ARTICLE IN PRESS

Waste Management xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Leaching capacity of metals–metalloids and recovery of valuable materials from waste LCDs

Vasiliki Savvilotidou, John N. Hahladakis, Evangelos Gidarakos *

School of Environmental Engineering, Technical University of Crete, Politechnioupolis, Chania 73100, Greece

A R T I C L E I N F O

Article history:
Received 24 March 2015
Accepted 20 May 2015
Available online xxxx

Keywords:
WEEE
LCDs
Polarizer
ITO glass
Metal recovery
Metalloid recovery

A B S T R A C T

The purpose of Directive 2012/19/EU which is related to WEEE (Waste Electrical and Electronic Equipment), also known as "e-waste", is to contribute to their sustainable production and consumption that would most possibly be achieved by their recovery, recycling and reuse. Under this perspective, the present study focused on the recovery of valuable materials, metals and metalloids from LCDs (Liquid Crystal Displays). Indium (In), arsenic (As) and stibium (Sb) were selected to be examined for their Leaching Capacity (*R*) from waste LCDs. Indium was selected mainly due to its rarity and preciousness, As due to its high toxicity and wide use in LCDs and Sb due to its recent application as arsenic's replacement to improve the optimal clarity of a LCD screen. The experimental procedure included disassembly of screens along with removal and recovery of polarizers via thermal shock, cutting, pulverization and digestion of the shredded material and finally leaching evaluation of the aforementioned elements. Leaching tests were conducted under various temperatures, using various solid:liquid (*S*/*L*) ratios and solvents (acid mixtures), to determine the optimal conditions for obtaining the maximum leaching capacities. The examined elements exhibited different leaching behaviors, mainly due to the considerable diversity in their inherent characteristic properties. Indium demonstrated the highest recovery percentages (approximately 60%), while the recovery of As and Sb was unsuccessful, obtaining poor leaching percentages (0.16% and 0.5%, respectively).

1. Introduction

Recycling is a process neither beneficial nor particularly efficient at all times. In order to address the problematic implementation of recycling, it is necessary to identify the point at which its successful completion suffers. For example, gold recovery from Printed Circuit Boards (PCBs) has previously been estimated to yield a less than 60% of useful material. Hence, the essential gold loss takes place during disassembly and not during the chemical recovery process of gold (Keller, 2006; Song and Li, 2014). It is clear, therefore, that major issues in WEEE management are involved in the disassembly process, which is, perhaps, the most basic stage for a proper and efficient recycling. Furthermore, the implementation of a recycling program as a viable option should always include any potential adverse effects on human health. For instance, in some recycling plants in Sweden, significantly high concentrations of In, Cr, Co, Pb and Hg were measured in the blood and urine of employees that worked in the recycling units compared to the ones that worked in the offices (Julander et al., 2014). Furthermore, air pollution derived from As and Sb has been observed in the recycling facilities/plants of 13 villages in Guiyu, China (Bi et al., 2011). These cases indicate that WEEE recycling could, potentially, be an important pollution source. Such studies are important for identifying any potential risks involved during recycling activities. Apart from the impact on human health, the possible environmental effects should also be taken into consideration. Last but not least, any huge economical cost that outweighs recycling benefits, reduces the revenues of recycling companies, thereby inhibiting any financial benefit (Soo and Doolan, 2014).

To the authors' best knowledge, limited research has been performed in the field of the recovery/reuse of valuable materials from LCDs. Literature reports the manufacturing of construction aggregates using secondary recycled materials. More specifically, the waste glass of LCDs may be reused in concrete, a material known as LCDGC (Liquid Crystal Display Glass Concrete). In this case, a portion of the collected sand (e.g. from a river) is replaced by sand manufactured from a LCD glass. The addition of 20% LCD glass sand meets the specific slump requirements, while at the same time improves the strength and durability of concrete (Wang, 2008;

* Corresponding author. Tel.: +30 2821037789/2821037725; fax: +30 2821037850.

E-mail addresses: vsavvilotidou@hotmail.com (V. Savvilotidou), john_chach@yahoo.gr (J.N. Hahladakis), gidarako@mred.tuc.gr (E. Gidarakos).

http://dx.doi.org/10.1016/j.wasman.2015.05.025
0956-053X/

Wang and Huang, 2010; Fan and Li, 2013). The production of ceramic glass via waste LCD glass sintering is also another recycling choice (Lin et al., 2009). The current recycling of WEEE is mainly oriented to the recovery of rare earth elements (REEs), an increasingly important research path for a potential transition to a greener economy. There are three main applications of REEs: magnets, nickel-hydride batteries and fluorescent lamps. In LCDs, fluorescent lamps at the end of their life cycle are considered a rich source of REEs such as europium (Eu), terbium (Tb) and yttrium (Y), hence posing both a high research interest and a great challenge (Binnemans et al., 2013).

Although the European Union (EU) sets targets on the mass fraction (wt%) of the original material to be recovered and/or reused and/or recycled, no emphasis is given on the recovery of scarce/insufficient resources, or to a significant number of special and precious metals such as In, Ag and Pd (Nelen et al., 2014). However, the recovery techniques on the treatment of LCDs vary, depending on each of the following focused areas: (a) production of insulating ceramic glass of LCD waste glass and calcium fluoride sludge (Fan and Li, 2013), (b) pyrolysis to remove the organic segments/portions of the LCD glass (Lu et al., 2012), (c) chemical processes through which elements such as Y and Eu are obtained at high percentages (Innocenzi et al., 2013, 2014) and (d) microbial methods aiming at the recovery of In (Ogi et al., 2012). As for the recovery of metals oriented from waste LCDs leachates, literature has reported Cr recovery via a supercritical water oxidation procedure (Veriansyah et al., 2007).

Among the parts of a typical LCD unit, the LCD panel has a complex structure, consisting of a polarizing film, liquid crystals and glass substrates (Wang and Xu, 2014). The liquid crystals are placed between the two glass-substrates which are externally surrounded by polarizing membranes (Li et al., 2009; Zhuang et al., 2012; Wang et al., 2013; Savvilotidou et al., 2014). More specifically, a LCD unit contains 86.52 wt% glass, 12.81 wt% organic materials and approximately 0.02 wt% In which is located in the indium-tin oxide (ITO) layer in between the two glass substrates (Ma and Xu, 2013). This material is of particular interest, mainly due to being a source of In recovery. Recently, research interest has also been focused on the separation of the polarizer to its components; tri-acetyl cellulose, (TAC) and polyvinyl alcohol, (PVA) (Lu et al., 2012).

In general, transparent conductive films (TCFs) are used in a variety of photoelectron devices, such as LCDs, organic light emitting diodes (OLEDs), photovoltaic cells, sensors and lasers, mainly due to their specific visible light transmission and good electrical conductivity (Li et al., 2014a,b). Among the aforementioned films, ITO combines the best properties (Kameda et al., 2007; Li et al., 2014b). ITO is a solid solution consisting of 90% w/w In_2O_3 and 10% w/w SnO_2 (Dodbiba et al., 2012; Li et al., 2014a; Yoshida et al., 2014). It is estimated that ITO layer in a functional LCD display has a thickness (dITO) of approximately 150 nm and a density (pITO) of 7.14×10^6 g/m^3. Despite the great interest, research on ITO still remains incomplete and unclear. There are various measured data on the amount of In existing in an LCD panel. According to Yang et al. (2013) the specific weight of a 17 inches LCD screen panel (Mglass) was measured about 3.2 kg/m^2. As a consequence, assuming that the thickness of ITO is uniform/stable, In content was estimated about 0.25 g-ln/kg-glass (250 ppm). Other studies report that In content in ITO glass is 102 mg/kg (Li et al., 2009; Wang et al., 2013), or according to Lee et al. (2013), an amount of 234 mg/m^2 In was estimated in an ITO with an approximate thickness of 125 nm. It is noteworthy the fact that ITO production represents 70% of the global In consumption (Yang et al., 2013), thereby creating the need for its recovery, or at least its replacement by another element. Given the limited earth's availability in In, major research attempts have been oriented toward the perspective of using alternative materials. Graphene has recently attracted considerable interest due to its excellent properties. However, despite its synthesis, graphene is unsuitable for mass production, mainly because it requires specific substrate materials which limit its applications (Zheng et al., 2014). In short, at present, recovery of ITO is probably the only predominant choice to prevent a plausible future depletion of In.

On the other hand, the LCD materials' recovery sector has successfully been developed by researchers over the last years. Among the precious materials (metals, metalloids) that can be recovered from waste LCDs, as mentioned above, is the critical indium (Weiser et al., 2015). Taking into consideration this year's market data about metals, In price is estimated to approximately 550–700 $/kg (Metal-pages, 2015).

The present work focused on the qualitative and quantitative determination of In, As and Sb in waste LCD panels, with the view of investigating the recovery possibilities of the aforementioned elements by the use of various acids while examining the effect of various parameters on the recovery percentages, such as solid:liquid (S/L) ratio, temperature and time.

1.1. Why recovering In, As and Sb?

A LCD unit contains a variety of metals as recent studies report (Maragkos et al., 2013; Kolias et al., 2014; Savvilotidou et al., 2014). Based on literature data, In is mainly detected in ITO (Li et al., 2009; Li et al., 2011, 2014a), As is used in the panel due to its capability of improving the optical clarity of screens (Lim and Schoenung, 2010; Salhofer and Tesar, 2011) and Sb has recently been used as a replacement of As, mainly because it has similar behavior and properties while being at the same time far less toxic than As (Bi et al., 2011; Ungureanu et al., 2015). The metalloids (As, Sb) have also been used as anti-foamers in the glass of the LCD panels, raising concern about their speciation and possible presence in elevated concentrations in landfill leachates (Ungureanu et al., 2015). However, to the authors' best knowledge there are no studies either confirming or rejecting the above mentioned concern. Taking, also, into consideration the limited literature data on As and Sb recovery from waste LCDs, the study of the aforementioned elements was considered, therefore, of utmost importance.

The selection of In was mainly done due to its limited earth's availability, preciousness and wide spectrum of reuse/recycling alternatives. The study of As was performed on account of its high toxicity, even at relatively low concentration levels and consequently for environmental purposes. Finally, Sb was chosen to be studied for further recovery.

2. Materials and methods

2.1. Sample preparation and experimental procedure

Prior to any recovery (leaching) attempt, a total digestion of the examined samples was performed (100 mg of LCD sample in powder form mixed with 10 mL of HNO_3:HCl in a 1:5 ratio, for 20 min under 180 °C), using a sophisticated microwave (MARS 6) and a subsequent analysis by using an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, Agilent 7500cx) to determine their total metal content. Finally, in order to investigate the recoverability of In, As and Sb, sub-samples of chopped screens were prepared and further subjected to different leaching conditions. Parameters associated with the sample preparation, analysis and experimental procedure are presented in detail below.

The experimental procedure included the following steps: collection of waste LCDs, dismantling, removal of polarisers, shredding, pulverisation to quantify and qualify the composition of the