mobilized metals was minor, especially aluminum.

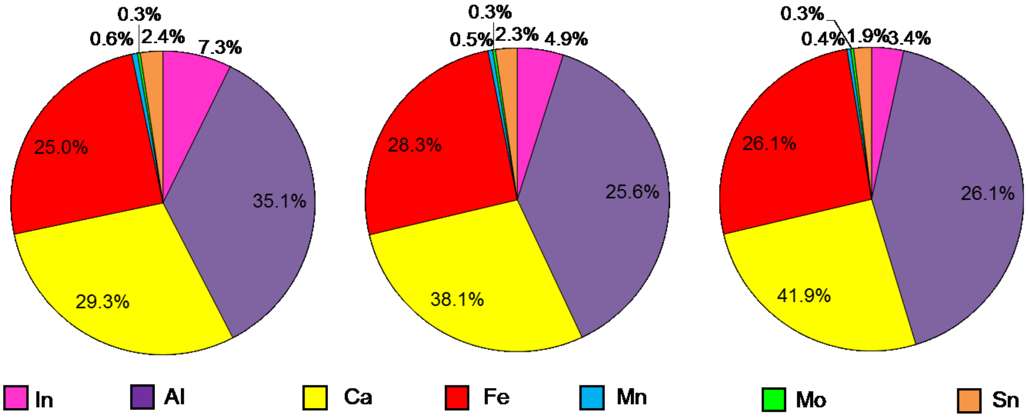

Fig. 1.6. Percentage of metals in the leach liquor collected after 10, 30 and 60 min (treatments 7-8-9 in Table 1.1).

3.7 Effect of the number of steps in the cross-current leaching

The main aim of cross-current leaching was to concentrate indium to obtain a cost-effective process, given the low content of indium in LCDs. Once the best conditions had been determined (2 M H_2SO_4, 10 min leaching at 80°C), the number of leaching steps, necessary to mobilize as much indium as possible, maintaining a satisfactory efficiency, was investigated. Fig. 1.7 shows that as the number of leaching steps increased, the concentration of indium in the solution also increased, as expected. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Conversely, the mobilization efficiency significantly decreased from a step to the next one. For example, in the first step indium leaching was complete, whereas in the second step it was in the range 85-90%, and with 6 steps it was about 50-55%. Also for the other metals analyzed and co-mobilized with indium (iron, aluminium and calcium; data not shown), a lower efficiency was observed when the number of leaching steps increased.

The decreased mobilization efficiency is the reverse of saving the acid solution. Indeed, as the same acid solution is used to sequentially leach metals from LCD panels, eventually adding a small amount of new acid lost from a leaching step to the next, as a result the mobilization capacity decreases. Nevertheless, indium is more concentrated and the amount of leaching solution to treat in the following steps to recover indium is significantly minor. This observation is true for 6 steps (investigated in the present study), but the same trend should be observed also for a higher number of steps. Considering the low indium concentration in end-of-life LCD, no more than 6 stages were tested since the indium lost becomes too much significant. The model described in Eq. 2 well fits experimental data of indium leaching efficiency in the treatment of 6-step cross-current leaching (dotted lines in Fig. 1.7).

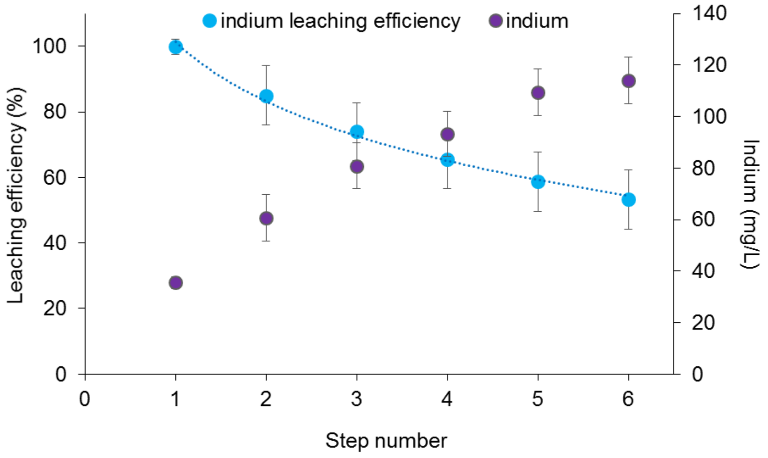

Fig. 1.7 Theoretical trend of indium mobilization efficiency (line) compared with real data (symbols) in the treatment of cross-current leaching (based on treatment 10 in Table 1.1). Data of indium concentration are also reported.

3.8 *Advantages of cross-current configuration*

This last part of the chapter focused on a draft estimation of the possible economic income determined by indium sale in a simulated scaled-up process. Fig. 1.8a shows that the possible income from indium sale increases almost by 4-fold when 10 steps of leaching, rather than only 1, are carried out (predicted by Eq. 2). Conversely, the costs of the process per kg of LCD treated drastically reduce by increasing the number of steps of leaching. The process costs were estimated for cross-current leaching with 10 steps, as predicted by Eq. 2 (Fig. 1.8a), followed by indium cementation. Therefore, 2 curves were drawn, which represent the maximum (about 500 \$/kg) and the minimum (about 100 \$/kg) income. One of the main advantages of cross-current leaching is reagent saving (0.7 kg acid/kg LCD treated; Table 1.1). In the phase of leaching, the amount of sulfuric acid is lower than conventional leaching, as the leaching solution used to mobilize metals from a LCD amount is then used in the following steps, eventually adding a small amount of new acid. Therefore, the cost of reagents considerably decreases with the number of leaching steps, and benefits to the environment are achieved.

Analogously, both the CO_2 emissions produced by the simulated 10-step cross-current leaching process and the CO_2 saved thanks to the hypothesized recovery of secondary indium were evaluated. Figure 1.8b shows that CO_2 emissions are remarkably reduced when the number of leaching steps increases, starting from an average value of 1.7 kg CO_2-Eq./kg LCD treated in the first step, they are about a half in the second step. Environmental benefits were assessed in terms of CO_2 saved, calculated as avoided primary production of indium. In this case, it can be observe that since at the first step about 20 kg CO_2-Eq. are saved, with 10 steps the emission of about 90 kg CO_2-Eq. could be avoided, considering to recover about 150 g of indium treating 1 ton of LCDs in a plant with a volume of 5 m^3.

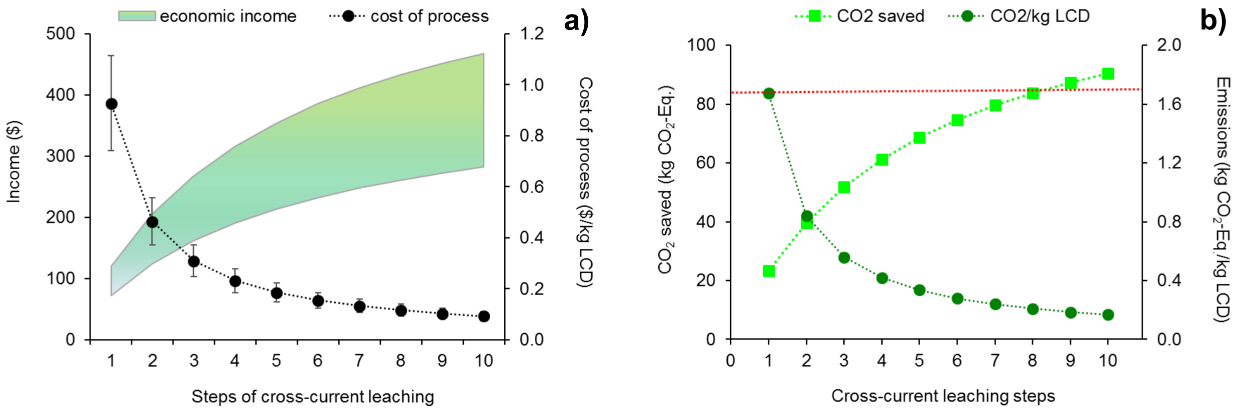

Fig. 1.8. a) Cost of process for indium recovery from LCD panels and income from its sale. b) Emissions of CO_2 produced in the treatment of cross-current leaching and avoided emissions of CO_2 as a result of secondary production of indium. In both the cases, we considered a hypothetical scaled-up process based on cross-current leaching, (treatment 10 in Table 1.1), followed by cementation. The red dotted line represents kg CO_2-Eq. /kg LCD treated by a single step leaching.

4. Conclusions

The concentration of indium in end-of-life LCDs was about 150 mg/kg. The heterogeneity within each sample is acceptable, with maximum variations of 20%. Indium concentration in LCDs is comparable or even higher than that in minerals making LCD scrap an interesting source of metals. In the present work, a cross-current leaching to LCD scrap was applied for. The results showed that the best leaching conditions for a complete indium leaching were 2 M sulfuric acid at 80°C for 10 min. With longer leaching time, indium leaching was always complete, but this increased the co-extracted element concentrations. The use of the cross-current design with a multiple step configuration represents an essential factor since it may overcome the challenge of economic and environmental sustainability, due to lower content of indium. Indeed, thanks to the application of several steps of leaching (6 steps), the content of indium in the leach liquor is enhanced, and the expense of reagents is reduced. Indium concentration in the leachate was about 35 mg/L after the first step of leaching, almost 2-fold at the second step and about 3-fold at the fifth step. Moreover, hypothesizing a cross-current leaching scale-up process followed by cementation, the process for indium recovery would determine a reduction of CO_2 emissions, with important benefits to the environment. The results show that cross-current leaching is a promising process for the effective mobilization of indium from LCDs. Considering the risk of supply of critical raw materials such as indium, new effective methods to leach them from urban mines should be optimized and used at industrial scale. The process of cross-current leaching may represent a solution to concentrate critical elements and a step forward economical sustainability of processes for the recovery of elements with concentrations on the order of hundreds of ppm in WEEE.

5. Products

Results illustrated and discussed in this chapter were used to support a peer reviewed article published on Waste Management, Elsevier (Fig.1.9).

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Cross-current leaching of indium from end-of-life LCD panels

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Fig. 1.9. Articles published on *Waste Management*

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Chapter 2

RECOVERY OF INDIUM FROM LIQUID CRYSTAL DISPLAYS

Abstract

Indium is a critical raw material with economic importance and high supply risk. In the present study, indium was recovered by means of cementation from a leaching solution of waste liquid crystal display (LCD) panels. Cementation with zinc powder was optimized through the investigation of the effects of different variables (zinc concentration, pH, cementation time) on cementation efficiency and purity of the solid product. Almost all the indium present in the leaching solution passed to the solid phase when cementation was performed with a low (2-5 g/L), a medium (15-20 g/L) and a high (100 g/L) concentration of zinc, at pH 3. At pH 2, a complete cementation was obtained only with the highest concentration of zinc. Moreover, the highest purity of the indium product (62% indium percentage in the solid product, calculated in the 4-metal system indium-aluminum-calcium-iron) was achieved after a cementation of 10 minutes, whereas the presence of impurities increased with time. An empirical model successfully fitted the experimental data and suggested that the highest purity of the cemented product was expected at pH 2. A quantification of the environmental impact of the process for indium recovery from end-of-life LCDs was also carried out through a life cycle analysis approach, and it outlined that relevant benefits to the environment were obtained thanks to the recovery of indium from waste electric and electronic equipment (WEEE). The results obtained in the present study are promising since this is the first time that cementation was applied to a leaching solution of waste LCD panels. Indeed, the approach presented here is considered extremely useful in the frame of urban mining strategies.

Content

1. Introduction

The state of the art about the leaching technologies applied to LCD panels to extract indium is described elsewhere, along with an innovative promising approach based on cross-current leaching (Rocchetti et al., 2015). For the purification and recovery of secondary indium from the leaching solution, many approaches can be used, such as ion exchange resins, ionic liquids, solid separation, extractants (Hasegawa et al., 2013; Kubota et al., 2009; Liu et al., 2012). Some metals, such as iron and aluminum, show precipitation properties similar to indium, making it difficult to separate and to obtain a high purity indium product. Cementation is a potentially effective way to recover indium from solutions, based on the different oxidation potential of indium when compared to other elements. For this purpose, aluminum, zinc and magnesium are used to deposit indium on their surfaces (Hsieh et al., 2009; Jiang et al., 2011). Although indium cementation is a quite consolidated method, further investigation is necessary to identify the best operating conditions, that allow a selective recovery of indium from a leaching solution that contains other metals. Only a few studies in the scientific literature address the cementation to recover indium from ITO and/or LCDs. Li et al. (2011) and Li et al. (2014) recovered indium from waste ITO using zinc plates. Moreover, cementation with aluminum plate (pH 2, 60 °C) was reported to be effective to obtain indium sponge from ITO scrap (Park, 2011). Some patents have also been granted, but either the methodological approach is not detailed and clear, or they are not written in the international language. Indium cementation with zinc seems a feasible way for the recovery of indium from waste LCD panels. On the basis of the reduction potential, the reaction of indium reduction is favored in presence of zinc as cementation agent (Table 2.1). Indeed, zinc has a lower reduction potential than indium, therefore In^{3+} is reduced to metallic In. Cementation time, pH of the reaction and the choice of the amount of zinc, when zinc powder is used, is controversial. Especially for the quantity of zinc powder used, most of the available information can be found for other systems. Koleini et al. (2010) carried out indium cementation from a stripping solution of zinc sulfide concentrate at pH 3 for 6 h at 25 °C. The amount of zinc powder consumed was 1.5 times the stoichiometric quantity of indium, and its recovery ratio and purity of the precipitate were more than 95%. Other authors, using a higher amount of zinc powder (1.8 times the stoichiometric quantity of indium) in similar cementation conditions (pH 3 for 7 h at 25 °C), obtained a recovery ratio of indium and purity of the product above 97% (Jiang et al., 2011). Barakat (1998) used zinc powder to recover indium from alloy wire scrap through the cementation in a stoichiometric ratio of 1.2 at pH 1.4 at 30 °C, and obtained an indium recovery of 98.8%. According to this researcher, although increasing the ratio of zinc could slightly enhance the indium recovery, this is detrimental to the indium purity, as the excess of zinc contaminates the indium sponge. In all the papers found in the scientific literature about indium cementation, the amount of indium and the stoichiometry of the reduction reactions are used to determine zinc dosage. Conversely, pH is a key variable in order to achieve the right zinc dosage: indeed, also zinc consumption for hydrogen formation has to be taken into account.

Consequently, the aim of this study was to identify the best process conditions for the downstream section of the process to recover indium from LCD displays, considering both the cementation efficiency of indium and the purity of the indium product as targets.

Table 2.1. Standard reduction potential of aluminum, calcium, iron, indium and zinc (25°C, 101 kPa, 1M; Habashi, 1999).

Half-reaction	Reduction potential (V)
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$2\ H^+ + 2\ e^- \rightarrow H_2$	0
$In^{3+} + 3\ e^- \rightarrow In$	-0.34
$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
$Zn^{2+} + 2\ e^- \rightarrow Zn$	-0.76
$Al^{3+} + 3\ e^- \rightarrow Al$	-1.66
$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87

2. Materials and methods

2.1. Cementation with zinc powder

Cementation tests were carried out with solutions that resulted from cross-current leaching with sulfuric acid of end-of-life LCD panels (Rocchetti et al., 2015). Different experimental conditions were investigated, for a total of 16 treatments. The experimental factors considered were the concentration of zinc powder, pH and cementation time. The concentration of zinc was chosen on the basis of 2 main aspects: the concentration of indium in the leach liquor and the consumption of zinc due to the hydronium ion reduction. Three intervals of zinc concentration were evaluated: low zinc (2-5 g/L), medium zinc (15-20 g/L) and high zinc (100 g/L). Table 2 summarizes the experimental conditions of each cementation treatment. In each test, a volume of leach liquor was treated at a temperature of 55-60°C on a magnetic stirrer. When the temperature was reached, pH was adjusted with sodium hydroxide and then pure zinc powder was added to the solution. Samples were collected at final pH value to verify the possible metals precipitation (in hydroxide form) and at different time intervals to monitor the time course of the cementation.

Table 2: Operating conditions of different cementation treatments, indium cementation efficiencies and indium percentage in the solid product.

Treatment	Zinc concentration (g/L)	pH	Cementation time (min)	Volume (mL)	Indium recovery efficiency (%)	Indium in the solid product (%)
1	2	2.5	10, 20	50	77.7	51.5
2	2	4.0	10, 20	50	95.0	48.5
3	5	1.0	10, 60, 240	100	32.1	39.1
4	5	1.5	10, 60, 240	100	37.5	42.6
5	5	3.0	20, 60	50	98.0	41.0
6	15	2.0	5, 10, 20	50	47.6	38.9
7	15	2.0	5, 10, 20	50	54.4	43.9
8	15	3.0	5, 10, 20	100	95.0	35.9
9	15	3.0	5, 10, 20	100	96.2	36.2
10	20	1.0	10, 60, 240	50	46.0	37.8
11	20	2.0	10, 60, 240	50	35.8	42.2
12	20	3.0	5, 10, 20	50	98.6	36.0
13	20	3.0	10, 20, 30, 40, 50, 60	500	98.9	36.4
14	100	1.0	10, 60, 240	50	43.0	47.2
15	100	2.0	10, 60, 240	50	99.8	61.6
16	100	3.0	10, 20, 60	50	99.9	47.0

2.2. Chemical analyses

The concentration of metals in the liquid phase was determined by means of inductively coupled plasma-atomic emission spectrometry in accordance with Maxfield and Mindak (1985). The metals analyzed during the cementation treatments were indium, aluminum, calcium and iron. These elements were considered the most significant for their average concentration in the waste LCDs on the basis of a previous chemical characterization and on the literature information as well (Rocchetti et al., 2015).

2.3. Statistical analysis

Analysis of variance and regression analysis were carried out with the software UNISTAT 6.5 to evaluate the effects of zinc concentration, pH and cementation time on cementation efficiency and on the composition of the solid product.

2.4. Environmental impact evaluation

The effects of the recovery process described in the present paper were evaluated by means of the life cycle assessment (LCA). The goal of LCA was to identify the environmental benefits and impacts of leaching and indium cementation, and to compare this management option for waste LCD panels with incineration and disposal in landfilling sites for urban waste (European Parliament, 2012). The analysis referred to a simulated process to recover indium carried out in the industrial plant built within the HydroWEEE FP7 231962 project, with a capacity of 5 m^3, an energy consumption of 0.13 kWh/kg LCD panel treated and solid concentration 0.2 kg/L. Considering previous (Rocchetti et al., 2015) and present results, the process consisted of a 2-step cross-current leaching with 2 M sulfuric acid, followed by pH adjustment to 3 with sodium hydroxide and cementation with 5 g/L zinc powder. The system boundaries included the 3 management options described for panel LCDs after the disassembly. Transport, manual disassembly for the removal of back cover, steel superstructure, printed circuits boards, cables, hazardous backlights and recycling of plastic and other fractions, common to the 3 scenarios, were out of the system boundaries. The impacts in the categories of abiotic depletion and global warming were evaluated using the software GaBi 5 (PE International) following the CML 2001 - Nov. 09 method. The choice of the two categories is due to the modernity of these critical issues (Bereketli et al. 2011). The processes of the reagents and energy used were taken from the database of the software, integrated with the Ecoinvent database 2.0. The functional unit was set to 1 kg waste panel LCD treated (either recycled with the recovery of indium, or incinerated or landfilled).

3. Results and discussion

3.1. pH adjustment and metal precipitation

The leaching downstream started with the addition of sodium hydroxide, in order to meet the best pH conditions for cementation. Fig. 2.1 shows the precipitation efficiency of indium, aluminum, calcium and iron as a consequence of sodium hydroxide addition. In one case (treatment 1 in Table 2), the extent of metal precipitation at very acidic conditions (pH 0) was assessed during pH adjustment, and a negligible precipitation process took place, as expected. Indium precipitation displayed a clear pattern depending on changes in pH. Indeed, as the pH increased after the addition of sodium hydroxide, the amount of indium that precipitated increased accordingly. In particular, indium average precipitation efficiency was in the range 20-40% at pH values in the 1-3 interval. Aluminum and iron showed a precipitation trend similar to indium. Conversely, calcium precipitation seemed not influenced by pH changes.

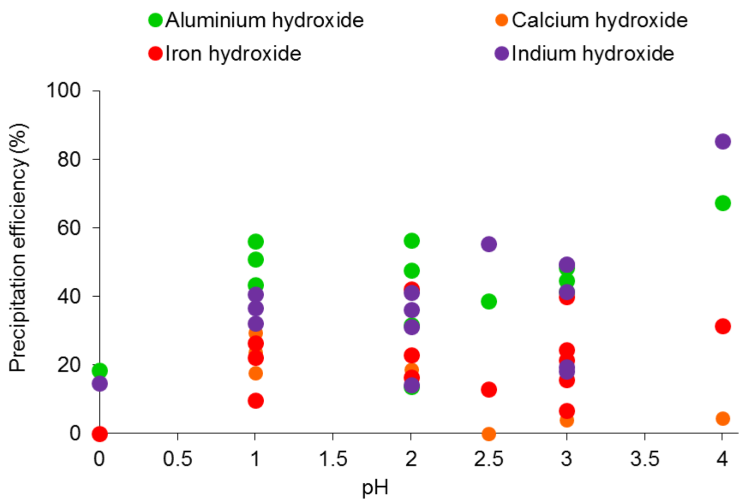

Fig. 2.1. Precipitation efficiency of indium, aluminum, calcium and iron as a function of pH (temperature 55°C, pH adjustment with sodium hydroxide).

3.2. Effect of zinc concentration and pH on the cementation process

The trend of metals during the cementation treatments was observed to define the best operating conditions. The recovery efficiency was determined for indium and aluminum, one of the major impurities found in the cemented material. Iron and calcium cementation were negligible (data not reported), and the presence of these elements in the final product was due to the precipitation with sodium hydroxide (Fig. 2.1; Park, 2008). Fig. 2.2a reports the recovery efficiency of indium in all the treatments, determined after 10 min from the start of the process. Indium cementation was affected by the operating conditions: at pH 1 cementation of indium was not effective, as most of the indium in the solid phase came from the precipitation with sodium hydroxide (Fig. 2.1). At pH 2 cementation was relevant only when a high concentration of zinc was used, reaching an indium recovery of 99.8%. The best results were found at pH 3. Indeed, the percentages of indium recovery, including also precipitation besides cementation, were: 98.0% with a low concentration of zinc, from 95.0% to 98.9% with a medium concentration of zinc and 99.9% with the high concentration of zinc. A low concentration of zinc was still effective for indium precipitation at pH 4, where an indium recovery of 89.7% was achieved. It would be difficult to compare our data with the literature, given the novelty of the subject. However, Li et al. (2011) reported a mostly complete recovery of indium using cementation with zinc plate. Similar results were obtained by other researchers using different techniques (hydrometallurgical process and hot immersion, cementation with zinc plate, solvent extraction and vacuum carbon-reduction; He et al., 2014; Hsieh et al., 2009, Yang et al., 2013).

Fig. 2.2b reports the recovery efficiency of aluminum in all the treatments, determined after a 10-min cementation. During the process of indium cementation, generally aluminum was not involved, and most of the recovered aluminum had precipitated in the previous phase of pH adjustment. However, a high recovery of aluminum was observed at pH 3 with a medium and high concentration of zinc. This is due to the increase in pH during the cementation, and not to the aluminium reduction. Indeed, the lower reduction potential confirms that aluminum (III) cannot be reduced by metallic zinc (Table 2.1).

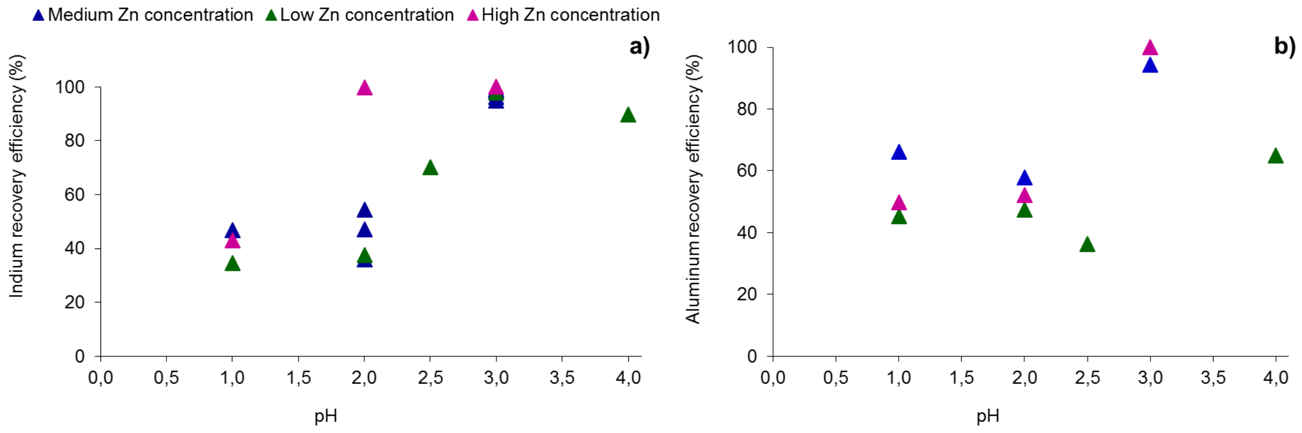

Fig. 2.2. Recovery efficiencies through precipitation and cementation of a) indium and b) aluminum at 55-60°C with low (2-5 g/L), medium (15-20 g/L) and high (100 g/L) zinc concentration.

Fig. 2.3 shows the speciation of indium in the recovered solid, for the operating conditions that gave a complete indium recovery, in order to identify the relevance of the 2 prevalent forms of indium in the recovered solid (hydroxide and metallic). It can be observed that the metallic form of indium was 46-59%.

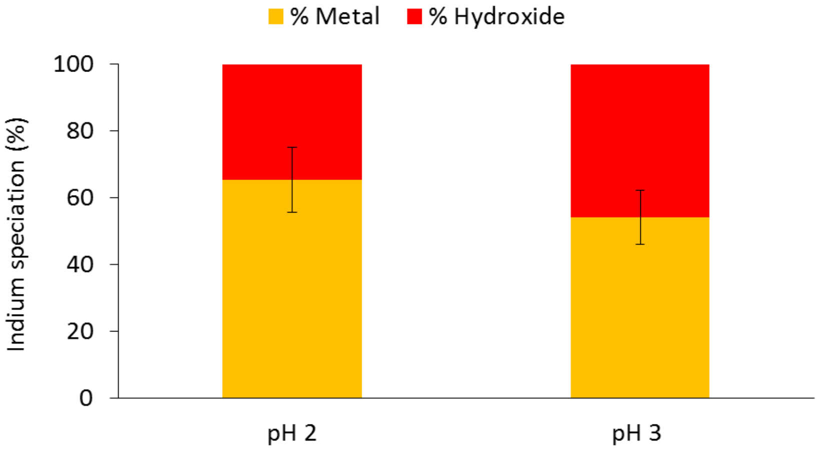

Fig. 2.3. Indium speciation in the solid product where a complete recovery was achieved.

3.3. *Effect of time on the cementation process*

Fig. 2.4 reports the temporal profiles of indium recovery, as well as of the other metals, considered as impurities in the solid product, achieved in the treatment with initial pH 3 and with the medium concentration of zinc. The sampling time 0 min represents the condition at the end of pH adjustment, before zinc addition. After 10 min from the start of the cementation process, indium recovery reached a value of 90%, with the minor amount of co-extracted metals. Conversely, at time 20 min a small increase of indium cementation (about 99%) was observed, but with a high efficiency of aluminum cementation (> 90%). Therefore, in order to gain a product as pure as possible, the cementation process should last 10 min, a time extremely short if compared with that described by Li et al. (2014), on the order of 1-2 days using zinc plates. The change in pH was used as an indicator of the proceeding of the cementation process. The increase of pH values favored the transfer to the solid phase of all the considered metals, including the impurities calcium, iron and aluminum, which precipitate as hydroxides (Fig. 2.1).

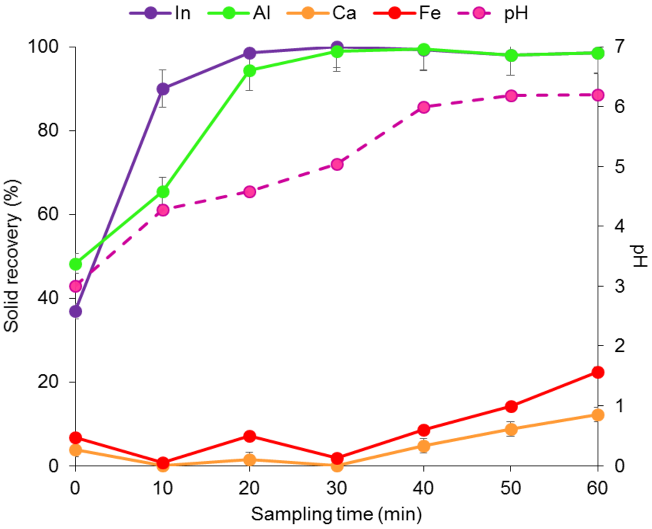

Fig. 2.4. Temporal profiles of metal recovery and pH, during cementation (Treatment 13 in Table 2).

3.4. Quality of the solid product

Generally the results of the present study showed that the longer the cementation time is, the higher is the recovery of indium, as observed also by other authors (Barakat, 1998). However, a shorter cementation time allowed to find a minor amount of co-extracted metals. The high quality of the solid produced after 10 min of cementation was verified by the determination of the composition of the 4-metal system indium- aluminum- calcium-iron. As an example in Fig. 2.5 reports the composition of the solid obtained in treatment 15 of Table 2. The lowest cementation efficiency of the other metals allowed to obtain the highest percentage of indium (about 62%) in the final solid product. Further processes such as solvent extraction could be applied to obtain indium with a higher purity (>95%).

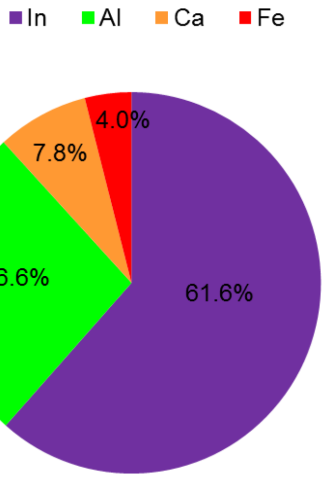

Fig. 2.5. Composition of the solid product in the indium-aluminum-calcium-iron system (treatment 15 in Table 2, 10-min cementation time).

3.5. Statistical analysis and empirical models

A first analysis of variance points out the very high statistical significance ($p<0.001$) of zinc concentration and pH on cementation efficiency, as it can be observed in Fig. 2.2a. Furthermore, a high statistical significance ($p<0.01$) of the following main factors and interactions was also observed (reported in order of significance): the 3-way interaction pH-zinc concentration-time and time as main factor.

The preliminary analysis of variance applied to the indium percentage in the solid product, calculated in the 4-metal system indium-aluminum-calcium-iron, revealed a very high statistical significance ($p<0.001$) of zinc concentration, a high statistical significance ($p<0.01$) of the 2-way interaction zinc concentration-time and a medium significance ($p<0.05$) of the 3-way interaction pH-zinc concentration-time, the 2-way interactions time-zinc concentration and time-pH, and pH. These observations highlight the importance of the use of a suitable amount of zinc powder for cementation, able to contrast the presence of the hydronium ions and bring indium from the liquid to the solid phase, and the non-linear inverse function between zinc concentration and cementation length.

Linear regression tools was applied to forecast both indium cementation efficiency and its percentage in the solid product, considering as independent variables only the significant main effects and interactions. The following empirical equations were obtained, with regression coefficients R^2 of 0.80 and 0.65, respectively:

$$In\ cementation\ eff\ (\%) = 16.0 + 1.43\ t + 0.21\ Zn + 24.8\ pH + 0.04\ t\ Zn\ pH$$

(eq. 1)

$$In\ percentage\ (\%) = 40.4 - 0.2\ Zn - 2.2\ pH - 0.9\ \mathrm{pH}\ \mathrm{t} + 0.2\ Zn\ pH + 0.06\ t\ Zn - 0.03\ t\ Zn\ pH$$

(eq. 2)

where *In cementation eff(%)* is indium cementation efficiency, *pH* is the value of pH, *Zn* is zinc concentration, *t* is cementation time and *In percentage(%)* is the percentage of indium in the solid product.

Fig. 2.6a shows the values for zinc concentration and cementation time predicted by eq. 1 in order to obtain a cementation efficiency of 100%. For a short cementation time, the concentration of zinc is very variable. Zinc concentration is very high at pH 1, this is to contrast the consumption of zinc as a result of the presence of hydronium ions that is favored at low pH and has quick kinetics. Conversely, the quantity of zinc necessary to cement indium decreases with pH. Fig. 2.6b shows the values predicted by eq. 2 for indium percentage in the cemented solid, with cementation efficiency 100%. Cementation at pH 1 results disadvantageous for the too high request of zinc, therefore it has not been considered. Experimental data achieved under similar operating conditions are also shown for comparison. According to the model, the highest indium percentage (around 60%) is obtained at pH 2, and the presence of impurities increases with time during cementation. The good agreement between experimental and calculated data is evident in Fig. 2.6a and 6b.

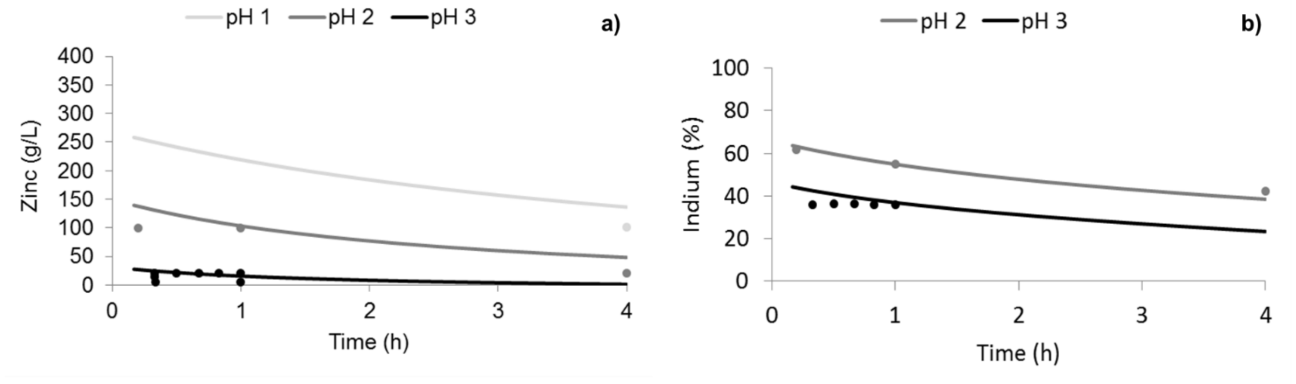

Fig 2.6. a) Zinc concentration and cementation time predicted by eq. 1 in order to obtain a cementation efficiency of 100%. b) Indium percentage in the solid product (calculated in the 4-metal system indium-aluminum-calcium-iron) predicted by eq. 2, with cementation efficiency 100%. Experimental data observed under similar operating conditions are also shown (points).

3.6. Environmental perspective

An environmental perspective of the process for indium recovery was provided by means of LCA. The impacts of the recycling process developed in this work are compared with conventional end-of-life LCD panels management routes, i.e. incineration and disposal in landfilling site, in terms of abiotic depletion and global warming (Fig. 2.7a and b, respectively). The option of LCD recycling through leaching followed by cementation determined a net environmental credit in the impact category of abiotic depletion, equal to $-8.5 \cdot 10^{-6}$ kg Sb-Equiv. for 1 kg of panel LCD treated, thanks to the recovery of indium (Fig. 2.7a). Incineration determined an impact of $4.7 \cdot 10^{-6}$ kg Sb-Equiv., whereas landfilling was negligible. In the category of global warming, the use of sulfuric acid for leaching and of sodium hydroxide to adjust pH prior to the cementation were the main causes for an estimated impact of $0.6 \cdot 10^{-6}$ kg CO_2-Equiv. for 1 kg of LCD treated, similar to the impact of landfilling (Fig. 2.7b). When compared with the other 2 management options, the impact of incineration was about 3-fold in the category of global warming. Generally, the impacts of landfilling were minor than incineration. As a whole, these results support the advantage to the environment associated with indium recovery from end-of-life LCDs, despite the quite low indium concentration in the panel. The benefit of recycling approach could be further increase by the possible recovery of residues of the recycling process as building materials (Wang, 2009).

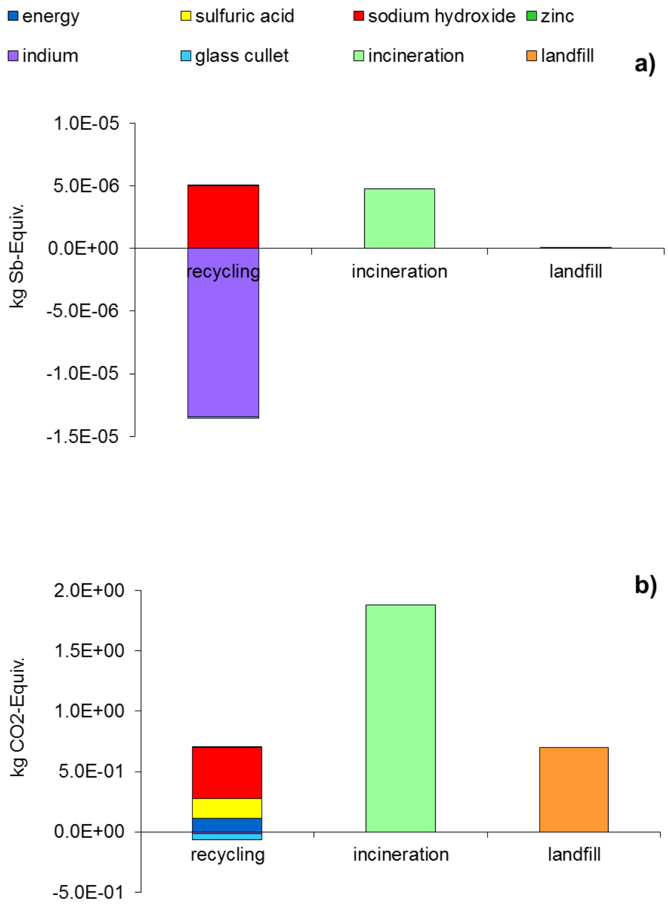

Fig. 2.7. Impact evaluation in the categories of a) abiotic depletion and b) global warming for a simulated scaled-up process based on 2 steps of cross-current leaching and cementation with 5 g/L zinc powder (functional unit 1 kg LCD panel).

4. Conclusions

The development of effective strategies for the recovery of secondary indium from WEEE is a hot topic, since it could decrease the dependency on the import from other countries (Ardente and Mathieux, 2014). In this frame, treatments were carried out for the recovery of indium by means of cementation with zinc powder from a solution produced through a cross-current leaching of LCDs. The highest indium recovery, equal to 99.8% was achieved at pH 2 when a relatively high concentration of zinc was used (100 g/L). Moreover, indium cementation was almost complete at pH

3, even with quite low zinc concentration (5 g/L). Cementation also involved aluminum, which was one of the main impurities in the final product (about ¼ of the mass). In such product, indium was about 62% with a short cementation time (10 min), with the minor amount of co-extracted metals.

A statistical analysis confirmed the positive effect of pH, time and zinc concentration on the cementation efficiency and the negative effect of time and pH on indium percentage in the solid product. LCA results for a simulated recovery of indium at industrial scale involving cross-current leaching and cementation with zinc revealed that from an environmental point of view the process was better than other management options. In particular, in the category of abiotic depletion significant benefits to the environment were due to the recovery of indium.

Further investigations are still in progress aimed on the one hand at the achievement of high indium purity through solvent extraction strategies, and on the other at improving the environmental sustainability of the process, through wastewater recirculation and recycling of the panel glass, solid residue of leaching. The results described are promising as this was one of the first times that indium was recovered from a leaching solution of waste LCD panels. The process described furthers a method to recover indium from end-of-life LCDs rather than from reserves. It can help ensure progress towards sustainable societies, encourage industrial innovation of the recycling companies and the implementation of cleaner processes.

5. Products

Results illustrated and discussed in this chapter were used to support peer reviewed articles and congress paper. They have published on Journal of cleaner production, Elsevier (Fig. 2.8), Chemical Engineering Transactions, AIDC (Fig. 2.9) and Physica Status Solidi C, Wiley Online Library (Fig 2.10).

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Recovery of indium from liquid crystal displays

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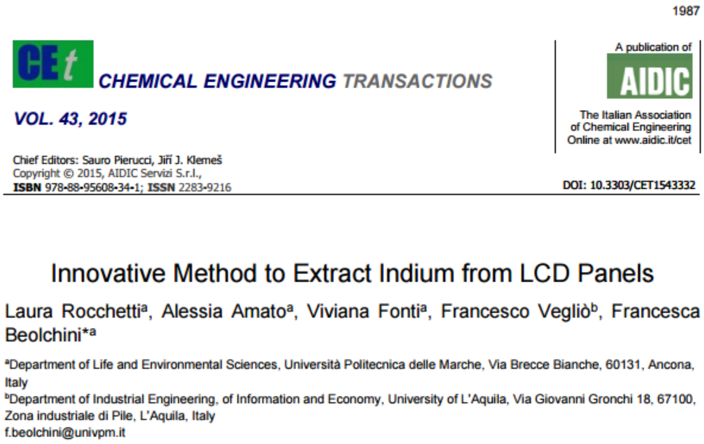
Fig. 2.8. Articles published on *Journal of Cleaner Production.*



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Innovative Method to Extract Indium from LCD Panels

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Fig. 2.9. Articles published on *Chemical Engineering Transaction*

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Valorizing end-of-life LCD scraps
after indium recovery

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Fig. 2.10. Articles published on *Physica Status Solidi C.*

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Rocchetti L., Amato A., Fonti V., Beolchini F. End-of-life liquid crystal displays: a secondary source of indium. Ecomondo, Rimini, 3-6 November 2015

Rocchetti L., Amato A., Fonti V., Ubaldini S., De Michelis I., Kopacek B.,Vegliò F., Beolchini F. Hydrometallurgical processes for the recovery of precious and critical metals from liquid crystal displays. Conference Going Green – Care Innovation 2014, Vienna, 17-20 November 2014.

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Amato A., Rocchetti L., Fonti V., Ruello M.L., Beolchini F. Secondary indium production from end-of-life liquid crystal displays. 2016 Spring Meeting of European Materials Research Society, Lille 2-6 May 2016.

Amato A., Rocchetti L., Fonti V., Abo Atia T., Altimari P., Moscardini E., Toro L., Pagnanelli F., Beolchini F. Recovery of critical metals from LCDs and Li-Ion batteries. Electronic Goes Green 2016+, Berlin 7-9 September 2016.

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Chapter 3

ENVIRONMENTAL IMPACT ASSESSMENT OF DIFFERENT END-OF-LIFE LCD MANAGEMENT STRATEGIES

Abstract

The strong growth of the electrical and electronic equipment production combined with its short lifespan are causing the production of a significant amount of waste to treat. In particular, the present paper focuses on end-of-life liquid crystal displays (LCDs) for their significant content of valuable materials, like plastic, glass and metals that could be recovered after dismantling. In the recent literature, traditional LCD recycling processes are combined with innovative treatments, which allow to recover critical raw materials, such as indium. In this context, we have evaluated the environmental impact of four different strategies of end-of-life LCD management: the disposal in landfilling sites, the incineration, the traditional recycling treatment and an innovative process also addressed to the recovery of indium. The traditional recycling treatment resulted to be the best scenario for the environment. Indeed, a life cycle assessment study gave following environmental burdens (if negative they are credits): 18, 81, -68, -60 kg CO_2-equiv. and 0.08, 0.01, -0.25, -0.18 mol H^+-equiv., for the four scenarios in the categories of global warming and acidification, respectively. The limit of the variability of LCD composition was overcome including additional literature data in the study. In order to improve the innovative process sustainability, a system of water recirculation was optimized with a consequent impact decrease of 35% in the global warming category. Nevertheless, this action should be combined with an increase of indium concentration in the panel because the low metal content represents the bottleneck of the overall approach. In this regard, a sensitivity analysis showed that an increase of at least five times in indium concentration in the waste

is needed to observe an advantage of the innovative vs the traditional recycling process, when the impact category of climate change is considered. As a whole, the life cycle assessment was confirmed as a key tool for the choice of the best option of WEEE management.

Content

1. Introduction

The end-of-life liquid crystal display (LCD) monitors treatment represents a delicate issue for the significant content of substances with effects on the environment and human health, such as metals (mercury, cadmium, lead, etc.) and brominated flame retardants (Binnemans et al., 2013; Cui and Forssberg, 2003; Tsydenova and Bengtsson, 2011). Nevertheless, the negative potential of LCD, and in general of waste from electric and electronic equipment (WEEE) if improperly managed, is combined with the possibility to recover many valuable materials. Indeed, the typical composition of WEEE includes five categories of materials: ferrous metals, non-ferrous metals, glass, plastics and other materials (Widmer et al., 2005), each one with different potential of recovery. Generally, this kind of waste is disposed in landfill or incinerated, but these management options require high attention levels. Taking into account the toxicity of the substances previously described, the application of these strategies can cause several effects on different environmental compartments if the waste is not properly pretreated (Bereketli et al., 2011; Spalvins et al., 2008). For example, the copper contained in many devices can catalyze the formation of dioxin during the incineration of flame retardants (Cui and Zhang, 2008) also by the combustion of bromine organic compounds in inappropriate combustion conditions (Wu et al., 2008). Moreover, other problems are associated to the disposal in landfill sites, as the leaching and the evaporation of pollutants can determine consequences for soil, water and air (Tsydenova and Bengtsson, 2011). In order to reduce these negative effects, recycling strategies should be used with the final target to make the waste a source of secondary raw materials. In this regard, literature reports many recycling treatments applied to LCDs, mainly classified as pyrometallurgical and hydrometallurgical (Cui and Zhang, 2008). On the other hand, additional new and novel technologies, often suitable for small scale applications, include: biometallurgical, electrochemical, supercritical and vacuum metallurgical technologies (Zhang and Xu, 2016). The interest for LCD is due to the content of different valuable fractions, including indium, a metal classified by the European Commission as critical raw material (European Commission, 2014), with a medium concentration of about 160 ppm (Ma and Xu, 2013; Wang, 2009). This metal is used in oxide form combined with tin, to form a film called ITO (indium tin oxide), an optoelectronic material with the characteristics of transparency to visible light, electric conduction and thermal reflection (Li et al., 2011). Fig. 3.1 shows the detail of the main components of an LCD monitor including the panel, the frame and the electric and electronic parts. The backlighting components, reported in the figure, make this WEEE a hazardous waste for the possible presence of fluorescent lamps with a mercury content (Binnemans et al., 2013; Li et al., 2009; Park et al., 2006).

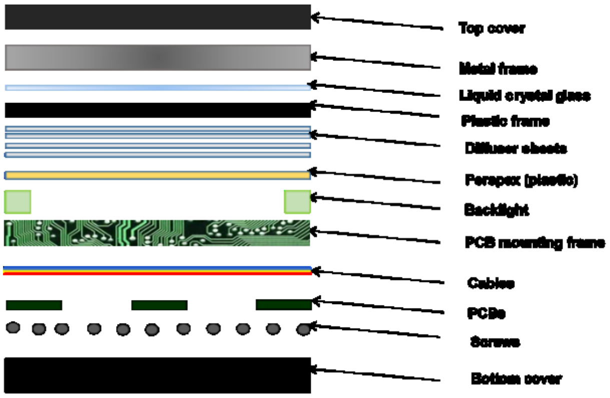


Fig. 3.1. Typical LCD cross section (adapted from Ryan et al., 2011).

Nowadays, the application of the new legislation combined with modern technologies, allowed the reduction of this metal content introducing advanced system, environmentally benign, as light emitting diodes (LEDs), that are replacing the fluorescent lamps (Savvilotidou et al., 2014). Nevertheless, considering that LED technology is a recent application, a significant percentage of end-of-life LCD contain the old backlighting system. In order to produce an evaluation of all potentially recoverable materials, Fig. 3.2 displays the composition of an LCD. Metals and plastic are the most significant fractions with percentages of 47% and 25%, respectively. The panel, containing the ITO film, represents 6% of the total weight of the monitor, and in turn it is made of 20% of glass and plastic, and 80% of material suitable for indium recovery processes.

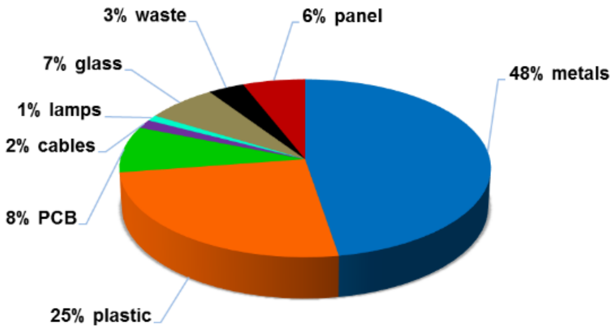


Fig. 3.2. Average composition of an LCD.

Considering the presented context and the valuable fractions in end-of-life LCD, the development of efficient systems for waste management is a priority. It is obvious that waste prevention is the best option in order to reduce environmental risks (Savvilotidou et al., 2014). However, it is not always possible and, as stated by Kolias et al. (2014), recycling strategies are the best route to avoid the disposal and the incineration. The possibility to make end-of- life LCDs a source of secondary raw materials would favor a proper management with a consequent reduction of toxic metals and hazardous materials dispersions. In addition, the application of this urban mining approach could represent a positive perspective also from a social point of view, playing a role in developing countries in providing broader access to technologies important to both consumer and industrial sectors (Williams et al., 2008).

The present work aims at the evaluation of the environmental impacts of different LCD treatment strategies. The options taken into account were: the disposal in landfilling sites, the incineration, a traditional recovery process for the most common fractions (e.g. plastic, glass, steel), and an innovative process that included also indium recovery. The life cycle assessment (LCA) approach was used, not only as tool to identify the best end-of-life LCD management option, but also to recognize the weak points of the innovative process to be improved in order to increase the sustainability of the treatment. Considering the LCA results, an experimental activity was carried out to perform a wastewater recirculation strategy that allowed to decrease the impacts of the innovative process.

2. Materials and methods

2.1 Processes for end-of-life LCD treatment

As shown in Fig. 3.3, the strategies for end-of-life LCD treatment can include several options, each one with different environmental impacts associated. The first two choices considered in this study are the most common and do not include a final recovery of materials. Considering the content of toxic materials, without a previous manual dismantling, the end-of-life LCD have to be disposed in landfill sites for hazardous waste (scenario 1). This option was chosen as baseline scenario. The same issue of hazardous components should not be underestimated in the case of incineration, independently from the beneficial effect of the energetic gain (scenario 2). The other two alternative strategies provide for a waste recovery with different treatments and targets. The recycling scenarios include a first dismantling step with the identification of all fractions potentially recoverable like metals, plastic, glass, printed circuit boards (PCB), cables and lamps. Nevertheless, the first recycling process, using a traditional approach, considers the remaining panel, containing the ITO film, as a waste for disposal (scenario 3). The fourth option includes an innovative process for the treatment of the panel with a complete indium recovery (scenario 4), following the conditions optimized by Rocchetti et al. (2015).

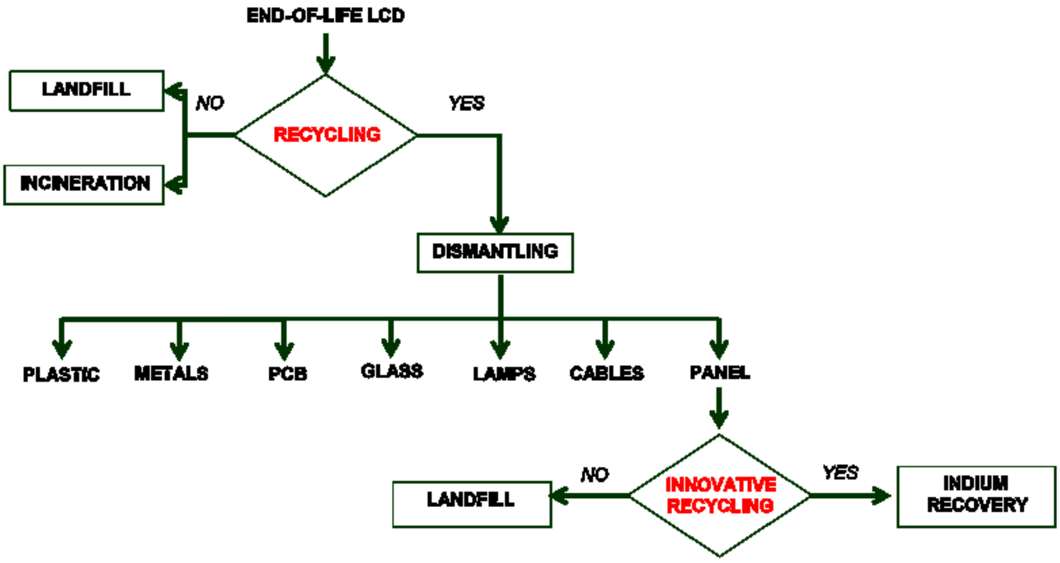


Fig. 3.3. Flow diagram of the management options for the end-of-life LCDs considered in the present paper.

The choice of the present hydrometallurgical treatment (Fig. 3.4), with the simplest design, is considered as the best option in the perspective of new recycling facilities that should be located near waste sources to minimize transportation distances. Indeed, this process was developed for the application in a mobile plant built within the research project called HydroWEEE-DEMO 308549 (Innovative Hydrometallurgical Process to recover Metals from WEEE including lamps and batteries), which was funded by the European Commission within the FP7 Capacities Work Program. More in details, the panel is subjected to a pretreatment that consists of a shredding/grinding phase and a washing with water to remove the organic liquid crystals. Thereafter, indium is leached by sulfuric acid using a cross-current configuration (Rocchetti et al., 2015) and recovered by a zinc cementation after the addition of sodium hydroxide up to pH 3 (Rocchetti et al., 2016). The process includes also the Fenton treatment of wastewater from the phase of panel washing, carried out using $FeSO_4$ and H_2O_2 (Kang and Hwang, 2000).

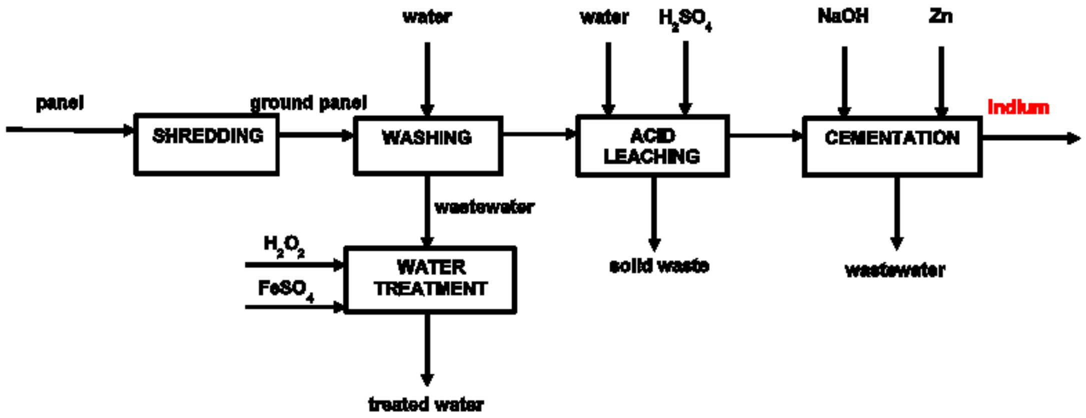


Fig. 3.4. Block diagram of the innovative recycling process to recover indium from end-of-life LCD panel.

Other effective hydrometallurgical processes are reported in the literature. In this regard, Li et al. (2009) and Savvilotidou et al. (2015) describe two processes for indium extraction from end-of-life LCD including an acid leaching with high efficiencies of about 90% and 60%, respectively. However, they are based on the use of nitric acid and of hydrochloric acid, that have a higher impact than sulfuric and that would complicate the application in the site of recyclers, that typically are small and medium enterprises. Table 3.1 reports the inputs required for each step of the innovative process, including the reagents and the energy necessary for the plant operations for the treatment of 100 kg of waste. The table shows also the recovered fractions that represent the credit of each step for the LCA analysis, following the percentages reported in Fig. 3.2.

Table 3.1. Main steps for the innovative recycling of end-of-life LCD, input of energy and raw materials and recovered materials.

Process	**Input**	**Input amount**	**Recovered materials**
dismantling	-		plastic, glass, cables, PCB, metals, lamps
shredding	electricity	0.17 kWh	plastic, glass
washing and water treatment	electricity water ferrous sulfate hydrogen peroxide (50%)	0.14 kWh 25 kg 12.25 kg 8.25 kg	-
leaching	electricity water sulfuric acid	0.65 kWh 11.57 kg 2.63 kg	glass cullet
cementation	electricity sodium hydroxide zinc	0.65 kWh 1.40 kg 0.04 kg	indium

2.2 Goal and scope definition of LCA analysis

The main goal of the first part of LCA analysis described in this paper was the identification of the environmental impacts due to the different management strategies of end-of-life LCDs, in order to identify the best option. Fig. 3.5 shows the system boundaries considered for the LCA and the processes included in the data elaboration. All scenarios (described in section 2.1) started from end-of-life LCDs, excluding the energy and materials used for the production of the new monitor, the energy consumed during the phase of use and collection once the end-of-life phase was reached.

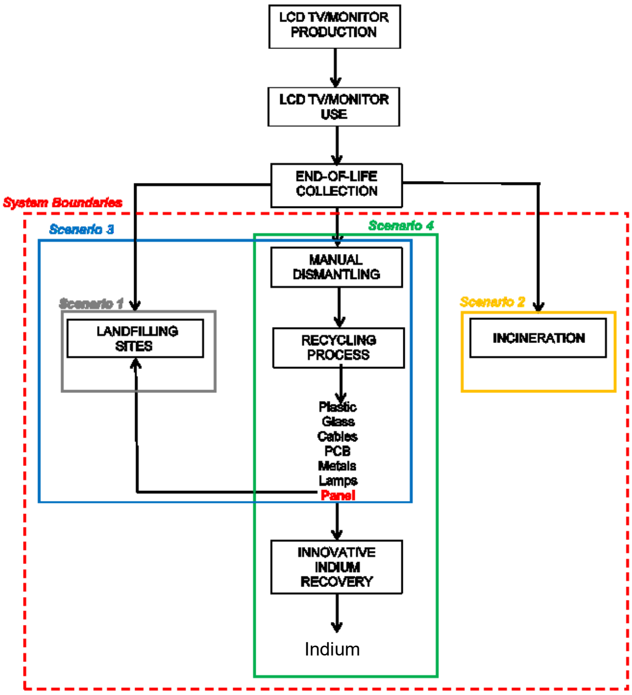


Fig. 3.5. System boundary for LCA analysis in the four scenarios taken into consideration: disposal in landfilling site, incineration, recycling by traditional and innovative approaches.

The second section of the analysis focused on the innovative treatment for indium recovery, identifying the steps to be improved in order to make the process more sustainable. To better understand the influence of indium content on the choice of the application either of the innovative process or the traditional process, we carried out a final sensitivity analysis. For this purpose, we considered an index expressed as a percentage, called “innovative vs. traditional”, calculated in function of several indium concentrations in the panel (hypothesizing to obtain them thanks to the concentration of indium with some pretreatments). The index was calculated as the difference of the algebraic sum of credits and debits of the innovative process minus the environmental credits of the traditional process, divided by the credits of the traditional process, in the impact categories of climate change and acidification. The positive effects of the recovery of secondary raw materials were quantified as avoided impacts for the primary production and reported as negative values.

2.3 Software and methods for the LCA

For the production processes of energy and raw materials and the estimation of the potential environmental impact of the processes considered in the four scenarios of interest, we used the GaBi 6 software (thinkstep) integrated with the EcoInvent 2.2 database. In addition, in order to confirm the results accuracy, data relative to incineration were processed also by the free software OpenLCA integrated with Needs database. The functional unit was 100 kg of end-of-life LCD with the composition presented in Fig. 3.2. The midpoint impacts of the waste management processes were evaluated according to the International Reference life cycle data system (ILCD) recommendation for the life cycle impact assessment (LCIA) (ILCD, 2010). We selected the following impact categories: climate change, evaluated with the Baseline model of 100 years of the IPCC, with the indicator of global warming potential (GWP100) expressed in terms of CO_2-equiv., and acidification, evaluated with the method accumulated exceedance (Posch et al., 2008; Seppälä et al., 2006), with the indicator accumulated exceedance expressed in terms of mole of H^+- equiv. The choices of these categories were due to the fact that climate change is a very topical issue, as also confirmed by the recent United Nations Climate Change Conference (Dalby, 2015), and because of the use of sulfuric acid for indium recovery process.

2.4 Experimental activity for water recirculation

The LCA was combined with an experimental activity that evaluated the possibility to reduce the water consumptions of the process for indium recovery. The experiment can be divided in two sections focused on: the wastewater from washing and the cementation solution. For the first part, water from a washing step was reused to treat a second amount of LCD scraps. The operation was carried out after the removal of the solution surface (about the 10% of the total) and the volume replacement. The procedure was repeated for a total of eight steps and each washed fraction was treated following the conditions described by Rocchetti et al.

(2015). A sample was collected to analyze indium concentration at the end of each leaching. For the second section, a first complete treatment was carried out including both the extraction and recovery steps (Rocchetti et al., 2016). The solution from cementation treatment was used for a new leaching after the replacement of 50% of the volume to ensure the achievement of the necessary acidic conditions. The procedure was repeated for a total of five leaching steps and samples were collected to determine indium concentration.

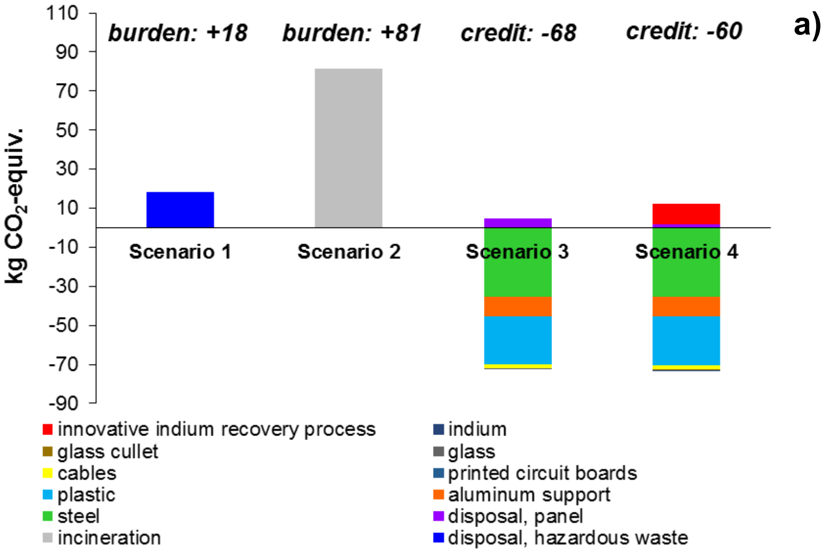
2.5 Chemical analysis

The concentration of indium in the aqueous phase samples was determined by inductively coupled plasma atomic emission spectrometry in accordance with EPA (2001). Before the analysis, liquid samples were centrifuged and diluted 2-fold with a solution of HNO_3 (pH 2) to avoid precipitation of metals. All metals determinations were conducted by an accredited chemical laboratory (UNI CEI EN ISO/IEC 17025).

3. Results and discussion

3.1 Assessment of the different management strategies

The first target of the present study was the identification of the best management strategy for end-of-life LCDs. The panel of Fig. 3.6 shows that the scenarios 1 and 2, referred to the disposal in landfilling sites and incineration, cause the highest environmental loads for the lack of materials recovery. Incineration produces a negative effect, particularly evident in the category of climate change (Fig. 3.6a), with an impact of 81 kg CO_2-equiv. due to the emission of carbon dioxide and gases with a global warming potential during the combustion. This data was also confirmed by OpenLCA software that reported an emission of 87 kg CO_2-equiv. On the other hand, the acidification category (Fig. 3.6b) highlighted the highest environmental load of landfilling, with a burden of 0.08 mol H^+-equiv., for the possible release of pollutants. As concerns the recycling processes, they both resulted in a net credit for the environment, due to the avoided impact for the primary production of raw materials, like plastic, steel, aluminum and glass. The advantage is also confirmed by some authors that studied WEEE management in different geographic areas (Biganzoli et al., 2015; Noon, 2011). More specifically, the most convenient resulted to be the traditional route, rather than the innovative one, with an overall credit of 68 kg CO_2-equiv. and 0.25 mol H^+-equiv, in the categories of global warming potential and acidification, respectively. The main contribution to such positive effect was due to the recovery of steel and plastic. On the other hand, the main weakness of the innovative process is that the amount of recovered products (indium and glass cullet) did not balance the impacts for the request of raw materials.



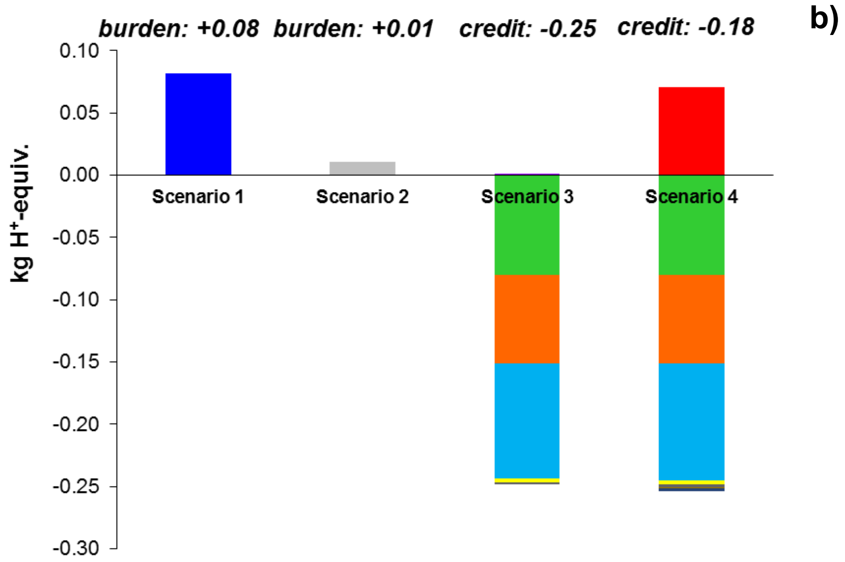


Fig. 3.6. Global balance on the environmental impacts generated by the four considered scenarios: 1) disposal in landfilling sites, 2) incineration, 3) recycling by traditional and 4) innovative processes in the categories of a) climate change b) acidification (functional unit 100 kg end-of-life LCD).

The assessment of the different management strategies, presented in this section, has two main limitations: i) the variability of end-of-life LCD composition due to the wide range of products available on the market and ii) the assumption of a complete recovery of all valuable fractions with a final purity typical of “ready for the market” recovered products. In the first case, an additional comparison taking into account different compositions of end-of-life LCD panels (Buzatu and Milea, 2008; Cryan et al., 2010) was carried out. The estimated range (Table 3.2) for the net credits obtained using this information, confirms the results above reported, suggesting that the products characteristics do not significantly modify the whole result for the environmental impact assessment. In the second case, some considerations suggested that the specific treatments for each material, with the relative efficiencies, were not relevant for the overall results.

Table 3.2. Estimated range for the net credits obtained using compositions available in the literature, for the scenarios of traditional and innovative recycling treatments.

Recycling process	**Impact category**	**Credit range**
Traditional	Global warming potential (kg CO_2-Equiv.)	70-80
	Acidification (mol H^+-Equiv.)	0.25-0.29
Innovative	Global warming potential (kg CO_2-Equiv.)	52-70
	Acidification (mol H^+-Equiv.)	0.14-0.24

3.2 Reduction of water consumption

The strategic relevance of indium recovery pushed our research toward the identification of the main weaknesses of the innovative recycling process. As shown in Fig. 3.7, the washing operation was the step with the highest environmental load, with a contribution greater than 60% on the total CO_2 emissions: more in details, the pie chart on the right demonstrates that about 80% of this negative effect is due to hydrogen peroxide used for the wastewater treatment. Consequently, it is evident that the decrease of wastewater could have an important effect on the reduction of the environmental impact of the whole treatment.

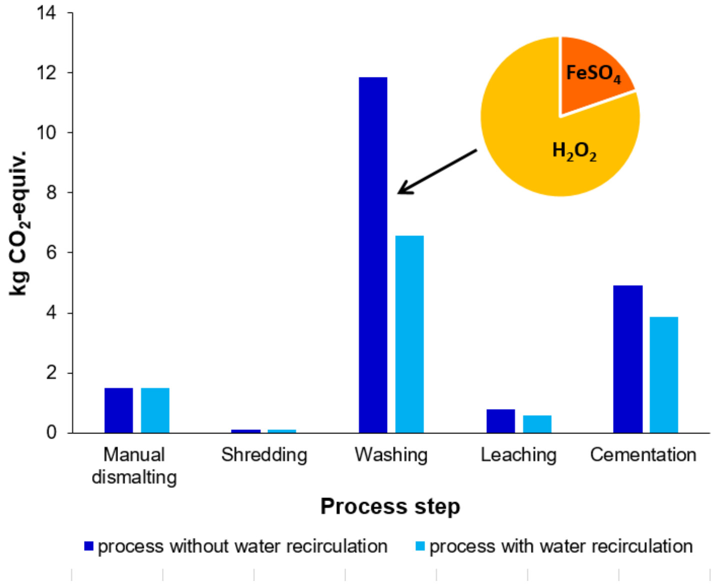


Fig. 3.7. Carbon dioxide emissions in each single step of the innovative recycling process (block diagram in Fig. 4, functional unit 100 kg end-of-life LCD), in the absence (dark blue) and in the presence (light blue) of a water recirculation strategy. The pie chart represents the contributions of hydrogen peroxide and ferrous sulfate on the environmental impact of washing step (water and electricity percentage are negligible).

In this regard, the results in panel of Fig. 3.8 show the effect of the number of water recirculation cycles on the indium leaching efficiency. More in details, Fig. 3.8a analyzes the possibility to reuse water from a first washing step to another one. It is evident that, starting from the second cycle, the increase of organic content, due to the liquid crystals presence, made the washing step ineffective. The final consequence is a negative effect on the successive leaching phase with an extraction efficiency loss of about 40%. However, a single recirculation was sufficient to obtain a 45% of water consumption saving in the washing step that can be translated into the improvement of environmental sustainability of the process. The positive effect was evident with a decrease of emissions due to the raw materials and energy consumptions from about 12.0 kg CO_2-equiv. to a value of 6.6 kg CO_2-equiv. (Fig. 7). On the other hand, the cementation solution could be recirculated for three times without evident effects on the leaching phase (Fig. 3.8b). The efficiency percentage decreased at the fourth step, up to a value of about 42%. Considering the necessary replacing of 50% of volume to ensure the acidic pH, three cycles allowed a further saving of

30% of water and sulfuric acid used for the leaching solution, with an overall decrease of 25% of emissions in the extraction and recovery steps. The combination between the experimental activity and LCA allowed to quantify the environmental consequences of water saving, combining the recirculation of washing and cementation solutions. Furthermore, the complete system was optimized in the perspective of a scale-up within the HydroWEEE-DEMO mobile plant.

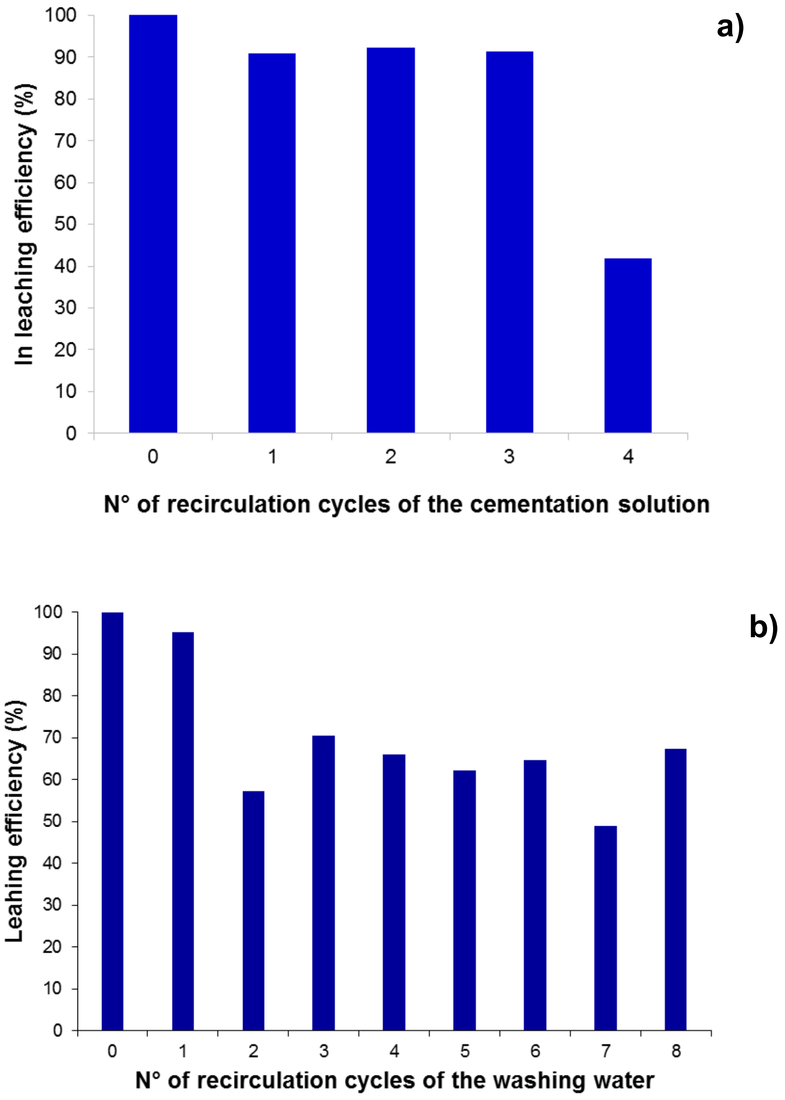
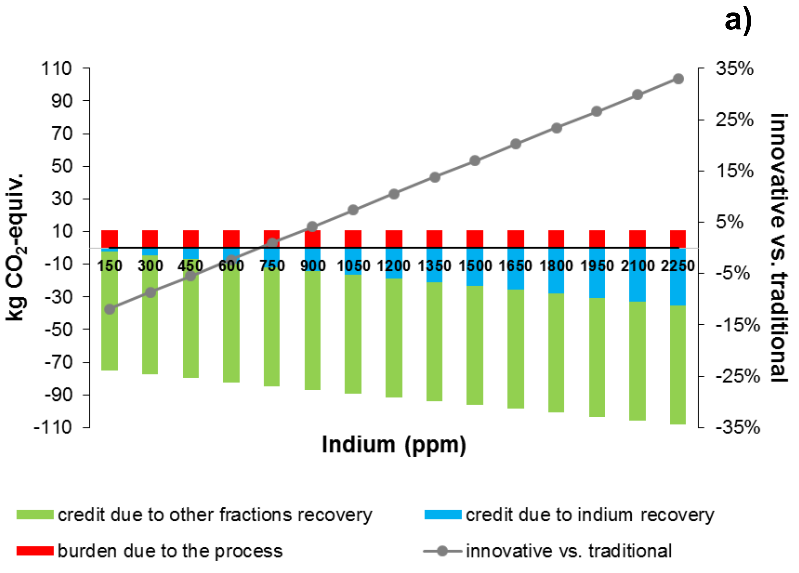


Fig. 3.8. Effect on indium leaching efficiency of the recirculation of the residual solutions produced after a) the panel washing step and of b) the cementation step (leaching operating conditions: temperature 80°C, 20% solid, 10 minutes (from Rocchetti et al., 2015).

3.3 *Increase of indium concentration in end-of-life LCD*

The fourth scenario relative to the innovative recycling treatment represents a promising option thanks to the high efficiency of indium recovery (about 100%). Nevertheless, considering the low indium concentration of 150 ppm identified in end-of-life LCDs by Rocchetti et al., 2015, we carried out a sensitivity analysis to quantify the real effect of an increase of the metal content on the process sustainability. With this aim, we decided to fix the values of the burdens for the innovative treatment and the credits for traditional valuable fractions. The trend of index “innovative vs traditional” showed the gradual increase of indium recovery process advantage in the categories of global warming and acidification. More in details, a growth of five times of indium content allowed to equal the CO_2 emissions of two recycling processes (Fig. 3.9a). An increase up to 2,250 ppm of indium concentration favored the innovative process up to 33%, at the expense of the traditional one. On the other hand, the doubling of indium content was enough in order to equal the two options in the category of acidification (Fig. 3.9b). The upgrading of metals concentration represent a typical issue in the WEEE treatment field that can be solved by mechanical-physical pretreatment, generally shredding/grinding (Cui and Forssberg, 2007; Cui and Zhang, 2008; Zhang and Xu, 2016).



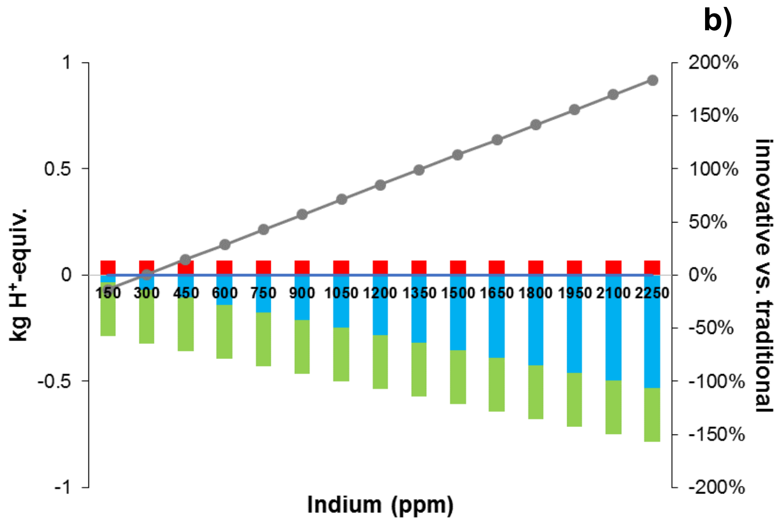


Fig. 3.9. Sensitivity analysis results. Effect of the indium concentration in end-of-life LCD on the innovative recycling process impact in the category of a) climate change b) acidification (functional unit 100 kg end-of-life LCD).

4. Conclusions

A LCA of four strategies of end-of-life LCD management: disposal in landfill sites (scenario 1), incineration (scenario 2), recycling with traditional approach (scenario 3), recycling by an innovative process with the additional indium recovery (scenario 4) was performed. Results showed that scenario 1 and scenario 2 were the worst waste management in the impact categories of climate change and acidification, respectively, because they do not involve any material recovery. According to the data processing, at the current state of the art, the best option for the considered impact categories seems to be monitor recycling without the panel treatment (scenario 3). This fact is due to high quantity of the recovered materials combined with the absence of impacts connected with the reagents used in the panel treatment. Nevertheless, as suggested by the European Union, the recovery of secondary raw materials represents a critical issue and the development of advantageous strategies of urban mining is a priority. For this reason, the combination of experimental activities and LCA allowed to identify the weakness of the process described for the recycling of the panel treatment. Consequently, a water recirculation strategy was performed with a final saving of about 35% of carbon dioxide emissions. In addition, the possibility to increase indium concentration in the waste, not less than five times the starting value, could make the innovative process the most sustainable option.

Considering the present high amount of WEEE to manage, recycling and re-use of their components is a necessity for the creation of a circular economy. This study reveals that the relatively low indium concentration of indium in end-of-life LCDs is the bottleneck for recycling treatments. The evaluation of the potential environmental impacts can be useful to understand if it is convenient to push recycling and recover also indium. From the results obtained in the present study, it seems that research should be addressed to identify a pretreatment of end-of-life LCDs able to concentrate indium.

5. Products

Results illustrated and discussed in this chapter were used to support peer reviewed articles and congress paper. They have published on Waste Management, Elsevier (Fig. 3.10) and Physica Status Solidi C, Wiley Online Library (Fig. 3.11).

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Environmental impact assessment of different end-of-life LCD management strategies

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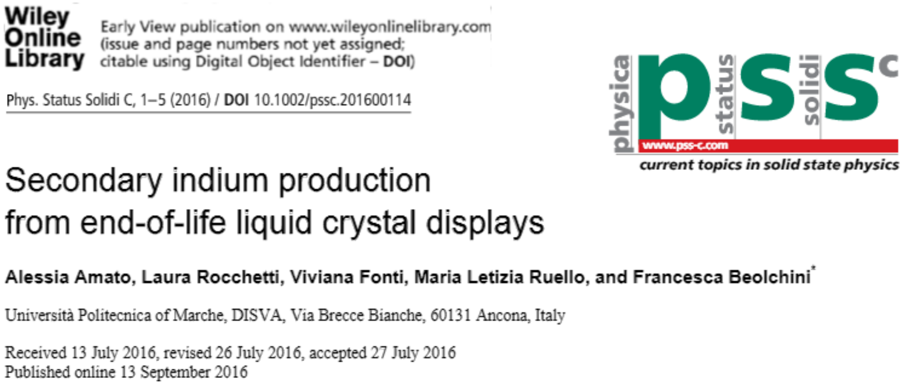
Fig. 3.10. Articles published on *Waste Management*.



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Secondary indium production from end-of-life liquid crystal displays

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Fig. 3.11 Articles published on *Physica Status Solidi C.*

The following list reports the congress contributions relative to data reported in present chapter:

Amato A., Rocchetti L., Beolchini F. Strategie di gestione di LCD a fine vita: un caso di studio e applicazione dell’LCA. Congresso Rete italiana LCA, Ravenna 23-24 Giugno 2016.

Amato A., Rocchetti L., Beolchini F. Environmental impact assessment of different end-of-life LCD management strategies. Symposium on Urban mining and Circular economy, Bergamo 23-25 May 2016

Amato A., Rocchetti L., Fonti V., Ruello M.L., Beolchini F. Secondary indium production from end-of-life liquid crystal displays. Spring Meeting of European Materials Research Society, Lille 2-6 May 2016.

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Chapter 4

ENVIRONMENTAL IMPACT ASSESSMENT OF WEEE TREATMENTS IN HYDROWEEE MOBILE PLANT

Abstract

Nowadays, electric and electronic equipment represent an integral part of life. The tendency to a frequent replacement of these devices is causing the production of significant amount of waste, better defined as waste electric and electronic equipment (WEEE). The content of valuable fractions, in particular metals makes them a possible resource of secondary raw materials, applying the urban mining approach. In particular, present chapter focuses on five kinds of waste: liquid crystal displays (LCDs), cathode ray tubes (CRTs), fluorescent lamps, lithium-ion batteries (LIBs) and printed circuit boards (PCBs). Currently, the traceable flows of this WEEE are pretreated for the recovery of traditional materials like plastic and glass. The residues, the fraction of interest of present study, are disposed in landfilling sites (LCDs, CRTs and LIBs) or treated in Umicore plant facilities (Belgium). Nevertheless, innovative treatments were developed within the European project HydroWEEE. The main introduced innovation is the possibility to carry out the recovery processes on a mobile plant, avoiding the impact due to residues transportation. In this context, present chapter assessed the environmental impacts connected with the treatment of each WEEE residue considered within HydroWEEE project. Further evaluations showed the improvement of environmental performances obtained during the processes optimization. A comparison between the current and the HydroWEEE management strategies, highlighted the relevant advantage of recycling compared to the disposal in landfilling sites and the environmental load of residues transportation (about 30-40%) on Umicore processes. The quantification of the advantage of HydroWEEE metals recovery compared to primary production (variable between 20 and 80%) closed the study.

Content

1. Goal and scope definition

1.1 General aspects

The relevance of waste electrical and electronic equipment (WEEE) issue for Europe is proved by the European WEEE Directive that deals with the reduction of waste disposal "to contribute to the efficient use of resources and the retrieval of valuable secondary raw materials" (European Parliament, 2012). Nowadays, hydrometallurgical and pyrometallurgical processes are the most common options for the recovery of raw materials, in particular valuable metals, from WEEE (Guo et al., 2015). Nevertheless, pyrometallurgical treatments need high temperature (often higher than 1000°C), with consequent significant energetic consumptions and economic costs (Leclerc et al., 2002). Currently, Umicore Precious Metal Refining (Hoboken, Belgium) is the biggest company in Europe that combines both pyro and hydrometallurgical treatments to recover metals from the residues of WEEE recycling processes. Considering its geographical position, there is a significant disadvantage, in particular for the South and East Europe countries, associated to the residues transportation for a long way to reach the plant. This aspect can be translated in high economic and environmental costs.

In this context, the project HydroWEEE Demo (Innovative Hydrometallurgical process to recover metals from WEEE including lamps and batteries) was funded by the European Commission within the FP7 Environment Work Program. The aim of the project is the recovery of base and precious metals from WEEE residues. The core of the activity is the realization of a mobile demonstration prototype, installed in a container lorry, for the application of processes optimized at a smaller Technology Readiness Level within a previous EU project, funded under the EU-FP7 Capacities Work Program, HydroWEEE. The system allows the recovery of In, Co, Y, Cu, Au and Ag from residues of the recycling processes of end-of-life liquid crystal displays (LCDs), cathode ray tubes (CRTs), lamps, Li-batteries (LIBs) and printed circuit boards (PCBs). The advantages and novelty of this plant include its cost-effectiveness and the possibility to reach and operate in the pemises of small and medium enterprise (SME) recyclers, avoiding the transportation of the residues.

Considering that the combination of technical and environmental approaches allows the development of sustainable recovery strategies, the aim of the present chapter is the quantification of the environmental impacts of all processes optimized for the HydroWEEE

Demo project plant. The whole chapter was written following the recommendation of ISO 14040:2006 norm (Environmental management - Life cycle assessment).

1.2 Goal of the study

The main goal of the present study was the identification of the important environmental aspects and stages over the life cycle of the recycling processes of WEEE residues, based on the treatments developed for the mobile plant built within the HydroWEEE Demo project. The identification of the possible critical points could suggest the steps to improve in order to increase the environmental sustainability of the processes. A comparison with the emissions produced by the processes optimized in the previous project (HydroWEEE) showed the progress for CRTs, lamps and LIBs, to determine whether the chosen approach follows the right direction for the protection of the environment. The evaluation of the current WEEE management and the innovative processes for metals recovery closes the chapter allowing the identification of the best strategy. The present study thus aims at being a suitable document for all companies involved in metal recycling from WEEE, to help with the choice of the most eco-friendly strategies.

1.3 Scope of the study

The functional unit chosen for present study was 1 ton of residue from traditional WEEE recycling, independently from the typology (LCDs, CRTs, lamps, LIBs and PCBs). The specific pretreatments, carried out according to the kind of WEEE with the aim to recover the main fractions (e.g. glass, plastics, metals), were not included in the system boundaries (Figures 4.1-4.2). The residues of this first step are not treated by most SME recyclers at present and represent the fraction of interest for this study. In particular, the pretreatments include crushing, sieving and Hg removal by distillation for the lamps, disassembly and CRTs recycling (e.g., with diamond cutting technology) for the CRTs, sorting, dismantling and grinding for the LIBs and LCDs (Figure 4.1) and sorting, shredding, magnetic separation and aluminum separation for the PCBs (Fig. 4.2).

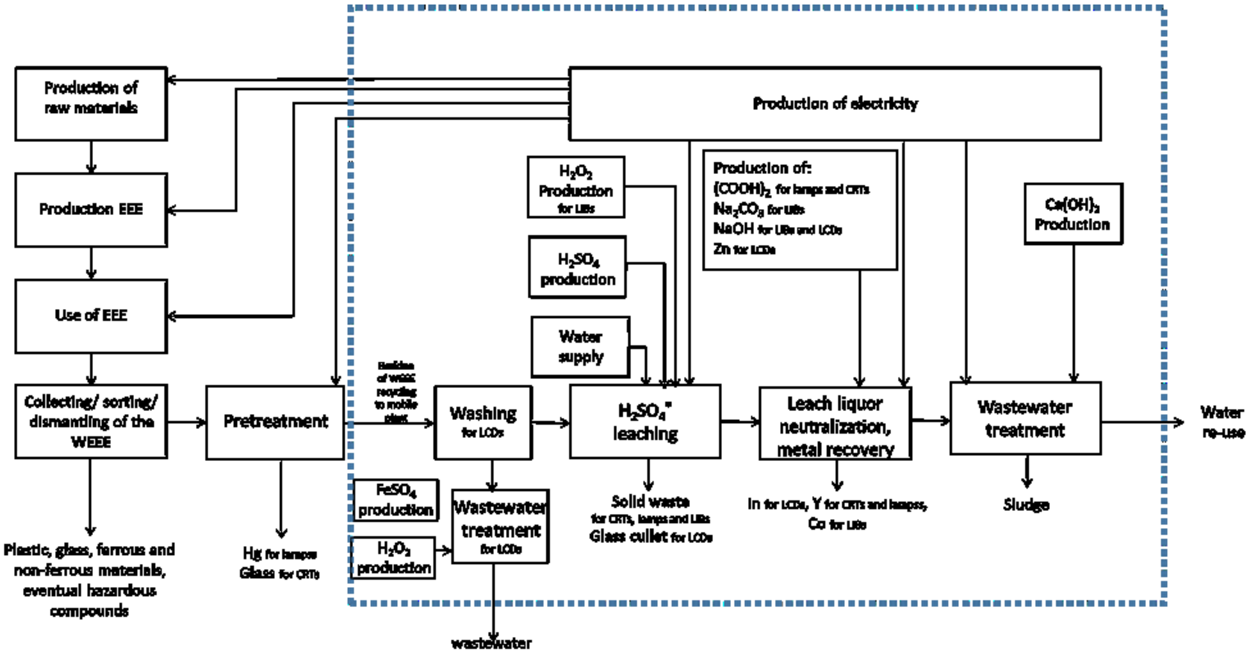


Fig. 4.1 System boundaries for the processes carried out in the HydroWEEE mobile plant for the metal recovery from the residues of traditional recycling processes of end-of-life lamps, CRTs, LIBs and LCDs. (Functional unit: 1 ton of WEEE from traditional recycling)

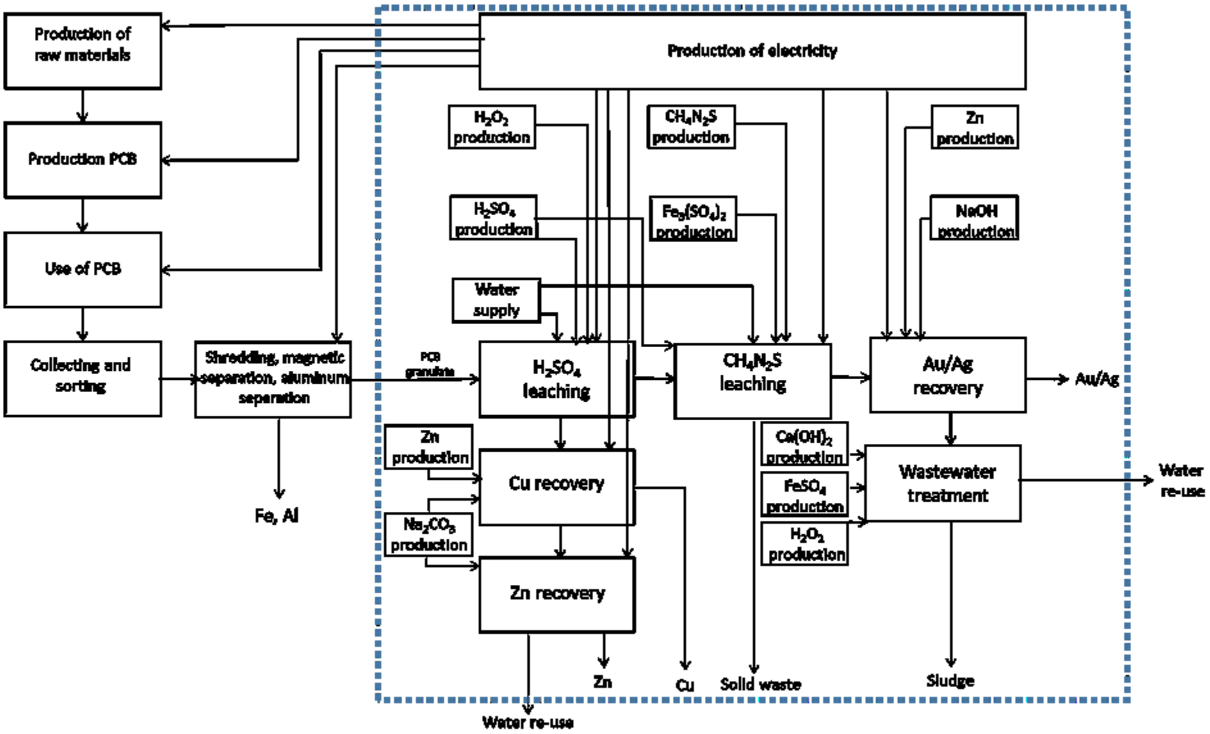


Fig. 4.2 System boundaries for the process carried out in the HydroWEEE mobile plant aimed at metal recovery from residues of end-of-life PCBs. (Functional unit: 1 ton of WEEE from traditional recycling)

Powders from these processes were used for the initial characterization to quantify the concentration of metals target. More in details, concentrations of 5-7% and 15-20% of Y were detected in lamps and CRTs, respectively and 2-3% of Co was identified in LIBs. On the other hand, PCBs showed Cu concentration between 25 and 28% and values in the range 0.04-0.08% and 0.14-0.19% for Au and Ag, respectively. Finally, LCDs had an In content of 0.006-0.16% These data were the starting point for achieving the most suitable and effective treatments for metals extraction and recovery. The feed materials for the portable plant were: fluorescent powders from lamps and CRTs, ground material (<1mm) from LIBs LCDs, and PCBs. A leaching operation with sulfuric acid was a common unit operation for the considered WEEE residues and included a washing with water in the case of LCDs for the liquid crystal removal. For LIBs residues, hydrogen peroxide was also added under acidic conditions, as a reducing agent. In the case of PCBs, this step was followed by a thiourea leaching for Au and Ag dissolution. The metal recovery from the leach liquor was carried out either by selective precipitation operations or by cementation, according to each of the specific metals to be recovered. The products were recovered with efficiencies higher than 90%. The variability of purity makes the products not suitable for direct commercialization (where at least 99% would be needed), but these products are marketable to companies that use them as feed for a final purification. An additional step of wastewater treatment was also considered, based on the use of lime for precipitation and neutralization processes. In the case of wastewater from LCDs washing and from the final Au/Ag recovery from PCBs, also a Fenton treatment (hydrogen peroxide and ferrous sulfate) was needed to oxidize organic contaminants. Considering the portability of the plant, the Italian power mix was assumed for the electricity data processing. Each described treatment represents an innovative option, alternative to the current methods of: disposal in landfilling sites for urban waste in the case of LCDs (European Parliament, 2012), disposal in landfilling sites for hazardous waste for residues of CRTs and lamps recycling (Slack et al., 2005; Techato et al., 2009) and metals recovery at Umicore plants for PCBs and LIBs (Gaines, 2014; Havlik et al., 2011). Fig. 4.3 represents the system boundaries considered for the evaluation of the different strategies of WEEE residues management. Considering the current practice, in the case of CRTs, lamps and LCDs, system boundaries were extended with the primary production of Y and In (Fig. 4.3a). On the other hand, this was not done for PCBs and LIBs, since both scenarios include the recovery of metals. The waste transportation was also considered for PCBs and LIBs, taking into account that the metal recovery plant is located in Belgium (Fig. 4.3b). With this aim, a representative distance of 2,000 km (roundtrip), travelled by a small lorry transport 7.5 T total weight, 3.3 T max pay load, was considered.

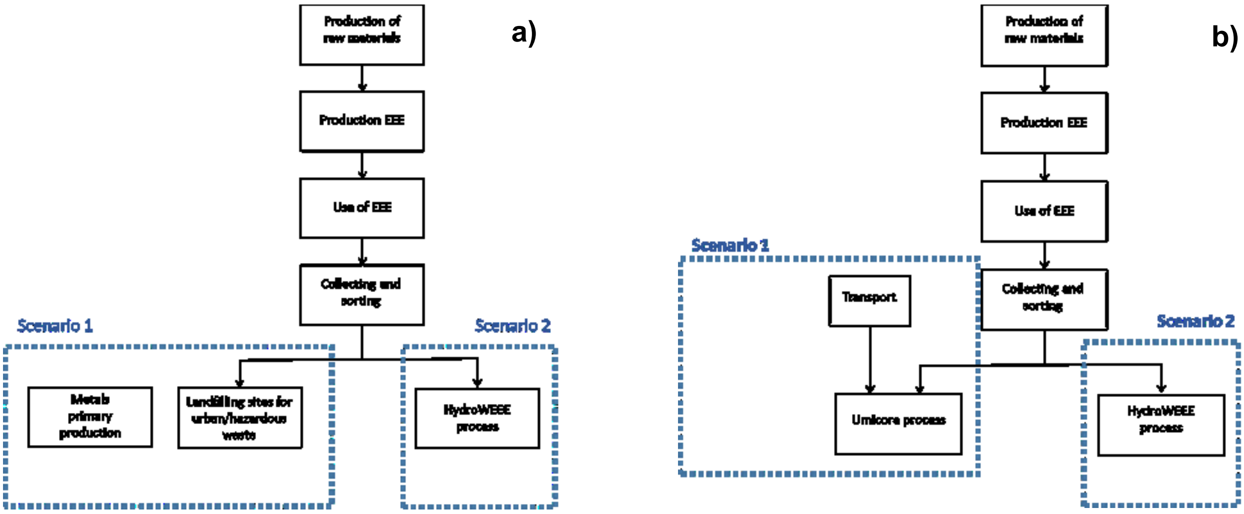


Fig. 4.3. HydroWEEE-DEMO vs. current recycling strategies: system boundaries a) CRTs, lamps, LCDs b) LIBs and PCBs (Functional unit: 1 ton of residue from WEEE traditional recycling)

2. Life cycle inventory analysis

The data used for present study are the results of the lab scale research activity of the three university partners of the HydroWEEE-DEMO project: Università Politecnica of Marche, Università degli studi dell'Aquila, Università Sapienza of Rome. Energy and raw materials production were elaborated using the GaBi 6 Professional software integrated with the EcoInvent (2.2) database.

Fig. 4.4 reports the output of the inventory analysis, in terms of consumption of energy resources, material resources and emissions to air. It can be observed that, in the cases of LCDs e LIBs (Fig.s 4.4 a-c, j-l), the recovery step was the most critical for all the three environmental burdens. On the other hand, CRTs and lamps showed the highest effect of this stage only on the material resource depletion, whereas the wastewater treatment showed the greatest request of energy resources (Figure 4.4 d,e). Different results were obtained for PCBs treatment, that did not highlight the criticality of a particular phase. Indeed, the two leaching steps and the two metal recovery steps showed comparable effects on emission production and resources consumptions (Fig. 4.4 m-o).

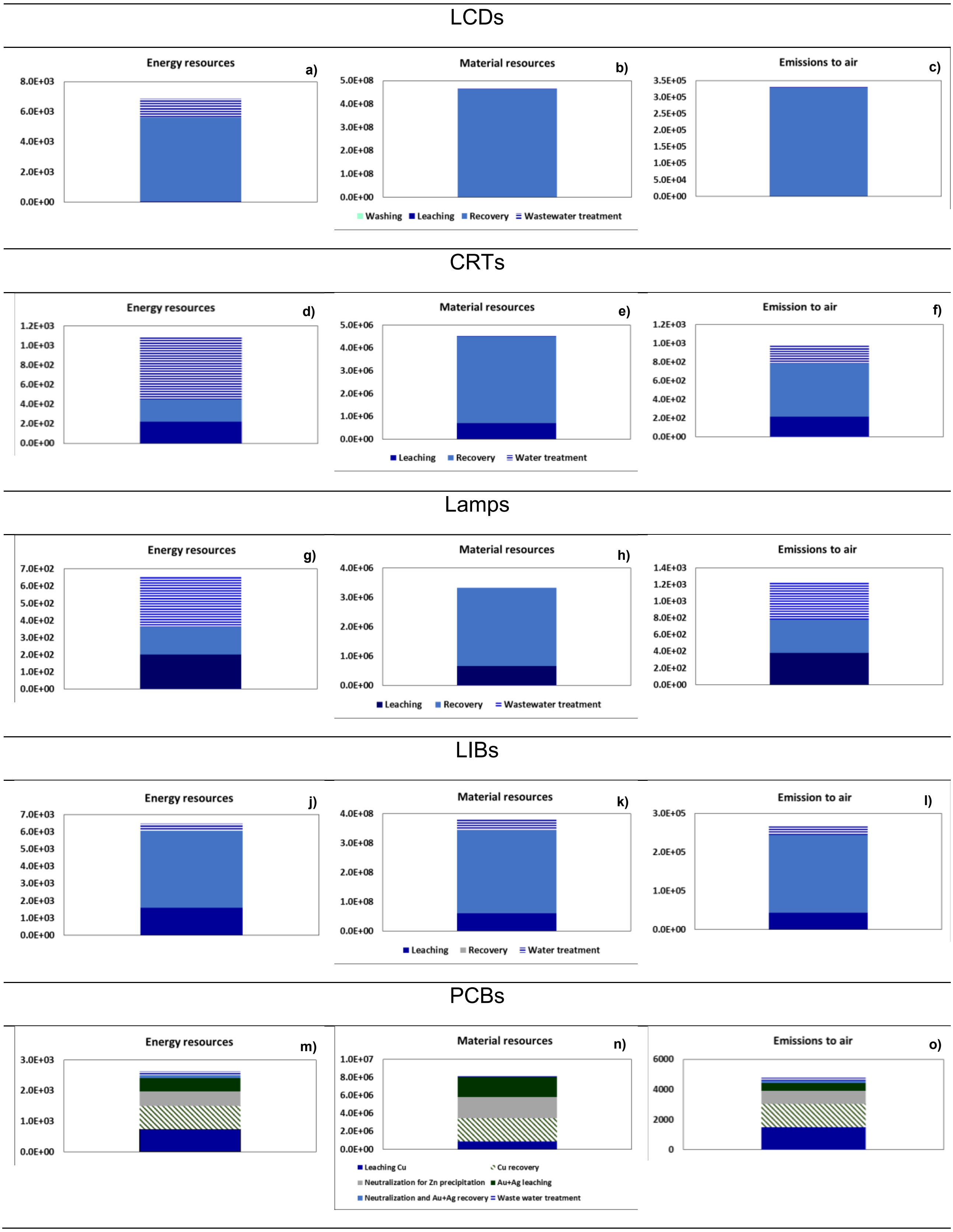


Fig. 4.4 Output of the inventory analysis for LCDs (a-c), CRTs (d-f), lamps (g-i), LIBs (j-l) and PCBs (m-o) HydroWEEE treatment. Results are expressed in kg.

(Functional unit: 1 ton of WEEE from traditional recycling)

3. Life cycle impact assessment

3.1 LCIA Classification

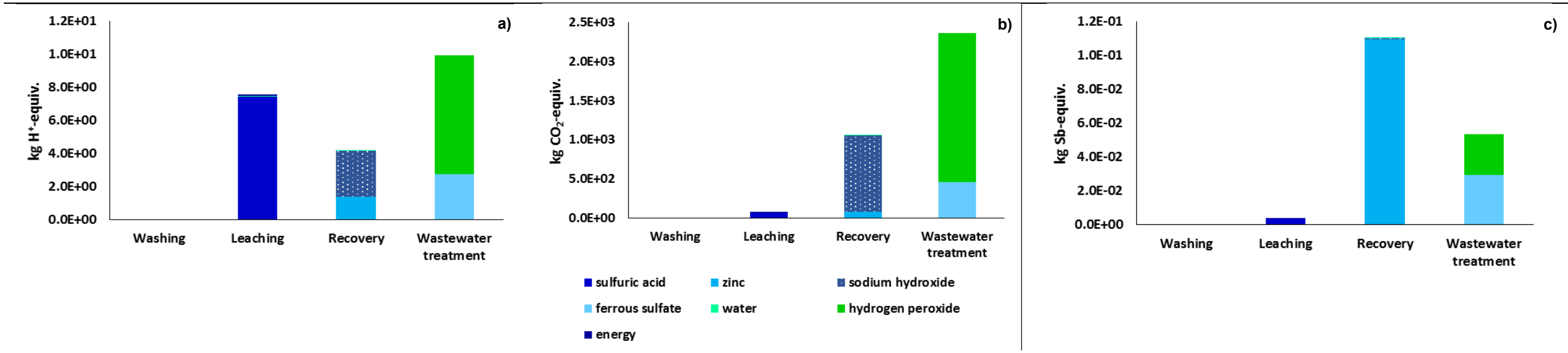
The midpoint impacts of the waste management processes were evaluated according to the International Reference life cycle data system (ILCD) recommendation for the life cycle impact assessment (LCIA) (ILCD, 2010). This methodology includes several categories; those selected for the present study are: climate change, evaluated with the Baseline model of 100 years of the IPCC, with the indicator of global warming potential (GWP100) expressed in terms of CO_2-equiv., acidification, evaluated with the method accumulated exceedance (Posch et al., 2008; Seppälä et al., 2006), with the indicator accumulated exceedance expressed in terms of Mole of H^+- Equiv. and resource depletion, evaluated on the basis of EDIP97 update 2004 (Hauschild and Wenzel,1998) and CML 2002 (Guinée et al., 2002) with the indicator of scarcity expressed in terms of kg Sb-equiv.. The reasons of these choices were the use of acidic conditions in the treatments and the topical issues of global warming and non-renewable resources consumptions, respectively.

3.2 LCIA results

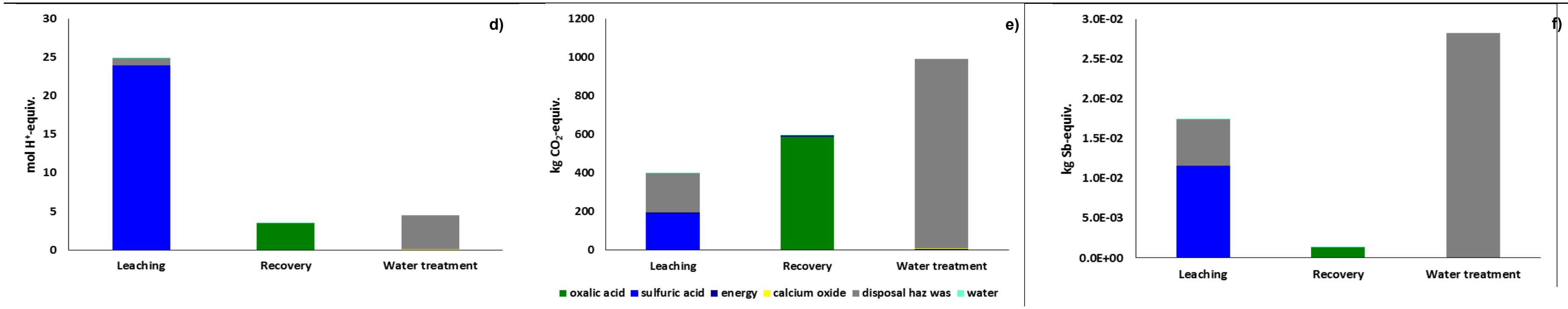
Fig. 4.5 shows the environmental impacts of the HydroWEEE-DEMO processes, in the categories of: acidification, global warming and resources depletion, for each considered WEEE residue (Fig. 4.5). All processes were divided into the main stages, in order to identify the most critical one in terms of environmental loads.

As showed in Fig. 4.5 a, b, for the LCD process the use of hydrogen peroxide for the treatment of wastewater caused the highest impact in the categories of acidification and global warming (10 mol H^+-equiv., 2300 kg CO_2-equiv.). On the other hand, the use of zinc in the recovery step is the reason of the most significant environmental load for the category of resources depletion (0.05 kg Sb-equiv.) (Fig. 4.5c). Comparable trends were obtained for CRTs and lamps, where the wastewater treatment caused the highest impacts in the category of global warming (990 kg CO_2-equiv. for CRTs and 470 kg CO_2-equiv. for lamps), mainly due to the hazardous waste disposal (Fig. 4.5 e, h). Similarly, the use of oxalic acid for the Y recovery is responsible for a relevant impact in the global warming category, for both the residues. The critical issue associated to the use of hydrogen peroxide was observed also in the LIBs treatment (Fig. 4.5 j-l). Indeed, the environmental load connected with this raw material in the leaching step, was very high in the categories of acidification (30 mol H^+-equiv.), global warming (1900 kg CO_2-equiv.) and resources depletion (0.03 kg Sb-equiv.). The estimated impacts for the PCBs treatment displayed in Fig. 4.5 m, n, show that Cu leaching caused the highest impacts in the categories of acidification and global warming (26 mol H^+-equiv., 1460 kg CO_2-equiv.) for the use of sulfuric acid in the first case and hydrogen peroxide in the second one (Fig. 4.5 m, n). On the other hand, Cu cementation is the reason of the most significant impact load in the category of resource depletion (1 kg Sb-equiv.), for the use of zinc powder (Fig. 4.5o).

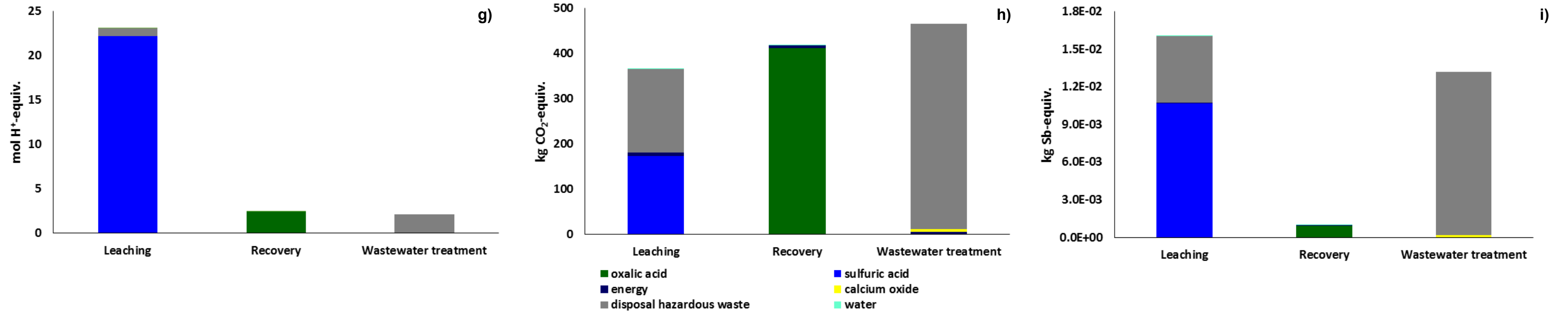
LCDs


a)
kg H⁺-equiv.
1.2E+01
1.0E+01
8.0E+00
6.0E+00
4.0E+00
2.0E+00
0.0E+00
Washing
Leaching
Recovery
Wastewater treatment
b)
kg CO2-equiv.
2.5E+03
2.0E+03
1.5E+03
1.0E+03
5.0E+02
0.0E+00
Washing
Leaching
Recovery
Wastewater treatment
sulfuric acid
zinc
sodium hydroxide
ferrous sulfate
water
hydrogen peroxide
energy
c)
kg Sb-equiv.
1.2E-01
1.0E-01
8.0E-02
6.0E-02
4.0E-02
2.0E-02
0.0E+00
Washing
Leaching
Recovery
Wastewater treatment

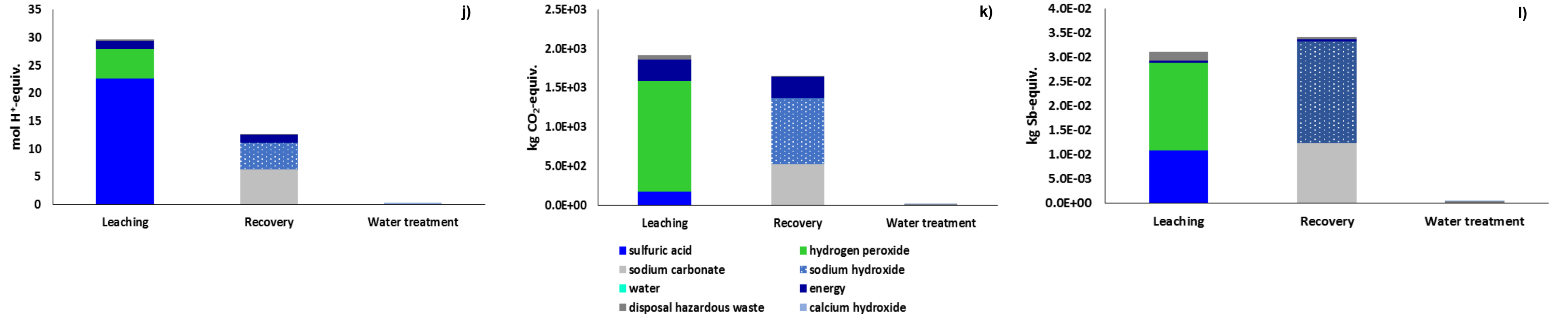
CRTs


d)
mol H⁺-equiv.
30
25
20
15
10
5
0
Leaching
Recovery
Water treatment
e)
kg CO2-equiv.
1200
1000
800
600
400
200
0
Leaching
Recovery
Water treatment
oxalic acid
sulfuric acid
energy
calcium oxide
disposal haz was
water
f)
kg Sb-equiv.
3.0E-02
2.5E-02
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
Leaching
Recovery
Water treatment

Lamps


g)
25
20
15
10
5
0
mol H⁺-equiv.
Leaching
Recovery
Wastewater treatment
h)
500
400
300
200
100
0
kg CO₂-equiv.
Leaching
Recovery
Wastewater treatment
■ oxalic acid
■ sulfuric acid
■ energy
■ calcium oxide
■ disposal hazardous waste
■ water
i)
1.8E-02
1.5E-02
1.2E-02
9.0E-03
6.0E-03
3.0E-03
0.0E+00
kg Sb-equiv.
Leaching
Recovery
Wastewater treatment

LIBs


j)
35
30
25
20
15
10
5
0
mol H⁺-equiv.
Leaching
Recovery
Water treatment
k)
2.5E+03
2.0E+03
1.5E+03
1.0E+03
5.0E+02
0.0E+00
kg CO₂-equiv.
Leaching
Recovery
Water treatment
■ sulfuric acid
■ hydrogen peroxide
■ sodium carbonate
▨ sodium hydroxide
■ water
■ energy
■ disposal hazardous waste
■ calcium hydroxide
l)
4.0E-02
3.5E-02
3.0E-02
2.5E-02
2.0E-02
1.5E-02
1.0E-02
5.0E-03
0.0E+00
kg Sb-equiv.
Leaching
Recovery
Water treatment

PCBs

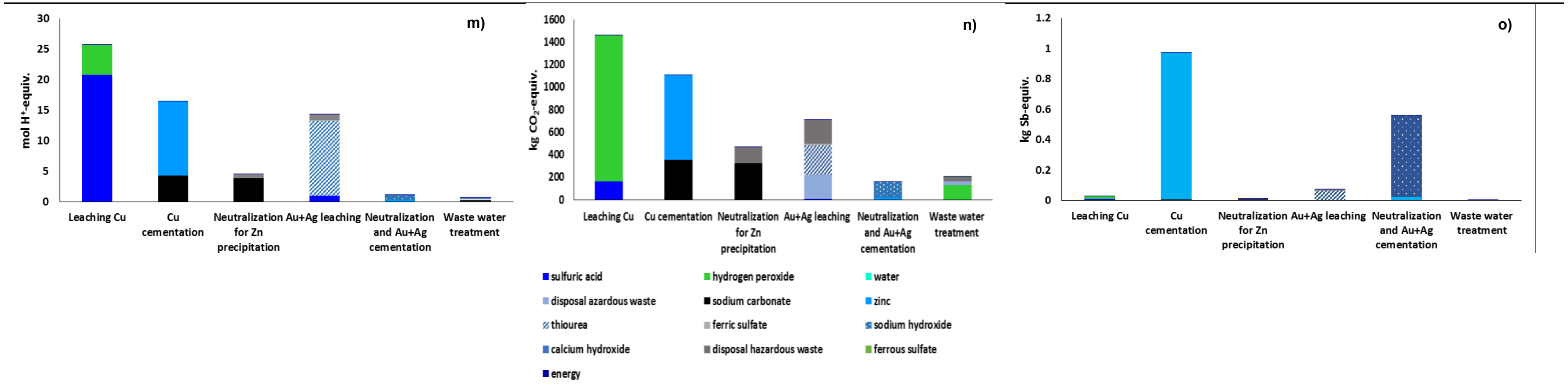


Fig. 4.5 Impacts of residues of LCDs (a-c), CRTs (d-f), lamps (g-i), LIBs (j-l) and PCBs (m-o) recycling process (classification and characterization according to ILCD recommendations).

(Functional unit: 1 ton of WEEE from traditional recycling)

4. Life cycle interpretation and discussion

The data reported in the previous paragraphs allowed to achieve an estimation of the environmental impacts of the five processes for metals recovery from WEEE residues, and to identify the most critical steps for the environmental load. Nevertheless, further elaborations were necessary to complete the environmental impact assessment of the HydroWEEE-DEMO processes. More specifically, the present chapter focuses on three main aspects: i) the environmental impact trend during process optimization (from the first HydroWEEE project to the HydroWEEE –DEMO project), ii) the comparison between this innovative approach and the current WEEE management and iii) the assessment of the metal recovery advantages, compared to primary production. For the evaluations, the global warming category was chosen since the climate change issue is a very topical question, as confirmed by the recent United Nations Climate Change Conference (Dalby, 2015).

4.1 From HydroWEEE to HydroWEEE Demo

The comparison between the HydroWEEE and HydroWEEE Demo is essential in order to assess the progress towards the environmental sustainability during the process technical optimization.

The discussion does not include LCDs (the previous HydroWEEE project focused mainly on In extraction rather than on recovery) and PCBs (the process was completely modified in the HydroWEEE Demo project, in order to make it feasible in the mobile plant). As showed in Fig. 4.6 the environmental load due to CRTs and Lamps treatment decreased of 30% in the first case and of 40% in the second one. Nevertheless, this positive effect was combined with the addition of wastewater treatment that caused the growth of emissions up to 2000 kg CO_2-equiv. and 1250 kg CO_2-equiv. in the CRTs and Lamps treatment, respectively. Anyway, an overall improvement of 4% was reached in HydroWEEE Demo Lamps treatment. The technical improvement did not cause negative effect also in the LIBs case. Indeed, comparable impacts were observed, in spite of the implementation of the wastewater treatment.

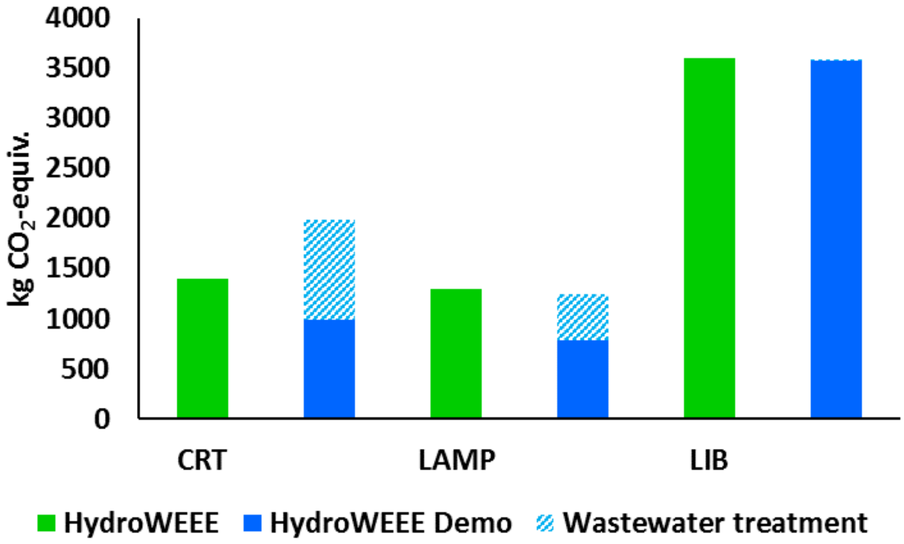


Fig. 4.6 Comparison between the first HydroWEEE and the HydroWEEE Demo processes in the category of global warming. (Functional unit: 1 ton of residue from WEEE traditional recycling)

4.2 Current management strategies of the residues vs. the HydroWEEE-DEMO approach

The comparison between the metal recovery processes and the current WEEE management strategies allowed the identification of the possible advantages of HydroWEEE research. The considered scenarios, previously described in Fig. 4.3a, include as current management strategies the disposal in landfilling sites, for urban waste in the case of LCDs and for hazardous waste in the case of residues of CRTs and lamps. On the other hand, as previously reported, the disposal in landfilling sites is not the reference scenario in the case of PCBs and LIBs, since currently traceable flows in Europe are mainly treated in the Umicore plant facilities (Fig. 4.3b). As showed in Fig. 4.7, the results of this LCA evidence that the recycling approach is very favorable for the environment if compared to the disposal in landfilling sites for hazardous materials, in the case of CRTs and Lamps (Fig. 4.7). Indeed, the environmental load of the HydroWEEE-DEMO processes was balanced by the credits due to the recovered metals and by the avoided residues disposal in landfilling sites. Conversely, the recovery of In from LCDs residues, had an impact higher than the traditional disposal of panel in landfilling sites. This negative result was expected, due to the low In concentration in the waste. However, as described in Chapter 3, a possible metal concentration in the waste would make the HydroWEEE-DEMO process sustainable (Fig. 4.8).

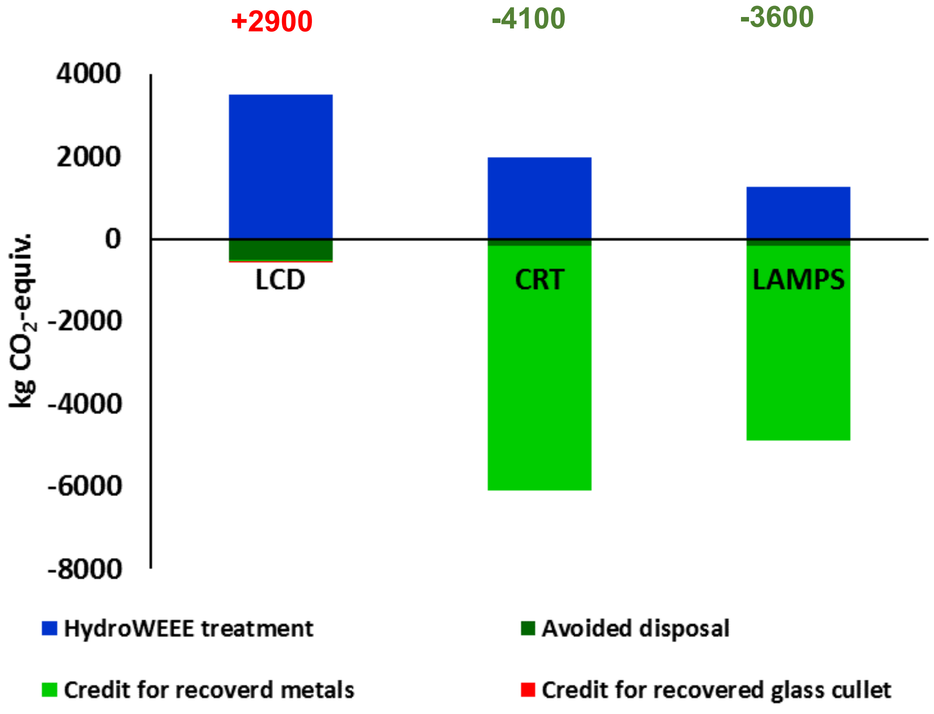


Fig. 4.7 Global balance on the environmental impacts generated by the treatment of residues of: LCDs, CRTs and lamps in the category of global warming (Functional unit: 1 ton of WEEE from traditional recycling)

As concerns LIBs and PCBs, available information regarding the environmental impact of the Umicore process is limited and the only public data report a CO_2 emissions saving of 80%, compared to the primary production (Meskers et al., 2015). This percentage is expressed in general terms, without any specification neither of the residues nor of the metals. However, an effort to compare HydroWEEE and UMICORE processes was performed anyway. A complete metal recovery was assumed for the Umicore process, with an impact in the global warming category calculated as the 20% of the primary production of the recovered metals: Co from LIBs, and Cu, Au and Ag for PCBs (Table 4.1). System boundaries have been extended, including the avoided transportation (Fig. 4.3b).

Table 4.1 Emissions associated to the primary production of metals recovered within HydroWEEE project, in the category of Global warming (Ecoinvent 2.2)

Metal	**WEEE residue**	**Primary process**
		kg CO_2-equiv. / kg recovered metal
In	LCDs	156
Y	CRTs, lamps	49.6
Co	LIBs	8.8
Au	PCBs	18,788
Ag	PCBs	55.5
Cu	PCBs	3.5

Results in Fig. 4.8 show the environmental advantage of Umicore processes compared to the HydroWEEE-DEMO ones. Nevertheless, as explained before, the uncertainty of the available data is significant and the environmental impact of the Umicore processes could likely be underestimated. Anyway, independently from this critical issue, it can be observed that the transportation has a relevant impact, around 30-40% of the total impact. Moreover, the results also highlight the environmental load connected with the hydrogen peroxide use in the HydroWEEE processes. The possibility of the substitution of this raw material, identified as critical in previous paragraphs, could significantly decrease carbon dioxide emissions

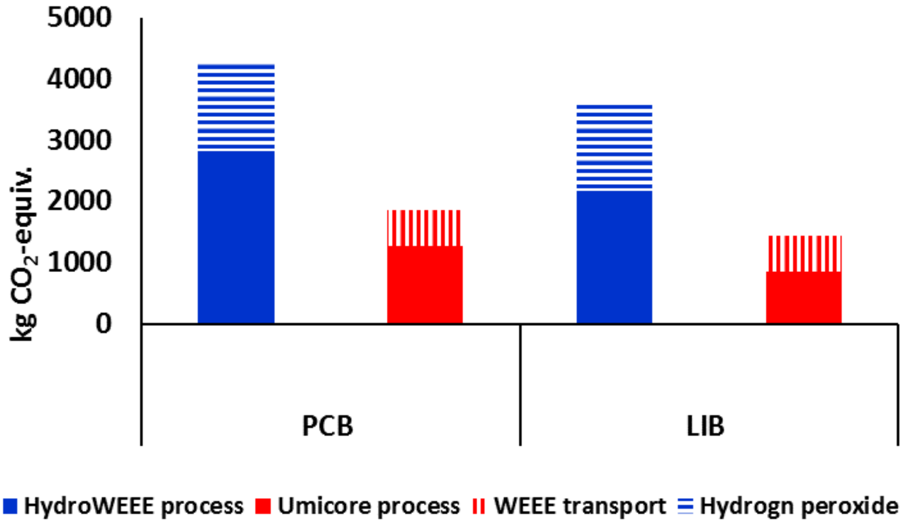


Fig. 4.8 Comparison between the environmental impacts generated by Umicore and HydroWEEE treatments for metals recovery from residues of PCBs and LIBs in in the category of global warming (Functional unit: 1 ton of WEEE from traditional recycling)

4.3 Secondary raw materials production

The recycling treatments allow to achieve both the decrease of waste to dispose in landfilling sites and the production of secondary raw materials. This paragraph has the aim to give value to the second aspect quantifying the advantage due to the avoided primary production. Even in this case, considering the geographic location of the company, the aspect of waste transportation was taken into account for the residues of PCBs and lamps. This impact can be eliminated by the residues treatment in the HydroWEEE mobile plant. Obviously, there is an impact of the plant transfer that, nevertheless, can be neglected with respect to waste transportation. In order to include this issue in the assessment, the HydroWEEE impacts were corrected and a "net HydroWEEE" calculated, where the previously estimated values are reduced by the savings associated to the avoided transportation. Fig. 4.9 shows that the HydroWEEE-Demo process allowed a CO_2 emission saving for kg of recovered metals of about 70% for CRTs and lamps, 30% for PCBs and 20% for LIBs, compared to metals primary production, . In addition, the avoided waste transportation increased the emission saving up to 42% for PCBs and 30% for LIBs (Fig. 4.9 c, d).

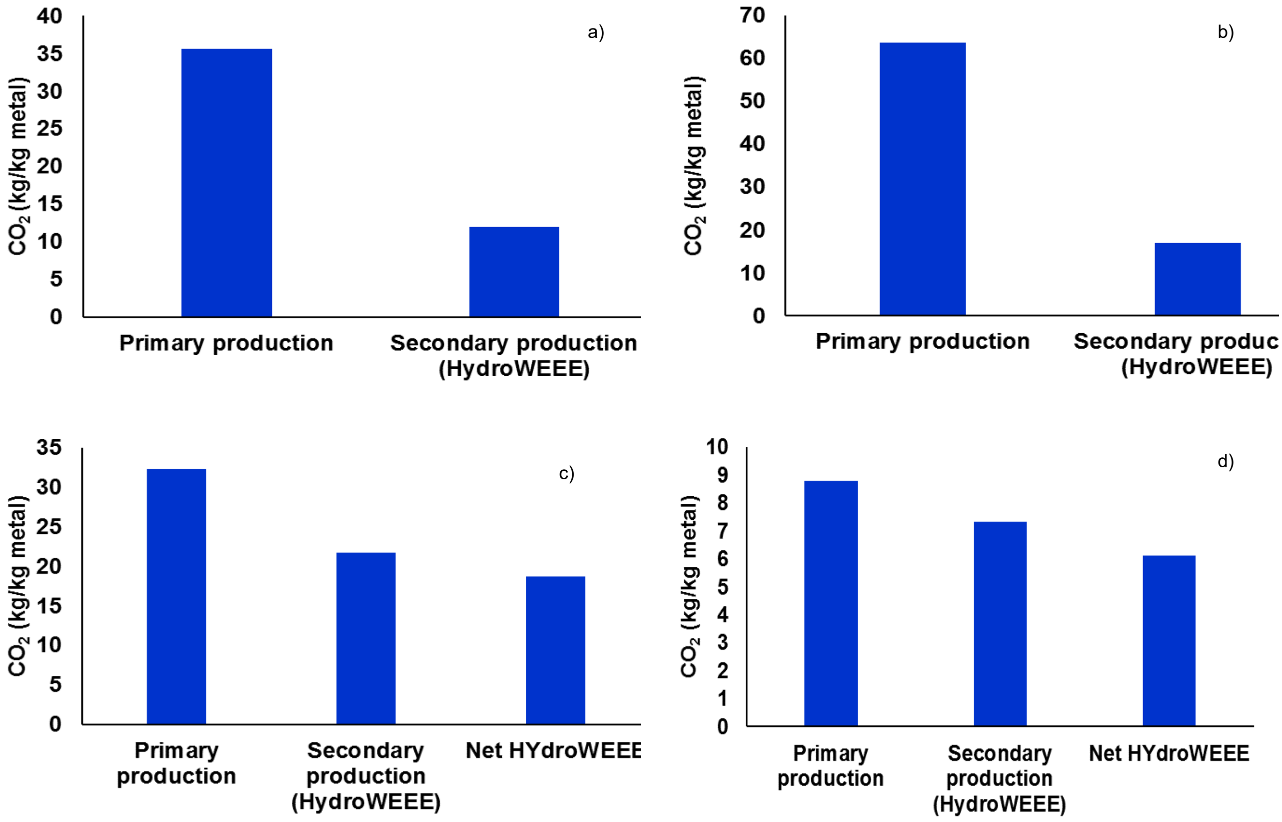


Fig. 4.9. Comparison of the CO_2 emissions of the primary process of metals production, secondary process developed in this study from a) CRTs and b) lamps and secondary process net of transportation for the recovery of metals from c) PCBs and d) LIBs. (Functional unit: 1 ton of WEEE from traditional recycling)

In order to compare the HydroWEEE strategy and the UMICORE processes for metals recovery from waste, Fig. 4.10 shows the estimated savings in CO_2 emissions compared with the primary metals production (secondary vs. primary production). As concern Umicore data, the saving in the emissions of 80% (Meskers et al., 2015) decreases to about 70% due to the environmental load of residues transportation.

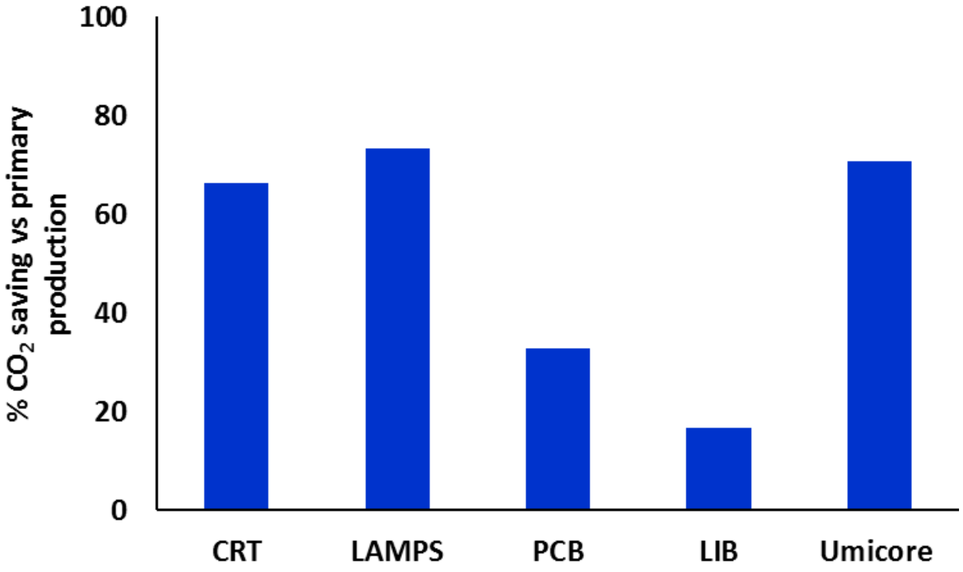


Fig. 4.10. Comparison of the CO_2 saving vs. primary production of HydroWEEE and other secondary metal production processes.

It is evident that the HydroWEEE approach resulted to be comparable, and in some cases even better, to other secondary production process in terms of environmental impact. CRTs and lamps showed the most sustainable treatments with a CO_2 emissions saving of 67% and 73%, respectively. LCDs are not represented in the figure since the treatment of the panel does not allow an environmental advantage for the low metal concentration in the waste.

5. Products

Results illustrated and discussed in this chapter were used to produce the Progress Report: Report on lamps, CRTs and LCDs, printed circuit boards, industrial and automotive catalysts, within the European project HydroWEEE Demo.

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Chapter 5

RISK ASSESSMENT OF HYDROWEEE MOBILE PLANT

Abstract

A correct process implementation should combine the technical and environmental optimization with a thorough risk assessment, since the scale-up of a treatment includes several risks for the workers. The main factors to consider are the probability that the hazardous source causes a damage and the severity of the damage. Therefore, a correct risk assessment should be adapted to the guidelines of the country in which the plant is placed. Present chapter took into account a mobile plant for the recovery of metals from residues of waste electric and electronic equipment (WEEE). Therefore, the challenge was the writing of a general and clear evaluation, suitable for each involved location, following the guidance on risk assessment at work of European Commission (1996).

Content

1. Introduction

Starting from the hazard definition "*the intrinsic property of ability of something with the potential to cause harm",* it is possible to describe the risk as "*the likelihood that the potential for harm will be attained under the conditions of use and/or exposure, and the possible extent of the harm"* (European Environment Agency 1998). The risk assessment is an essential step that has to precede the start-up of each process, in order to guarantee the workers protection. In particular, the risk estimation includes a measure of the probability of the hazard actually causing harm and a measure of the severity of harm in terms of the consequences for people or the environment (European Environment Agency 1998). In this regard, each country has different norms, for example, the 81/2008 legislative decree is the reference regulation in Italy. Nevertheless, European Commission drew up the document Guidance on risk assessment at work, (1996) with the aim to suggest the basics for the risk assessment in Europe. This guide has the target to help the Member States with the risk evaluation, following the main points of previous Directive 89/391/EEC. Considering the specific features of each work place, the document suggests that the best strategy for identification of hazards and control of the risks should be based on the participation and consultation of all those who work at the workplace, including workers and their representatives. The present chapter deals with the evaluation of safety at work of a plant for the treatment of waste electric and electronic equipment (WEEE) for metals recovery. The critical issue is the plant mobility that allows the operating in all European countries, each one with a different reference normative. Considering the described context, the Guidance on risk assessment at work was chosen as landmark in order to achieve a general document, as much as possible relevant for each place in which the plant will be positioned.

2. Methodology and criteria used for the risks assessment

The basics for the risk assessment are suggested by the document Guidance on risk assessment at work, by European Commission (1996). This guide has the target to help the Member States with the risk assessment, following the main points of Directive 89/391/EEC.

This choice is due to the plant mobility that causes the necessity to identify general norms applicable in all countries in which the plant will be positioned.

The evaluation includes:

- Identification of the hazards in all aspects of work.
- Identification of the individuals which might be exposed to the hazards.
- Estimation of the risk, taking into account the reliability and the adequacy of the existing preventive or precautionary measures.
- Decision on potential new measures to apply in order to eliminate or reduce the risks, taking into account the good practice as a guideline.

The risks are estimated as follows. With the aim to obtain a representative measure, risk is decomposed in two main factors: the probability (P) that the hazardous source causes a damage and the damage severity (G) (Table 5.1). The numerical product between probability and severity is the risk (R). The values are assigned on the basis of the following tables:

Table 5.1. Levels of probability and severity used for the risk estimation

	Probability level: **P**	Severity level: **G**
1	Very low= hardly or rarely	Negligible or small damage (Prognosis shorter than 3 days, without consequences)
2	Low = sometimes or probable	Moderate damage (Prognosis between 3 and 40 days without consequences)
3	Medium = often or very probable	Significant or serious damage (Prognosis longer than 40 days or reversable illness)
4	High = usually or often	Significant or very serious damage (Death, irreversible illness or permanent desamblement)

As showed in Table 5.2, combining the probability and the severity values, (algebraic product) we can obtain the risk matrix, defining the different levels (Table 5.3):

Table 5.2 Risk calculation

R = P x G		**Probability**			
		1	**2**	**3**	**4**
Severity	**1**	1	2	3	4
	2	2	4	6	8
	3	3	6	9	12
	4	4	8	12	16

Table 5.3 Calculation of risk level

Calculation of risk levels	**R = P x G**
Low	1-3
Medium	4-6
High	8-9
Very high	12-16

3. System description

3.1 Plant description

The considered plant is an industrial mobile plant that has been realized within the HydroWEEE-Demo project. The plant can treat several types of residues of the WEEE recycling processes, in particular:

- fluorescent lamps (LAMP)
- cathode ray tubes (CRT)
- ground printed circuit boards (PCB)
- Li-ion batteries (LIB)
- liquid crystal displays (LCD).

The whole mobile plant has been realized in two containers and its capacity has been optimized in order to be the largest possible.

The plant has the following features, considered as very relevant for its transfer to the sites of typical European SME WEEE recyclers:

- strengthened structure and special robust, flexible fixtures for piping and equipment, in order to reduce the risk of eventual breaks during transport;
- normal electricity/water requirements;
- wastewater treatment included, aiming at closing the water loop – limit the amount of fresh and waste water as well waste water in a quality that can be dumped in the normal sewage system;
- special set-up of mobile plant for outside operation (with rain, snow, wind, …);
- thermal insulation for operation in winter time/cooling for summer time;
- precautionary measures to protect “untrained” personnel and the environment from any damage;
- allowing not only the 5 current input materials, but flexible processes with different inputs in future;
- only 1 person necessary to operate the plant including feeding, storing output material;

- “self-healing”/ robust processes and programming;
- “plug and play” – self testing, self-calibration, … at set-up/ramp-down;
- automatic reporting (operation/failure/mass balance/…) per day, week, month, … accessible from office location .

As showed in Figure 5.1, the plant was realized in two mobile units. The first one contains the main equipment to leach the initial material with acid solution and to filter the suspension. Thereafter, the solution is sent to the container 2 in which the reactor and filterpress to recover rare earths, base metals and precious metals are positioned together with the equipment dedicated to wastewater treatment. In particular, the 3D image of the plant shows:

- Leaching reactor (pink reactor), R1
- Storage tank, T1
- Filter press for leaching suspension, FP1
- Recovery reactor (green reactor), R2
- Filter press to recover final products, FP2
- Wastewater treatment section with two reactors, R3-1 and R3-2
- Scrubber for air treatment, S1, that ensures the emissions suction.
- Boiler to heat the leaching reactor, B1.

The three reactors include a stirring system.

The plant is also equipped with:

- compressor for pneumatic control devices, electrical and PLC panels
- system of pipes and valves (piping) with the related transfer pumps, for the movement of acidic solution.

- sensors system (loading cell for the reactors, level indicator for the tanks…) and servo control system (electro-pneumatic valves, etc.) to achieve the data acquisition and the control during the implementation of the process.

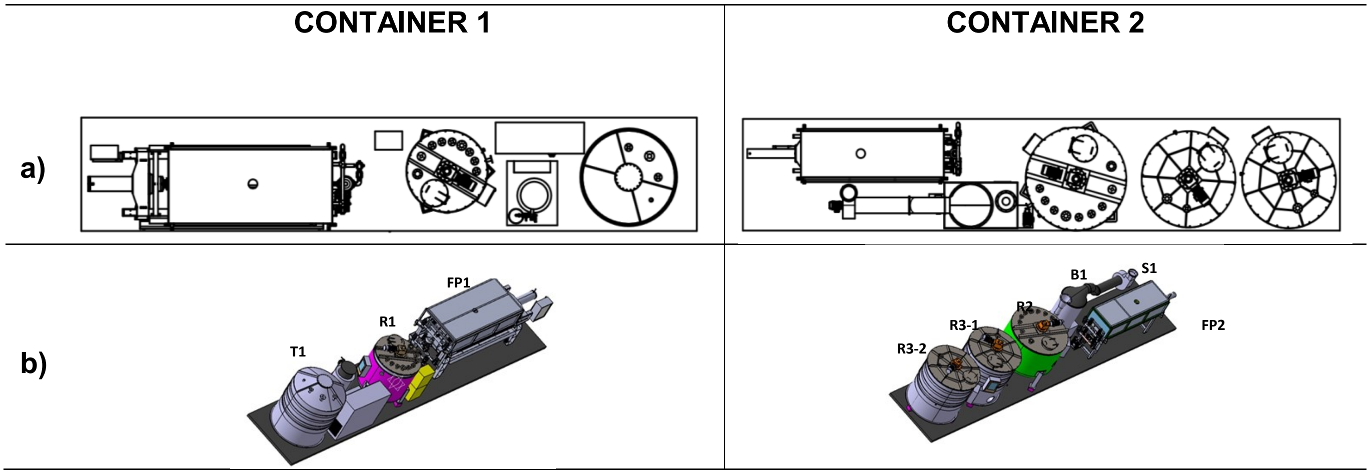

Fig. 5.1: Mobile plant equipment in the two containers, a) layout and b) 3D visualization

The materials for plant and piping were chosen to resist both acid and basic conditions of the hydrometallurgical processes. Furthermore, it has been designed limiting the times that the personnel should enter into containers.

The following figures show the 3D images and the real photos of some equipment installed inside the containers.

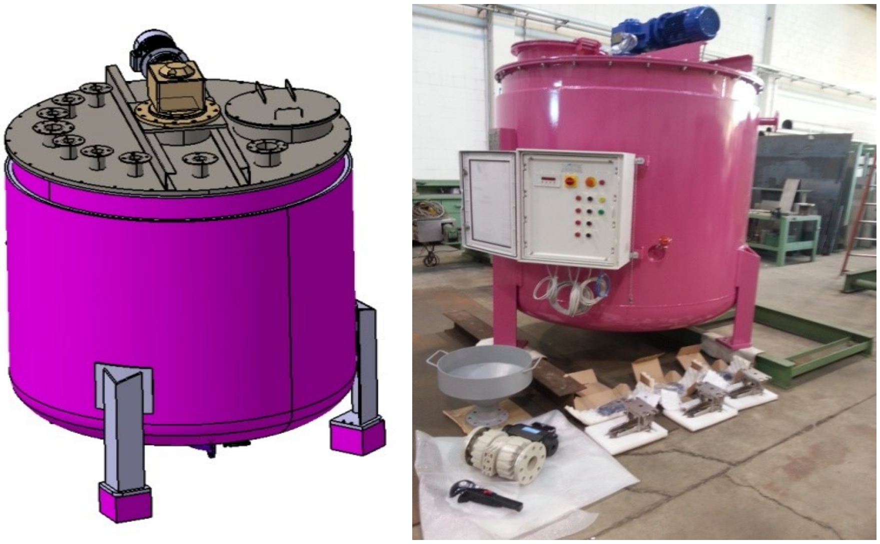

Fig. 5.2: Leaching reactor R1 – Mobile plant, HydroWEEE demo

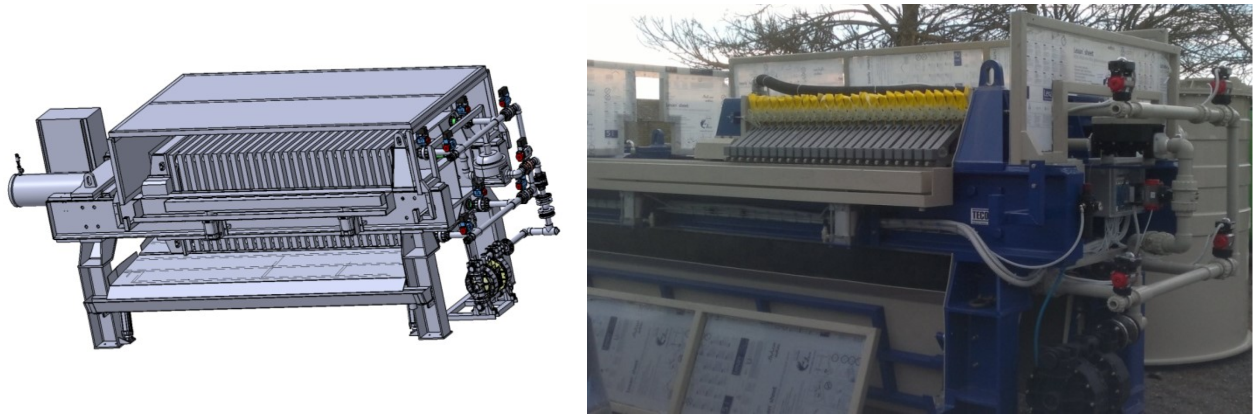

Fig. 5.3: Filter press FP1 – Mobile plant, HydroWEEE demo

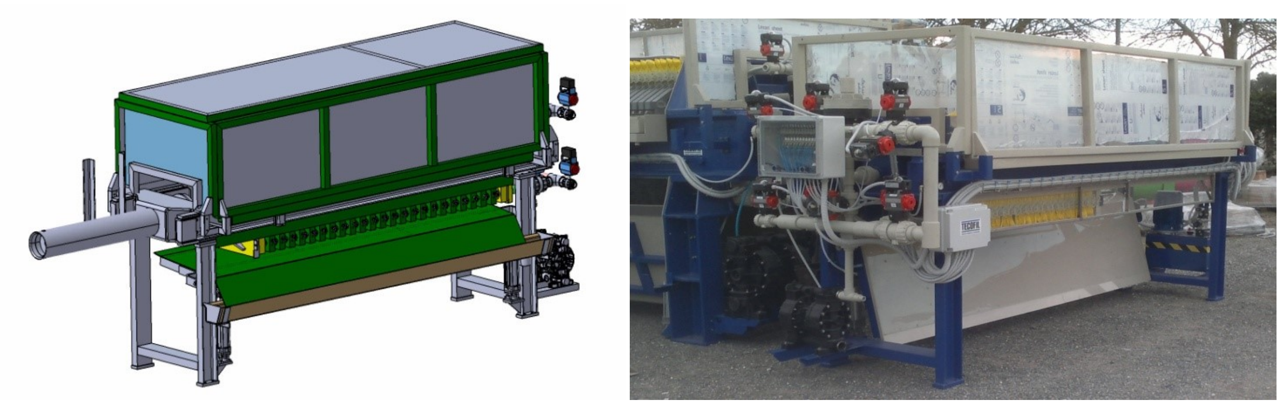

Fig. 5.4: Filter press FP2 – Mobile plant, HydroWEEE demo

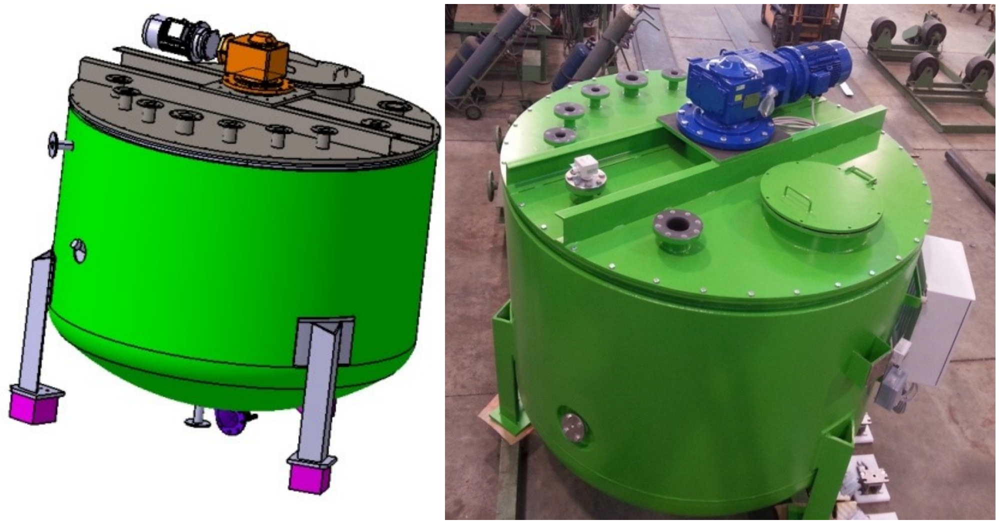

Fig. 5.5: Recovery reactor R2 – Mobile plant, HydroWEEE demo

The reactors are equipped with mixing system fundamental for the kinetics of the reactions and to keep the solids in homogeneous suspension. Fig. 5.6 shows the mixing system of reactor R1, as example.

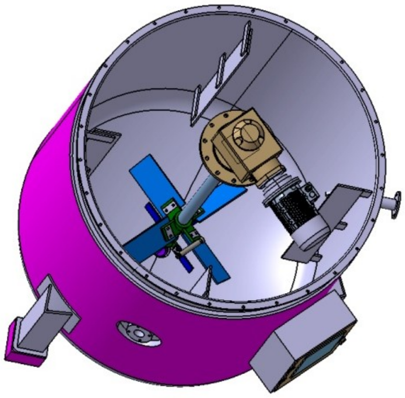

Fig. 5.6: Mixing system for R1 – Mobile plant, HydroWEEE demo

As regards the positioning inside the container, it allows the staff entrance for the possible maintenance. Indeed, several opening on the walls of the containers were planned and the phases of the unit modifications are reported in Fig. 5.7.

Fig. 5.7: Modification’s phase of the containers – Mobile plant, HydroWEEE demo

Additional information are those relative to the criteria to put piping inside the units, to connect the equipment with reagent tanks outside the plant and to connect the two containers. Fig. 5.8 shows the opening for the tubes that connect container 1 and 2.

Fig. 5.8: Opening for piping – Mobile plant, HydroWEEE demo

Considering the plant mobility, additional process equipment should be present in the SME host site. In particular:

- Storage area for waste to treat (contained in supply sacks).
- Storage area for the reagents, in powder form (contained in supply sacks).
- Tanks for the storage of acidic solution

3.2 Process description

As previously described, the plant was built for the treatment of the residues from traditional recycling of five WEEEs: CRT, LAMP, LIB, PCB and LCD. The specific hydrometallurgical processes were optimized thanks to the research activity of the three university partners of the HydroWEEE-DEMO project: Università Politecnica of Marche, Università degli studi dell'Aquila, Università Sapienza of Rome. The present paragraph has the aim to summarize the operative conditions and the flows streams.

3.2.1 CRT and LAMPS residues processes

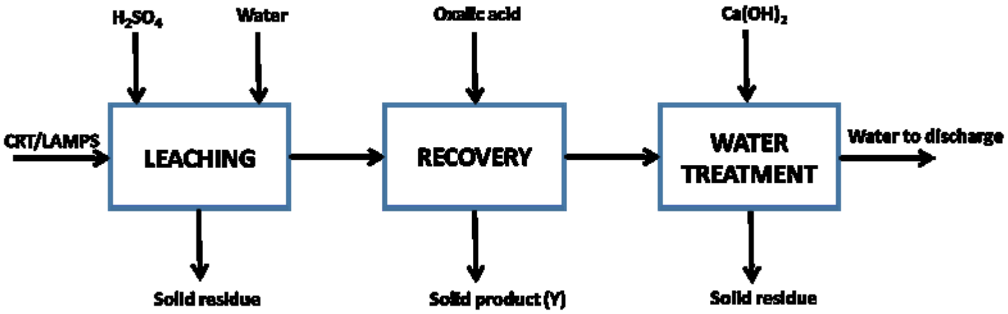

Fig. 5.9: CRT/LAMP residues treatment

The treatments of CRT and LAMP residues have a similar design that allows the recovery of rare earths in oxalate form (Fig. 5.9). A first metal extraction is carried out using sulfuric acid, diluted by water. The reaction product is filtered by a filterpress. Thereafter, the produced solid is discarded and the liquid (containing metals) can be stored in a storage tank before the recovery treatment. This second step is carried out by the manual dosing of oxalic acid and the final product is collected by a second filterpress. The obtained liquid solution is stored in a tank and then treated, in the third reactor, by a chemical-physical process by milk of lime addition. After the reaction and the flocculation, the flow is filtered by the filterpress and the resulting sludge is discarded (and managed as hazardous waste). On the other hand, the treated water is stored in the storage tank and used for the filterpress washing, or added to the first reactor. Periodically, water is disposed because it can not be used for additional recycle within the process. Currently, water treatment line (by milk of lime) is not operative and water is directly recirculated and finally disposed. Summarizing, the additives used in the plant are: sulfuric acid, oxalic acid and milk of lime.

3.2.2 LIB residues process

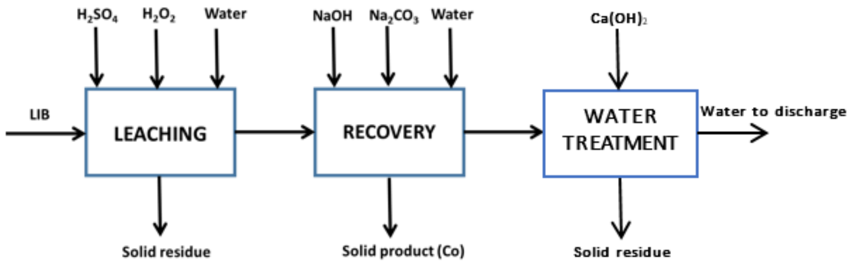

Fig. 5.10: LIB residues treatment

As showed in Fig. 5.10, LIB residues in powder form are treated into the leaching reactor using sulfuric acid and hydrogen peroxide, in aqueous solution, at 70°C.Thereafter the leach liquor is cooled and treated, in the same reactor, with sodium hydroxide pellets up to a pH value between 3.8 and 4.0. After the precipitation, the solution is separated from the solid residue by filtration using the filterpress. The treated leach liquor is then fed to the second reactor for the recovery of Co. Here, sodium carbonate (dissolved in aqueous solution) is added and the solution is kept under stirring. After precipitation the solid product is recovered by filtration in the filterpress and wastewater is collected in a tank and then treated, in the third reactor, by a chemical-physic process by milk of lime addition. After the reaction and the flocculation, the flow is filtered by the filterpress and the resulting sludge is discarded (and managed as hazardous waste). On the other hand, the treated water is stored in the storage tank and used for the filterpress washing, or added to the first reactor. Periodically, water is disposed because it can not be used for additional recycle within the process. Summarizing, the additives used in the plant are: sulfuric acid, hydrogen peroxide, sodium hydroxide sodium carbonate and milk of lime.

3.2.3 PCB residues process

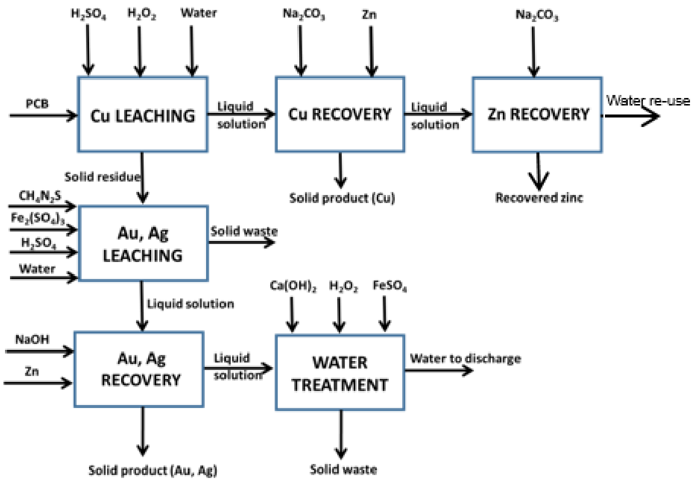

Fig. 5.11: PCB residues treatment

PCB residues process (Fig. 5.11) includes two leaching stages for selective dissolution of base and precious metals. Leaching solutions are treated to obtain the final outputs by cementation for copper and neutralization-cementation for gold and silver. It is worth to mention that all procedures are performed at atmospheric levels of temperature and pressure.

The first leaching stage uses sulfuric acid and hydrogen peroxide, in aqueous solution in which a filtration by filterpress is provided at the end of both the phases. The cementation process by zinc, followed by a filtration, ensures a fast reduction of copper ions to its metallic form and also a high recovery efficiency. Moreover, the dissolved zinc is recovered, in a following step, by a precipitation with sodium carbonate. On the other hand, the residual solid of the leaching procedure is further used to recover its gold and silver content by dissolution into a diluted sulfuric acid solution, after the addition of thiourea and ferric sulphate as oxidizing agent. Thereafter, these precious metals are recovered by performing a neutralization step by sodium hydroxide, followed by Zn cementation and a final filtration.

During the leaching stage, thiourea is oxidized to formamidine disulfide (FDS), this being after decomposed to elemental sulfur and cyanamide. The presence of these dangerous organic substances, makes the wastewater treatment necessary. This process is obtained by Fenton reagent (hydrogen peroxide and ferrous sulfate) and a consecutive impurities removalby basification with a lime solution and a final filtration by filterpress. Summarizing, the additives used in the plant are: sulfuric acid, hydrogen peroxide, sodium carbonate, zinc powder, thiourea, ferric sulfate, ferrous sulfate, sodium hydroxide and milk of lime.

3.2.4 LCD residues process

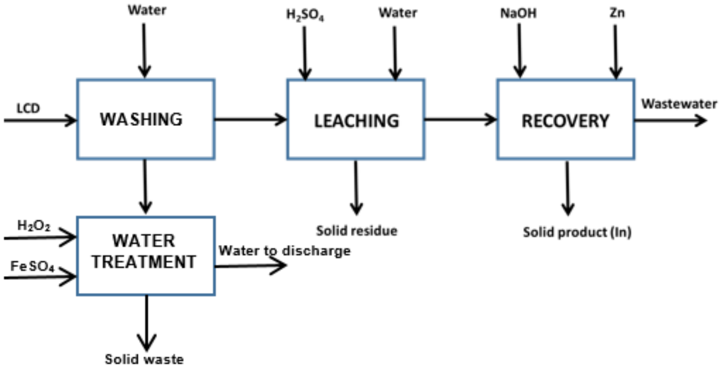

Fig. 5.12: LCD residues treatment

As displayed in Fig. 5.12, the indium recovery process from LCD residues starts with a first washing followed by a filtration. The liquid fraction is collected, used for a second washing and then stored in a tank for the final treatment by Fenton reagent (hydrogen peroxide and ferrous sulfate). On the other hand, the filtered solid is treated by leaching using sulfuric acid solution at 80°C, adopting a cross-current configuration. At the end of each extraction step, the leach liquor is filtered in a filterpress. The produced solid is collected for a possible recycling and the liquid (containing metals) can be stored in a storage tank before the recovery treatment. This second step consist of a pH adjustment with sodium hydroxide up to pH 3 and a cementation with zinc powder, carried out at 55-60°C. At the end of process, the solution is sent to the filterpress and the liquid fraction is stored in the first reactor for a new leaching treatment, after the refresh of 50% of volume.

Summarizing, the additives used in the plant are: sulfuric acid, sodium hydroxide, zinc powder, hydrogen peroxide and ferrous sulfate.

For all the processes described, workers do few manual operations:

- Liquid reagents receiving and connection of dosage pipes
- Loading of fluorescent powders: hoisting by forklift and loading by hopper
- Manual cleaning (possible) of the filterpress
- Manual loading of the solid reagents (as oxalic acid) with opening bag and overturning in the hopper located above the reactors
- Movement of filtered sludge containers, by forklift truck
- Valves opening and closing if they are not electrically controlled
- Sampling of the liquids and solids from the reactors and filterpress for analysis (if requested)
- Cleaning of the reactors and tank by water
- Coordination of possible ordinary maintenance operations (inspection reactors, inspection of the other components of the plant, general cleaning) and straordinary maintenance (variable in each case).

3.3 Operation steps

In order to have an overview of activities carried out in the mobile plant, irrespective of the selected process, Fig. 5.13 reports the flow chart of the work cycle.

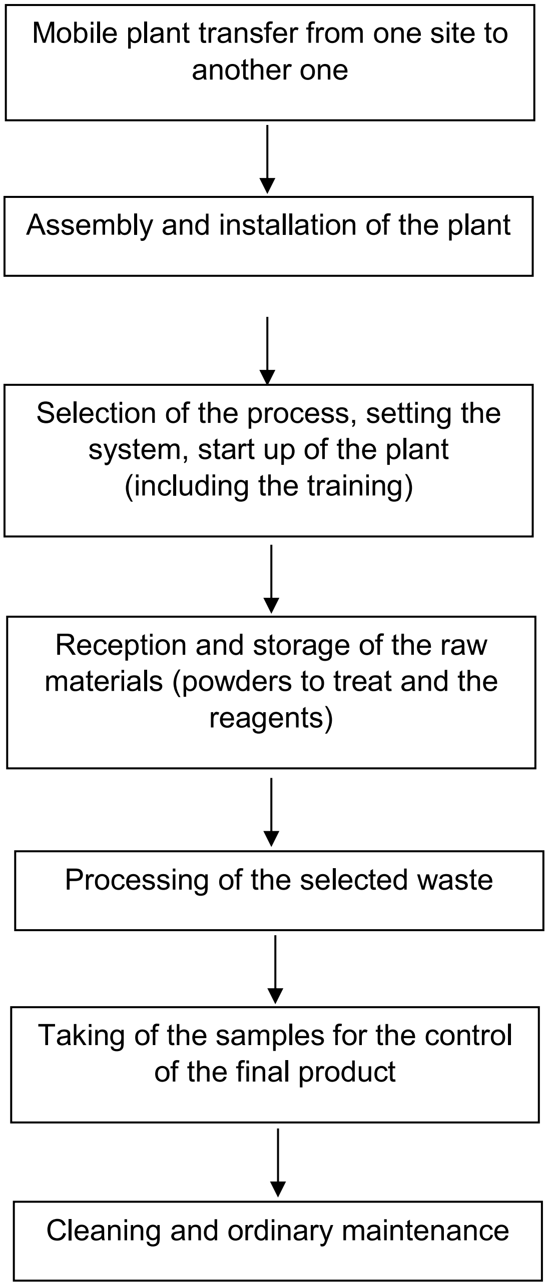

Fig. 5.13: Flow chart of the work cycle

In the Fig. 5.13 are reported the main operation steps of the work cycle from transfer of the mobile plant to a site until to the end of the production cycle or/and to a further transfer to another site. After the transport the plant needs to be partially assembled and checked in its integrity including the inspection of the piping, valve, pump and all controls. Once the process is selected among the HydroWEEE processes described before, the plant is set to work the selected waste. This phase includes the setting of the system controls; start up of the plant and the training period for the operator. At the same time or immediately later the plant and the operators should be ready to receive the raw materials and the reagents. These materials should be stored in appropriate containers, be sure for the operators and the people that works near the store site. The operators directly involved in the activities of reception and reagents placing must use the appropriate individual protection systems. After training of the personnel and control of the entire plant the selected waste is treated in according to the hydrometallurgical processes described in the previous section.

The treatments include: feeding of the reagents, dissolution of the materials, filtration by filterpress, recovery of the products and their recovery by another filterpress and finally wastewater treatment.

The activities of the operator are: manual feeding of the waste powders and solid reagents using a hopper located upper the reactors, opening of the manual valves, for example for the loading of the liquid reagents, removal of the solid on filterpress (the filtration systems are automatic but in some situations the intervention of the operator is required), activation of the manual controls and sampling of the final product for laboratory controls. The operator in the ordinary cycle monitors the progress of the processes from computer, in the case of the malfunction the personnel intervenes to repair the system and eventually replace the faulty component. In some case the intervention of the specialized operators is required.

The normal cycle provides also the ordinary maintenance, the inspection and the cleaning of the components of the mobile plant.

4. Risks assessment results

4.1 Identification of hazardous areas

Considering the process steps described in previous paragraph, Table 5.6 and 5.7 identify the description of the process steps and the specific areas with a potential risks.

Table 5.6 Description of the process steps

Process steps	**Description**
Plant transfer	Road involved in containers transport
Assembly, installation, start up, setting and training	Operation of mobile plant downloading Assembly and setting of the components not installed Connections with the loading of the liquid reagents and with the disposal systems Connections with the power sources, in particular with electrical systems and air compressors Setting and checking all components of the plant Setting and checking all parameters of the plant as velocity, pressure, dosage of the reagents, etc. Functional tests and checks Testing the plant with water Setup and replacement of components if requested during the start up phase Checking of the programming First tests with the waste to treat Checking of the final products
Operation	Control and inspection Loading of the reagents Loading/unloading Small settings of the functional parameters Small interventions by personnel during normal operation, regulation of the manual valve and other commands, local cleaning, etc. Supervision Checking of the final products
Cleaning and maintenance	Regulations and ordinary cleaning Removing of accidental spillages Dismantling of components parts of the plant Ordinary maintenance Replacements of obsolete components
Searching of the faults	Setting Dismantling of components parts of the plant Isolation and energy dissipation Repair service Replacements of components Setting the repaired and replace parts Checking of the plant

Table 5.7 Hazardous areas identified in the mobile plant

Hazardous area	**Description**	**Figure**
Itinerary	Road involved in containers transport during the plant transfer	
Provided area	Working area during the starter	
Provided area	-Area for the stationing of workers involved during the ordinary operation of the plant -Area for the intervention on liquid reagent tanks - Area for the ground waste and powdered reagents loading - Area for the manual dosage of powdered reagents - Area for the intervention near the filterpresses - Area for the samples collection from the tanks -Areas near the reactors during the inspection -Areas near the control panel	 
Mobile and motorized parts	-Areas for the mobile plates of filterpress movement -Areas under the filterpress box	

Maintenance areas	All areas for the ordinary and extraordinary maintenance intervention: - Area near the hopper for the powders loading - Areas for the mobile plates of filterpress movement - Movement area of box under the filterpress - Areas in close proximity of electrical cabinets - Areas near the cabinets for chemical agents - Areas above the reactors near the mixer - Areas interested from piping and pumps	 
Parts that can be moved by electrical, pneumatic and hydraulic actuators	Near the mobile, shifted and rotating parts: - Areas for the mobile plates of filterpress movement - Areas above the reactors near the mixer	
Parts of the machine accessible to the staff	Area with staff access: - Liquid reagents storage area - Solid reagents, powders and residual solid storage area - Delimited area near the containers - Area under the filterpress (solid phases unload) - Place for the operations of reactors feeding - Area near the electrical cabinet	
Loading area	Areas for the materials load: - Area for the liquid reagents storage - Area for the powders and solid reagent storage - Place for the powder feed and other solid reagents	
Whole machine	The whole machine, all the areas	
Electrical panel and casings of electrical components	- Near electrical panel and electrical components - Into electrical panel	

4.2 Risks assessment, prevention and protection realized measures, improvement program

Considering the process steps described in previous paragraphs, Table reports the risks for all the involved operations and the relative safety measures suggested for the staff.

Table 5.7 Evaluation of risks at mobile plant

Task	**Risk for health and safety**	**Applied measures**	**Possible support instruments**	**P**	**G**	**Risk= PxG**
Placement of the cubes of liquid reagents (moving by forklifts)	Mechanical accidents (i.e. impact, crush, …) Possible release	Verify that the store and the adjacent areas are properly free from obstacles and that other people are not present in these zones.		1	3	3
Connection of the pipe lines to the liquid reagents cubes	Contact with strong acid and bases (i.e sulfuric acid, hydrogen peroxide and sodium hydroxide)	Supplied and use of DPI: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits. Drain lines before performing the operation.	SDS of the liquid reagents	2	4	8
Loading of the ferric sulfate (Globally Harmonized System of Classification and Labelling of Chemicals, GHS hazards statements H302, 319, 335)	Harmful powder contact	Use the hopper located above the reactors. Supplied and use of DPI: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits.	Ferric sulfate SDS	2	2	4
Loading of ferrous sulfate (GHS hazards statements H302, 319, 315)	Harmful powder contact	Use the hopper located above the reactors. Supplied and use of DPI:: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits.	Ferrous sulfate SDS	2	2	4
Loading of thiourea GHS (GHS hazards statements H302, 351, 316d, 411)	Harmful powder contact	Use the hopper located above the reactors Supplied and use of DPI:: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits	Thiourea SDS	2	4	8
Loading sodium carbonate (GHS hazards statements H319)	Contact with a solution irritating for skin and eyes in case of accident	Supplied and use of DPI:: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits.	Sodium carbonate SDS	2	2	4
Loading sodium hydroxide (GHS hazards statements H314, 290)	Danger pellet contact	Use the hopper located above the reactors	Sodium hydroxide SDS	2	4	8

		Supplied and use of DPI: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits.				
Loading zinc	Not-harmful contact	Use the hopper located above the reactors Supplied and use of DPI:: face shield, safety goggles, chemicals resistant gloves, chemicals resistant suits.	Zinc SDS	2	1	2
Loading oxalic acid (GHS hazards statements H302, 312, 318)	Harmful powders contact	Use the hopper located above the reactors Supplied and use of DPI: gloves and visor FFP2.	Oxalic acid SDS	2	2	4
Loading of calcium hydroxide (GHS hazards statements H318)	Irritant compound contact	Use the hopper located above the reactors Use gloves and safety goggles	Calcium hydroxide SDS	2	2	4
Powders dosage (moving by forklifts)	Hazardous waste powders contact Mechanical accidents (i.e. impact, crush, …)	Use the hopper located above the reactors Provide and use of masks FFP2-3, gloves and protection suits Correct harness and lifting loads		1	4	4
Filterpress unloading and cleaning	Contact with acidic solutions or solids	In the presence of localized suction. Use gloves and safety goggles and operate by a spoon. Verify the absence of the staff in the underlying area. Verify the presence of the target container.		2	2	4
Filterpress unloading and cleaning	Contact with basic solutions or solids	In the presence of localized suction. Use gloves and safety goggles and operate by a spoon. Verify the absence of the staff in the underlying area. Verify the presence of the target container.		2	2	4
Handling of sludge boxes	Contact with basic solutions or solids Risks associated with overexertion	Supplied and use of DPI: Use gloves and safety goggles, acid-proof overalls Working footwear		2	2	4
Plant operation – operating machines and other equipments (compressors and electric system)	Blast of the compressors, ejected objects and fire	Read carefully equipment manuals, perform ordinary and extraordinary maintenance of the machine		1	4	4
Plant operation – release of the liquids from piping and	Contact with acid and basic solutions	Intervening in plant with suitbale DPI: gloves and		1	3	3

other components of the plant	Collision with equipment inside the plant	safety goggles, acid-proof overalls Working footwear The operator should be extremely careful during the operations			
Ordinary maintenance	Contact with acid and basic solutions	Intervening in plant with suitbale DPI: gloves and safety goggles, acid-proof overalls Working footwear	2	2	4
	Collision with equipment inside the plant	The operator should be extremely careful during the operations			
Plant operation	Fire for a malfunctioning of heating reactors system	Avoid the treatment in the periods in which the plant is not overseen. Inner temperature monitoring system. Available fire extinguisher.	2	3	6

(legend: 🟨 low risk, 🟧 medium risk, 🟥high risk)

Table 5.8: List of potential person exposed to the risks

Exposed person	**Description**
Personnel during the assembly and start up	Internal personnel and/or external specialist
Personnel during the ordinary operations, ordinary maintenance, cleaning	Internal personnel
Personnel during the extraordinary maintenance	External specialist
Other inexpert personnel	Personnel present near the mobile plant
Visitors	Visitors during presentations, demonstrations, students, providers, etc.
Other people	All the people who can interact with the plant, also occasionally

4.3 Reagents storage information

In order to guarantee a safe storage of reagents, Table5.8 reports the best conditions to implement.

Table 5.8 Conditions for a safe reagent storage

Reagent	**Hazard statement(s) (1272/2008)**	**Precautionary statement(s)**	**Conditions for a safe storage**	**Personal protective equipment**
Calcium hydroxide	H318 - Causes serious eye damage.	**P280** – Wear protective gloves/protective clothing/eye protection/face protection. **P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing. **P313** – Get medical advice/attention.	Store in cool place. Keep container tightly closed in a dry and well-ventilated place.	Respiratory protection: full face particle respirator Hand protection: gloves in nitrile rubber Eye protection: Face shield and safety glasses Skin and body protection: Complete suit protecting against chemicals
Ferric sulfate	H302: Harmful if swallowed H319: Causes serious eye irritation H335: May cause respiratory irritation	**P261** – Avoid breathing dust/fume/gas/mist/vapors/spray. **P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing.	Store in cool place. Avoid storage near extreme heat, ignition sources or open flame. Store away from oxidizing agents. Keep container tightly sealed	Respiratory protection: No required under normal condition uses Hand protection: chemical resistant gloves Eye protection: Safety glasses with side shields or goggles Skin and body protection: suitable protective clothing
Ferrous sulfate	H302: Harmful if swallowed H319: Causes serious eye irritation H335: May cause respiratory irritation	**P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing. **P302** – IF ON SKIN: **P352** – Wash with plenty of soap and water.	Store in cool place. Keep container tightly closed in a dry and well-ventilated place.	Respiratory protection: suitable respirator with filter. Hand protection: safety glasses with side shields (or goggles) Eye protection: Safety glasses with side shields or goggles Skin and body protection: suitable protective clothing
Hydrogen peroxide	H314 - Causes severe skin burns and eye damage	**P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes	Store in cool place. Keep container tightly closed in a dry	Respiratory protection: suitable respirator. DO NOT use any form of air-purifying

	H302 - Harmful if swallowed H332 - Harmful if inhaled H335 - May cause respiratory irritation H272 - May intensify fire; oxidizer	+ **P338** – Remove contact lenses, if present and easy to do. Continue rinsing. **P220** – Keep/Store away from clothing/…/combustible materials. **P261** – Avoid breathing dust/fume/gas/mist/vapours/spray. **P280** – Wear protective gloves/protective clothing/eye protection/face protection. **P310** – Immediately call a POISON CENTER or doctor/physician.	and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage. In case of release, spillage should flow to safe area. Containers should be visually inspected on a regular basis to detect any abnormalities (swollen drums, increases in temperature, etc.).	respirator or filtering facepiece, especially those containing oxidizable sorbants such as activated carbon Hand protection: gloves in nitrile, PVC, or neoprene Eye protection: Safety glasses in polycarbonate, acetate,polycarbonate/acetate, PETG or thermoplastic Skin and body protection: Suitable protective clothing in SBR rubber, PVC Gore-Tex or other specialized materials
Oxalic acid	H302: Harmful if swallowed H312: Harmful in contact with skin H318: Causes serious eye damage	**P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing. **P280** – Wear protective gloves/protective clothing/eye protection/face protection. **P264** – Wash … thoroughly after handling. **P301** – IF SWALLOWED: **P312** – Call a POISON CENTER or doctor/physician if you feel unwell.	Store in cool place. Keep container tightly closed in a dry and well-ventilated place.	Respiratory protection: dust mask Hand protection: suitable gloves Eye protection: Safety glasses Skin and body protection: suitable protective clothing and safety shoes
Sodium carbonate	H319: Causes serious eye irritation	**P260** – Do not breathe dust/fume/gas/mist/vapours/spray. **P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing.	Store in a cool dry area, away from incompatible products (acids)	Respiratory protection: respirators or dust masks Hand protection: suitable gloves (Cotton gloves for dry product; rubber, neoprene, when handling solutions) Eye protection: Safety glasses with side shields

				Skin and body protection: suitable protective clothing
Sodium hydroxide	H314: Causes severe skin burns and eye damage H290: May be corrosive to metals	**P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing **P280** – Wear protective gloves/protective clothing/eye protection/face protection. **P301** – IF SWALLOWED: **P330** – Rinse mouth. **P331** – Do NOT induce vomiting. **P309** – IF exposed or if you feel unwell: **P310** – Immediately call a POISON CENTER or doctor/physician.	Store in a cool, dry, well ventilated place, in securely closed original container. Keep away from aluminium, zinc, lead, tin and acids.	Respiratory protection: respirators in insufficiently ventilated woking areas Hand protection: suitable gloves in butyl rubber or PVC Eye protection: chemical safety goggles or face protection Skin and body protection: suitable protective clothing
Sulfuric acid	H314: Causes severe skin burns and eye damage H290: May be corrosive to metals	**P280** – Wear protective gloves/protective clothing/eye protection/face protection. **P301** – IF SWALLOWED: **P330** – Rinse mouth. **P331** – Do NOT induce vomiting. **P305** – IF IN EYES: **P351** – Rinse cautiously with water for several minutes + **P338** – Remove contact lenses, if present and easy to do. Continue rinsing **P309** – IF exposed or if you feel unwell: **P310** – Immediately call a POISON CENTER or doctor/physician.	Keep containers tightly closed in a dry, cool and well-ventilated place. Keep away from water. Corrosives area. .	Respiratory protection: respirators if the exposure limits are exceeded or if irritation or other symptoms are experienced. Hand protection: suitable gloves Eye protection: chemical appropriate protective eyeglasses or chemical safety goggles Skin and body protection: suitable protective clothing, long sleeved clothing
Thiourea	H302: Harmful if swallowed H351: Suspected of causing cancer H361d: Suspected of damaging the unborn child H411: Toxic to aquatic life with long-lasting effects	**P273** – Avoid release to the environment. **P281** – Use personal protective equipment as required. **P308** – IF exposed or concerned: **P313** – Get medical advice/attention.	Store in a cool, dry place. Do not store in direct sunlight. Store in a tightly closed container.	Respiratory protection: respirator if exposure limits are exceeded or if irritation or other symptoms are experienced Hand protection: suitable gloves Eye protection: protective eyeglasses or chemical safety goggles Skin and body protection: suitable protective clothing,

Zinc	Store in cool place. Keep container tightly closed in a dry and well-ventilated place.	Respiratory protection: respirator if ZnO or fumes are generated Hand protection: suitable gloves Eye protection: protective eyeglasses Skin and body protection: suitable protective clothing,

5. Conclusions

The present assessment allowed the identification of risks, and relative level, addressed to the plant personnel, visitors and external specialists. The results showed that the highest risk is connected with the raw materials use, in particular strong acids and basis and thiourea. Nevertheless, also the possibility of mechanical accidents deserves attention, especially during maintenance. It is clear that the magnitude of the damaging event can be reduced adopting the individual safety devices, observing carefully the operating procedures and taking into account the machinery manuals.

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7. Products

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