Waste Management 57 (2016) I–III

Contents lists available at ScienceDirect

Waste Management

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

A Glance at the World

Edited by Francesca Girotto

This column comprises notes and info not subjected to peer-review focusing on waste management issues in different corners of the world. Its aim is to open a window onto the solid waste management situation in any given country, major city or significant geographic area that may be of interest to the scientific and technical community.

Assessment of kitchen waste generated in a maternity hospital: A case study in Brazil

Due to lack of studies analysing the contribution of kitchen waste to the total mass of non-hazardous waste generated in healthcare facilities and also to examine their possible impacts, the Authors analysed the healthcare waste (HCW) generated from a maternity hospital in the state of Rio de Janeiro. The survey was conducted in three stages: two months, eight and seven days.

In the first stage, a non-participant observation was carried out in the HCW sector by monitoring the collection activities for four weeks in order to learn the management practices adopted and analyse the impact of kitchen waste on overall HCW management activities. The second stage and third stage consisted of measuring (weighing) the generated HCW.

Results of this study indicate that the minimum recorded masses of kitchen waste were between 7.25 kg and 8.15 kg. In both cases, although the bags were full, they contained mainly cardboard mixed with food. These observations indicate problems in the training process of both kitchen workers and collectors.

The maximum mass ranged between 80 kg and 100 kg causing troubles to collectors.

Table 1 presents some characteristics of other studies indicating kitchen waste contribution to the total mass of general waste.

In the present study, since kitchen waste was disposed directly in a specific temporary storage area, there was a greater facility to quantify the waste.

The period of non-participant observation of HCWM practices revealed several impacts of kitchen waste, mainly on temporary internal storage, external storage and cleaning of containers.

The results showed that kitchen waste has a substantial impact on the HCW management examined and this is an important issue, because the scraps from hospital meals as well as other kitchen waste, which could be reused in composting processes, are routed together with other non-hazard waste to landfills.

References

Mattoso, V.D.B., Schalch, V., 2001. Hospital waste management in Brazil: a case study. Waste Manage. Res. 19 (6), 567–572.

Patway, M.A., O'Hare, W.T., Street, G., Elahi, K.M., Hossain, S.S., Sarker, M.H., 2009. Quantitative assessment of medical waste generation in the capital city of Bangladesh. Waste Manage. 29 (8), 2392–2397.

Tivirolli, K., Tivirolli, S.C., Luz, P.C.D., Fujino, L.B.V., Shinzato, M.P., Skowronski, J., Hess, S.C., 2010. Management in three public hospitals of Mato Grosso do Sul, Brazil. Revista Brasileira de Promoção a Saúde 23 (1), 213–220.

L.de L. Moura
C.F. Mahler
Federal University of Rio de Janeiro, COPPE, GETRES, Brazil

H.M. Caullíraux
Federal University of Rio de Janeiro, COPPE,
Production Engineering Program, Brazil

S.A.M. Teixeira
Rio de Janeiro State University, Brazil

Table 1
Characteristics of different HCW research.

Reference	Research characteristics		
	Sampling period	Problems reported by the authors	Kitchen waste % in the HCW
Mattoso and Schalch (2001)	Weighing during every day of the week over two months	Kitchen and cafeteria waste could not be quantified because they were disposed together with the general waste. As a result, there was only the quantification of organic waste from the wards	13%
Patway et al. (2009)	Weighing for three days in each health institution	Kitchen waste was mixed with infectious waste, so the Authors had to segregate them first and then weigh them.	50,46–45,42%
Tivirolli et al. (2010)	Weighing for seven consecutive days in four campaigns in the first hospital, three campaigns in the second and five in the third hospital	Hospitals did not have any kind of segregation, so the authors used the parameters established by the WHO to estimate the amount of HCW types.	17,3–31,1%

http://dx.doi.org/10.1016/S0956-053X(16)30582-7

Seasonal variation in solid waste characteristics for urban and rural areas in Mauritius

Mauritius is an internationally recognized tourist destination and is considered to be an emerging Developing Country. Most of the MSW, commercial and industrial waste goes to transfer stations before being disposed of at the sole sanitary landfill of the island. Mauritian Authorities are trying to improve recycling, composting, and reuse to reduce the amount of solid waste to be landfilled. In order to achieve this goal, decision makers need relevant data on solid waste quantities and composition. This national waste characterization study will thus enable the creation of waste databases for Mauritius and may also be used for comparison with other Small Island Developing States (SIDS).

The direct analysis method (EPA, 1995) was used to determine the solid waste composition in the urban and rural areas of Mauritius. The characterisation study was conducted in conjunction with the Ministry of Local Government and Outer Islands at two transfer stations which receive wastes from three different sources namely domestic, industrial, and commercial sectors. The characterisation study was conducted over a period of 5 working days in each region for both summer and winter seasons.

A total of three trucks were randomly selected daily at three different time intervals: 9 a.m., 11 a.m., and 2 p.m. The gross load of the selected trucks was determined by using the weighbridge at each transfer station. The standard coning and quartering technique was used for the sampling of the solid waste and a sample size of 91–136 kg was retained. The solid wastes were then sieved (40 mm) and manual sorting of seven different fractions was carried out on the retained waste (see Table 1).

The moisture content, ash content and the calorific value on a dry weight basis of the mixed waste for both urban and rural areas was 38.13 ± 3.87%, 8.71 ± 2.26%, and 18,653 ± 1805 kJ/kg, respectively.

An overall analysis of the seasonal variations in waste composition demonstrated a high organic composition percentage (including paper) from the commercial (64%) and domestic (68%) sectors. This waste could be biologically treated through composting or anaerobic digestion. Results also showed that there could be a good recycling potential for glass, and gasification, pyrolysis or combustion for plastic and textile. Yard waste has decreased considerably from 43% in 2000 (Mohee, 2002) to 26% in 2014. This is in line with a rapid economic development taking place in Mauritius since the year 2000, resulting in large amount of green space being cleared for the construction of buildings and roads. The amount of food waste has also increased slightly from 25% (Mohee, 2002) to 31% as a consequence of the population growth from 2000 to 2014. Mauritius is changing from an agricultural to a more technological society. This paradigm shift has improved the standard of living as well as the consumption patterns of the population and at the same time the amount and types of waste being produced.

Table 1
Waste compositions (%) for the year 2014.

	Domestic waste	Industrial waste	Commercial waste
Yard waste	27	–	–
Food waste	27	–	42
Paper	14	29	22
Plastics	15	6	14
Metals	3	–	–
Glass	3	–	–
Others	6	4	22
Textiles	5	61	–

References

EPA, 1995. Characterisation of Municipal Solid Waste in the United States <http://www.epa.gov/osw/nonhaz/municipal/pubs/msw95.pdf>.

Mohee, R., 2002. Assessing the recovery potential of solid waste in Mauritius. Resour. Conserv. Recycl. 36, 33–43.

R. Mohee
N. Soobhany
G. Somaroo
S. Gunasee
S. Mauthoor
P. Jeetah
Department of Chemical and Environmental Engineering,
University of Mauritius, Mauritius

O. Gukhool
Department of Computer Science and Engineering,
University of Mauritius, Mauritius

Household waste management in rural of Chongqing, China

In Chongqing, located in southwest China, the total MSW generation was 16.38 million tons in 2014 (Delvoie, 2005). Only 6.28 million tons of waste were collected in urban areas and incinerated or landfilled in 2014 (N.B.S., 2014). Little attention was paid to the management of household waste in rural areas, which resulted in poor living conditions and environmental pollution. In order to figure out the current situation of household waste management in the rural areas of Chongqing, three typical regions (Changshou, Dazu, and Jiulongpo) were chosen to conduct a questionnaire and a field investigation (see Table 1).

The household waste generation and emission load were increasing with the income of the households. From this study, household waste resulted to range from 0.057 to 0.76 kg/p/d in Changshou, 0.13–0.20 kg/p/d in Dazu, and 0.037–2.40 kg/p/d in Jiulongpo. The final emission load of household waste ranged from 0.024 to 0.40 kg/p/d in Changshou, 0.08–0.16 kg/p/d in Dazu, and 0.03–2.00 kg/p/d in Jiulongpo. Overall, the average household waste generation and emission load in rural areas were 0.275 kg/p/d and 0.18 kg/p/d, which means about 1.32 million tons household waste in Chongqing. Organic waste (kitchen waste) was the main fraction with 73.23% in Changshou, 31.23% in Dazu, and 67.59% in Jiulongpo.

In Changshou, since 2010, public infrastructures, like waste stations, were built in a pilot village to manage household waste. However, due to the lack of labor, capital investment and participation, household waste was not collected and treated effectively.

In Dazu, parts of villages (covering from 30% to 40% of total households) were brought into a waste collection system. Waste transportation was not efficient and the uncollected waste was burned causing serious air pollution.

In Jiulongpo, residents' attitude and government's finance were insufficient, thus random dumping still existed even though there were trucks collecting waste at a fixed time.

Information on resident's environmental knowledge and awareness, and satisfaction about the current waste management services, were collected through 252 questionnaires. Results showed that more than 60% of the residents would like to pay 0.18–0.20 dollars/h/m for the collection and management of their waste. In term of source separation, Table 1 shows that recyclable waste (i.e. plastic, metals, and glass) accounted for about 15.37%, which means that its source separation would be acceptable and feasible.

Table 1
Generation, emission load, and composition of household waste in rural areas.

Region	Village	Income (dollars/p/y)	Household waste generation (kg/p/d)		Emission load (kg/p/d)	
			Range	Average	Range	Average
Changshou	Xindaolu	472.93	0.19–0.21	0.20	0.07–0.08	0.07
	Qilin	580.63	0.057–0.76	0.27	0.024–0.40	0.13
Dazu	Guansheng	618.47	0.15–0.20	0.17	0.12–0.16	0.14
	Gaopo	839.69	0.13–0.17	0.15	0.08–0.11	0.10
Jiulongpo	Hailan	1043.45	0.037–2.4	0.48	0.03–2.00	0.42
	Baihe	1015.72	0.08–0.86	0.38	0.06–0.57	0.25
Average		780.25		0.275		0.18

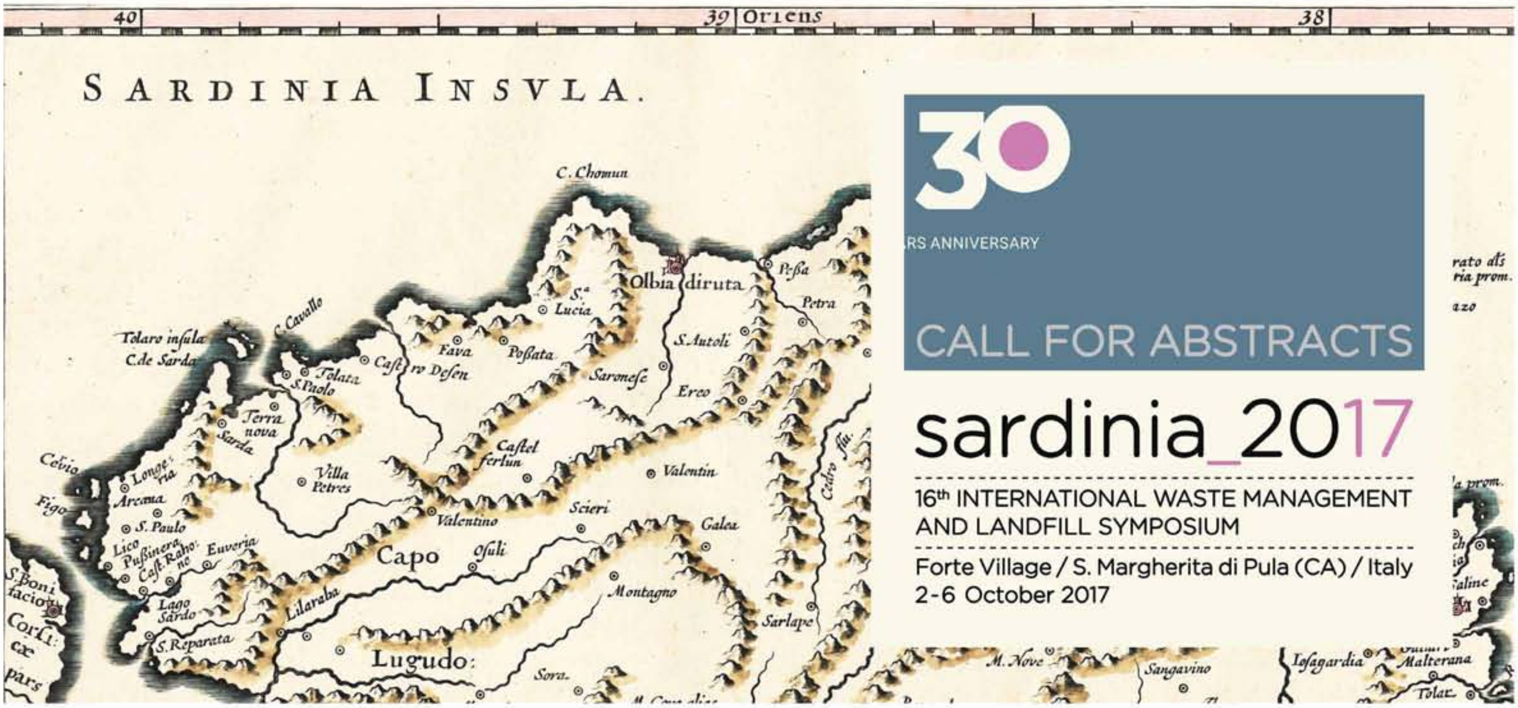
	Organic	Plastic	Paper	Textiles	Ashes	Glass	Metals	Others
Household waste composition (wt%)								
Changshou	73.23	6.53	1.93	0.77	5.1	6.73	0.58	5.58
Dazu	31.23	5.54	5.86	2.04	24.85	13.57	1.55	15.37
Jiulongpo	67.59	6.57	6.57	0.62	12.75	4.15	0.91	1.29

References

Delvoie, C., 2005. Waste Management in China: Issues and Recommendations. Infrastructure Department East Asia and Pacific Region.

N.B.S., 2014. Chongqing Statistic Yearbook <http://www.cqtj.gov.cn/tjnj/2014/indexch.htm>.

X. Zhao
L. Wang
College of Resources and Environmental Science and State Key Laboratory of Coal Mine Disaster Dynamic and Control, Chongqing University, PR China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Olbia diruta
S. Lucia
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Tolaro insula
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Waste Management 57 (2016) IV–VII

Contents lists available at ScienceDirect

Waste Management

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IWWG News & Views

Compiled by Marco Ritzkowski

In this issue: IWWG ART Gallery: The Green Team; Social aspects of waste management – examples presented on the IWWG webpage; an introduction about the Members Area on the IWWG webpage; announcement of VENICE 2016 – 6th International Symposium on Energy from Biomass and Waste, Workshop organized by the IWWG TG on Thermal Treatment during VENICE 2016; IWWG Asian Regional Branch: announcement of the 3rd IWWG-ARB Symposium; announcement of WasteSafe 2017 – 5th International Conference on Solid Waste Management in South Asian Countries, and details on future IWWG events.

IWWG ART Gallery: The Green Team

One of the sections contained in the IWWG Art Gallery is dedicated to "Projects". Beside many others you will find a success story, the initiative of a group of girls, known as the "Green Team", from Durban Girls' College (South Africa), whose mission is to transform their school into an environmentally conscious institution.

One of the projects the team undertook was to collaborate with Umcebo Design, already featuring in the IWWG Art Gallery, to make one of their beautiful chandeliers, now proudly displayed in their school, as a symbol of commitment to recycling and sustainability.

Plastic recycling at its best: A chandelier designed by the Green Team of Durban Girls' College.

To learn more about Durban Girls' College visit www.dgc.co.za and read the story about the Durban Girls'College Chandelier at the IWWG Art Gallery on www.iwwg.eu.

Social aspects of waste management

The social aspects of waste are often ignored or underestimated by present-day waste management strategies hinged on advanced technology to process the vast amounts of waste produced globally. There is however an increasing appreciation for the need to consider and value these aspects when solving waste problems and finding new solutions.

This is particularly true for developing and transient countries where the Informal Sector plays an important role in waste management. In parts of the world, such as Brazil, efforts have been made to organize and structure the work done by the Informal Sector and to incorporate informal activities into waste management plans. The challenges faced by workers in the Informal Sector are many, ranging from hazardous, unsanitary work conditions to poor remuneration. Waste pickers, also known as "scavengers", looking for recyclable goods on landfills are exposed to toxic fumes, bad hygienic conditions, dangerous compounds lurking in the heaps and ruthless dumping vehicles. The perils are many and the rewards are few however, in countries with high unemployment rates, this form of occupation is sometime the only means of survival for many people.

There are numerous examples of programs where the waste management activities of the Informal Sector have been successfully organized to build the capacity of disadvantaged communities and to improve their living conditions whilst increasing the volumes of waste recovered for recycling, cleaning up polluted areas and introducing treatment procedures that contribute to waste reduction.

Against this background the IWWG has set up a sub-section on its website (www.iwwg.eu) – the social aspects of waste management. Initiated by a joint approach of Cristina van der Westhuyzen and Rainer Stegmann, different aspects of this topic are introduced and reflected by guest editors. We would like to invite you to visit the page and to explore the presented examples. Please let us have your thoughts, suggestions and ideas but first visit the presented examples of projects from Brazil and Cameroon for some really interesting stories.

http://dx.doi.org/10.1016/S0956-053X(16)30583-9

Members Area on the IWWG website

Are you making use of the IWWG Members Area? One of the major benefits (beside the remarkable discounts on conference fees and publications) that IWWG is offering to its members is the access to a special section on the website – reserved for members only. Here you have access to more than 5500 conference papers from different IWWG events over the past 14 years, a fantastic opportunity from the scientific point of view. Moreover, a comfortable 'search-in-papers' function allows for the selection of particular papers through keywords, title and/or author information.

Your personal login-details to the Members Area are communicated to you soon after signing up to the IWWG. After login to the Members Area you may discover several other services provided by the group, such as selected PowerPoint presentations for download, reports from the Task Groups as well as reviews on previous conferences, statistical information on the development of the IWWG as well as our current Rules of Procedure. As special features we are offering our members access to the current as well as past Editorials and Newsletters (News & Views), both published in the official IWWG Journal Waste Management.

If you are already a member to the IWWG you are cordially invited to visit and use the IWWG Members Area; all others may take the opportunity to sign-up online (www.iwwg.eu) and discover a world of benefits.

VENICE 2016 – 6th International Symposium on Energy from Biomass and Waste

The production of energy from alternative sources and its impact on climate change are among the main strategic tools implicated in the sustainable development of our society. Numerous types of biomass and wastes contribute towards the production of energy and reduction in the use of fossil fuels by means of biological, chemical and thermal processes. Existing biomass and waste to energy technologies are currently undergoing rapid development. Despite growing interest in the use of these technologies, in many countries their implementation remains limited.

The aim of the Venice 2016 Symposium is to focus on the advances made in the application of technologies for energy recovery from biomass and waste and to encourage discussion in these fields. The previous edition of the Symposium, held in 2014, was attended by over 500 scientists and operators from approximately 54 different countries.

The sixth edition of the Symposium will feature:

- Three days of scientific presentations.
- One day of guided technical tours at biochemical and thermochemical plants.
- Six parallel oral sessions, poster sessions and an exhibition by companies working in the field.
- Expected attendance of over 600 delegates from tens of different countries worldwide.

The sixth edition of the Symposium will be held in the eminent meeting centre of Scuola Grande di San Giovanni Evangelista in Venice. Internationally renowned as one of the most relevant congress venue, lately it has begun encouraging and hosting famous and fascinating art and architecture exhibitions. It has always been supported by the most prominent institutions, such as the Municipality of Venice and the Veneto Region.

Scuola Grande di San Giovanni Evangelista

The Symposium is organized by the International Waste Working Group (IWWG) and Ordine degli Ingegneri della Provincia di Venezia, with the scientific support of the Universities of Padova, Hokkaido, Queensland, Rostock, Trento, Tsinghua and Hamburg University of Technology.

For any enquiries and information on registration, accommodation, etc., please contact the Organising Secretariat (info@eurowaste.it) or visit the official Symposium website (www.venicesymposium.it). **Please note: IWWG members are entitled to a 10% discount on all entrance fees.**

IWWG TG on thermal treatment: Workshop on "Waste-to-Energy: experiences, projects and expectations in the new markets" during VENICE 2016

The IWWG Task Group on Thermal Treatment already oriented in the past its activities in gathering evidences that the Waste-to-Energy treatments give an essential contribution to reaching the goals of technical reliability, environmental sustainability and economic viability in the waste management systems.

Past experiences were manly related to many European Countries and OECD countries, where several plants are successfully in

Umberto Arena and Lidia Lombardi, Leaders of the IWWG TG on Thermal Treatments

Seoul National University, Republic of Korea

operation, even if in many regions WtE plant capacity is still lacking also because of the local population strong opposition.

However, it is quite evident that WtE plants projects are presently quite few in the traditional west European Countries and the interest is moving towards new markets including the east European Countries and, even more, toward the growing economies as China.

According to this view, the aim of the workshop is to gather experiences, projects and expectations in relation to the above mentioned new markets. To this purpose it is essential to learn from the companies directly involved in those new markets, but also understanding the local rules and, in general, the boundary conditions for the realization of new projects.

More and up-dated information on the TG can also be found on the TG website: https://www.tuhh.de/iue/iwwg/task-groups/thermal-treatments.html

News from the IWWG-ARB

From 12 to 14 April, 2017, the 3rd IWWG-ARB Symposium will be held in Seoul National University, Seoul, Republic of Korea. The IWWG-ARB Symposium is a biennial academic event and one of the main activities of the regional branch. Initiated by the joint RG leaders Toshihiko Matsuto (Hokkaido University, Japan), Pin-jing He (Tongji University, China), and Jae Young Kim (Seoul National University, S. Korea) the 1st edition of the event was held in Hokkaido University, Sapporo, Japan in 2013.

Inspired by the successful Sardinia symposium the 3rd IWWG-ARB Symposium will cover all relevant aspects of waste management and may therefore be considered as the "Asian edition of Sardinia Conference". The organizing committee of the 3rd IWWG-ARB Symposium expects many experts in Asia are eager to join the event since more than 200 experts and students participated in the 2nd Symposium in Tongji University, Shanghai, China in 2015.

Even though the symposium is to exchange knowledge and experience among Asian countries, the symposium is not only for Asian experts but also any IWWG members are welcome. Through the symposium webpage further information will be available and an official announcement will be delivered to members of IWWG soon.

To learn more about the IWWG Regional Branches and to keep you up-dated on future and past activities please visit the Regional Branches section on the IWWG webpage (www.iwwg.eu). Here you may also find the contact details for each of the five RBs.

Group photo in the 2nd IWWG-ARB Symposium, Tongji University, China, 2015

Waste Safe 2017 – 5th International Conference on Solid Waste Management in South Asian Countries – 25–27 February 2017, Khulna, Bangladesh

The success of the previous four successive editions of WasteSafe conference has encouraged the organizer to continue this event at Khulna in every odd year in the month of February. This conference has become an excellent platform for young researchers mostly from developing countries to come in direct contact with world famous and experienced academics and researchers in the field of waste management for exchanging views on solid waste management concepts, innovation and sustainable technologies. Based on the experience of last four events, WateSafe 2017 is going to focus on the innovation of appropriate technologies and also the inclusion of faecal sludge and related waste water issues as thematic areas.

Wastes are normally solids, useless and unwanted. However, many of these materials can be reused, recycled and thus they can become a resource if managed and treated properly. Rapid growth of population, urbanization and industrialization poses sharp increase of waste generation and change of its nature. Due to organizational limitations, lack of people's awareness, absence of appropriate management, financial & resource constraints, ineffectiveness of legislation and law enforcement, wastes remain unmanaged and posed threat to human and nature, especially in the developing countries. To address this issue, Khulna University of Engineering & Technology (KUET) has taken several initiatives since 2002.

WasteSafe 2017 is scientifically supported by the IWWG and will be held in the campus of Khulna University of Engineering & Technology, Bangladesh at Civil Engineering Department. The conference is jointly organized by Khulna University, Bauhaus University Weimar, Germany, University of Padova, Italy and ORBIT Group.

Heartiest thanks to all organizations and/or individuals for rendering cooperation to accomplish this Conference in Khulna. Waste Safe 2017 welcomes all of you at Khulna and promise to have an interesting program and many stimulating discussions in an environment of traditional and simple Bengali hospitality.

To participate in the conference, registration is mandatory paying the conference fee (rates are available from the conference website, www.wastesafe.info). For any clarifications please do not hesitate to contact the WasteSafe 2017 Organizing Secretariat wastesafe.bd@gmail.com.

Future IWWG events

If you are looking for more information on past, present and future events, organized or co-organized by the IWWG, visiting the IWWG website is the straight tip (www.iwwg.eu/activities-events). Here you may find an event calendar, offering a well-structured overview on our events during the previous, present and next year, detailed information on individual conferences or symposia as well as links to the accordant conference websites. For a couple of events comprehensive reports as well as selected photographs are available from the same address.

For further information on IWWG activities, please:

- Access the IWWG Website: www.iwwg.eu
- Contact: Paola Pizzardini – IWWG Secretariat,
  Via Beato Pellegrino 23, 35137 Padova, Italy.
  Tel.: +39 049 8726986; fax: +39 049 8726987.
  E-mail address: info@iwwg.eu

Waste Management 57 (2016) 207–214

Contents lists available at ScienceDirect

Waste Management

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

Beneficiation and recovery of indium from liquid-crystal-display glass by hydrometallurgy

Basudev Swain [a,*], Chinmayee Mishra [a], Hyun Seon Hong [b], Sung-Soo Cho [a]

[a] *Institute for Advanced Engineering, Advanced Materials & Processing Center, Yongin 449-863, Republic of Korea*
[b] *Sungshin University, Dept. of Interdisciplinary ECO Science, Seoul 142-732, Republic of Korea*

ARTICLE INFO

Article history:
Received 9 December 2015
Revised 29 January 2016
Accepted 16 February 2016
Available online 2 March 2016

Keywords:
LCD recycling
Indium–tin–oxide, Indium recovery
Waste management
Recycling

ABSTRACT

Considering indium scarcity, the end-of-life (EOL) LCD, which accounts for up to 90% of market share can be a feasible secondary resource upon successful recycling. In the preferred hydrometallurgical process of such critical metals, leaching is the essential primary and essential phase has been investigated. In this process, LCD was mechanically separated along with other parts from EOL TVs through a smartly engineered process developed at our institute, Institute for Advanced Engineering (IAE), the Republic of Korea. After removing plastics and metals from the LCD, it was mechanically shredded for size reduction. The mechanically shredded LCD waste was leached with HCl for recovery of indium. Possible leaching parameters such as; effect of acid concentration, pulp density, temperature and effect of oxidant H_2O_2 concentration were investigated to identify the best conditions for indium extraction. Indium (76.16×10^{-3} g/L) and tin (10.24×10^{-3} g/L) leaching was achieved at their optimum condition, i.e. lixiviant of 5 M HCl, a pulp density of 500 g/L, temperature 75 °C, agitation speed of 400 rpm and time for 120 min. At optimum condition the glass, plastic and the valuable metal indium have completely been separated. From indium enriched leach liquor, indium can be purified and recovered through hydrometallurgy.

1. Introduction

Due to small weight and volume, low cost, and lower power consumption and heat emissions, currently liquid crystal displays (LCDs) are largely used in the place of the old technology of cathode ray tube (CRT). LCDs are widely used in notebooks, organizers, mobile phones, pocket calculators, measuring and control instruments, electronic games, hand-held miniature TVs, audio-video equipment, large signboards, automotive displays and more and more for PC monitors and TVs. The broad spectrum uses of LCD technology result increases in demand for indium–tin–oxide (ITO), which is a key component in LCD manufacturing. ITO is transparent conducting oxide and is widely used as a transparent conduction oxide thin layer in LCD manufacturing owing to its excellent optoelectronic properties; as transparency to visible light, electric conduction and thermal reflection (Swain et al., 2015a, 2015b). ITO is a mixture of indium (III) and tin (IV) oxides, with a typical composition of 90% In_2O_3 and 10% SnO_2 by weight. According to a recent European Commission report, distribution for worldwide use of virgin indium are as follows: flat panel display 56%, solders 10%, photovoltaics 8%, thermal interface materials 6%, semiconductor and LEDs 3%, alloy and compounds 4% and the others are 8% (European-Union, 2015). The market size of flat display panels, thin-film coatings (indium tin oxide, ITO) accounts for 84–90% (Lee et al., 2013; Polinares, 2012; Rocchetti et al., 2015; Wang, 2009). Worldwide total supply of indium was approximately 1200 tons for the year 2010, which includes 570 tons of primary indium production and the rest was from secondary resources (Charles Gibson, 2011). Charles et al. forecasted 15% annual growth rate for indium demand over the next two years (Charles Gibson, 2011). According to a United States Geological Survey (USGS) report, worldwide total primary production reported at 770 tons in the year 2013 (Jewell and Kimball, 2014). Almost all leading agencies of the world like; United Nations Environment Programme (UNEP) (Buchert et al., 2009), the US Department of Energy (DOE) (Bauer et al., 2010), the European Commission (European-Union, 2014, May), the US National Academy of Sciences (NAS) (Eggert et al., 2007), and the American physical society and materials research society (Jaffe et al., 2011) considered indium as a very critical metal in the supply chain for all terms, i.e., short, medium and long term.

Currently, indium is extracted from primary resources where it is present in concentrations of about 1–100 ppm (Alfantazi and

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* Corresponding author.
E-mail addresses: swain@iae.re.kr, basudevswain@yahoo.com (B. Swain).

http://dx.doi.org/10.1016/j.wasman.2016.02.019
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Moskalyk, 2003), whereas, from 100 to 400 ppm of indium is present in the LCDs (Rocchetti et al., 2015). Considering the lifetime of these electronic devices (generally 3–8 years) (Ma and Xu, 2013), these waste LCDs are a potential alternative secondary resource for indium production through urban mining and proper recycling (Park et al., 2009). A status report on recycling rates of metals reported by United Nations Environment Programme (UNEP) indicates hardly 1% indium bearing end-of-life (EOL) waste being recycled (Graedel, 2015; Graedel et al., 2011). Hence, LCD recycling can be a feasible option to address the critical raw material issue through urban mining. LCD recycling can address issues like environmental impact generated by waste incineration and/or disposal in landfill sites, health hazard from ITO pollution, and also can generate values from these wastes (Kolias et al., 2014; Li et al., 2009; Swain et al., 2015a, 2015b). Recycling of the LCD and recovery of indium can also address various directives like; the waste electrical and electronic equipment (WEEE) directive (became effective on 14 February 2014) (European-Union, 24 July 2012), and restriction of the use of hazardous substances in EEE (RoHS) directive (European-Union, 8 June 2011), UNEP e-waste management strategy and the waste management strategy of extended producer responsibility (EPR) (Swain et al., 2015e). Because of environmental, energy, and the economic benefit, among WEEE, the LCD recycling is becoming an important research focus in the field of urban mining (Rocchetti et al., 2013; Silveira et al., 2015).

Various reports have been reported for indium recovery from ITO through various routes. Park has reported recovery of indium from ITO target scrap by alkaline hydrothermal reaction (Park, 2011). Hong et al. reported recycling of the indium from ITO-sputtering waste, mostly deals with enrichment of indium containing waste powder from sputtering chamber wall (Hong et al., 2010). Hsieh et al. and Li et al. have proposed pure indium recovery method from ITO scraps using hydrometallurgical route (Hsieh et al., 2009; Li et al., 2011). Several waste resources are studied for the recovery of indium, i.e., ITO-scrap (Hsieh et al., 2009; Li et al., 2011; Virolainen et al., 2011), EOL LCD and etching waste (Kang et al., 2011; Liu et al., 2009) as prospective secondary resources for indium. Among all these methods leaching followed by solvent extraction should be the most versatile and flexible method. In the preferred hydrometallurgy process, leaching is the essential primary stage needs to be investigated and optimized. Several authors have reported leaching of indium from ITO of waste LCDs. Rocchetti et al. have reported cross-current leaching of indium from EOL LCD panels where sulfuric acid was used as lixiviant. The best leaching conditions for indium were 2 M sulfuric acid at 80 °C for 10 min, which allowed mobilizing indium completely (Rocchetti et al., 2015). But the leaching process reported is a multistage process to achieve the quantitative leaching. Savvilotidou et al. have reported metals–metalloids leaching method where waste LCDs screens along with polarizers were disassembled and removed via thermal shock, followed by cutting, pulverization and digestion of the shredded material and finally leaching of the metals was evaluated. In their investigation 60% indium leaching could be achieved (Savvilotidou et al., 2015). Considering the leaching efficiency, the reported leaching process by Savvilotidou et al. is hardly preferable in the industry even after scaled up. Dodbiba et al. reported leaching indium from obsolete liquid crystal displays, but the focus of the investigation is mainly associated with the effect of grinding on leaching efficiency rather leaching process optimization (Dodbiba et al., 2012). Li et al. have reported recovery of valuable materials from the waste LCD panel and the reported process for the pretreatment is similar to the process reported Savvilotidou et al., but different lixiviant like (HCl:HNO_3:H_2O = 45:5:50, volume ratio) was used for leaching (Li et al., 2009). The mixture of HCl and HNO_3 is not suitable for industrial application. Fontana et al. have reported indium recovery from waste LCD using 6 M HCl as a lixiviant and polyethylene glycol (PEG) as solvent (Fontana et al., 2015). The reported processes are associated with either tedious pretreatment procedure or complex lixiviant system, makes the industrial recycling a challenge.

In our current research, a simple, flexible, versatile, and worthy to scale up process has been investigated. In this paper, metal beneficiation and indium recovery from LCD glass by hydrometallurgy route have been investigated. Different operative conditions and process parameters like, the effect of HCl concentration, pulp density, and temperature were investigated to identify the best conditions for indium extraction. Unlikely other reported leaching processes, the effect of H_2O_2 was investigated separately to understand the advantages and disadvantages of the use of H_2O_2. Leaching kinetics was investigated to minimize the operation time and add economic values to the process. The investigation of leaching kinetics and the possible leaching without H_2O_2 uses should add value to the process. The approach consists of optimization of indium leaching efficiency and minimization of the other metals co-extraction into the leach liquor. The importance and novelty of the reported process explained below.

(i) The process eliminates tedious pretreatment process prior to leaching.
(ii) Eliminates the use of complex acid lixiviant system like HCl + HNO_3 + H_2O, aqua regia or nitric acid to recover indium, as complex lixiviant are environmentally hazardous and tedious to recover indium through further processing like liquid–liquid extraction.
(iii) Eliminates multistage leaching process, rather the same lixiviant can be used for multiple runs to concentrate and tune the leach liquor for further processing.
(iv) More importantly, the leach liquor generated and tuned by this process can be integrated with our commercially available process, reported elsewhere (Swain et al., 2015a, 2015b). Integrating current leaching process with our reported commercial indium recovery process (Swain et al., 2015b) can be a sustainable greener practical application of cradle-to-cradle technology management and circular economy.
(v) Supports WEEE, RoHS, and EPR directive. An efficient cradle-to-cradle waste management process for the circular economy.

2. Materials and methods

2.1. Materials

The indium rich ITO bearing LCD waste glass was collected from dismantling followed by beneficiation of waste LCD panels. Other chemicals as HCl and H_2O_2 were of analytical grade supplied by Dae-Jung chemical and metal Co, Ltd, the Republic of Korea. The ITO containing LCD glass from scrap LCD is now onward called waste LCD glass.

2.2. Apparatus

Fig.1 shows the leaching reactor used for leaching of the indium rich waste LCD glass. The main reactor vessel is 2000 ml flat-bottomed three-necked rounded top beaker equipped with an overhead agitator driven by a variable-speed motor. A heating mantle was used for heating and a thermostat attached to control the reactor temperature. A thermocouple equipped with digital measurement of temperature during continuous operation of the reactor was used to monitor temperature during leaching.

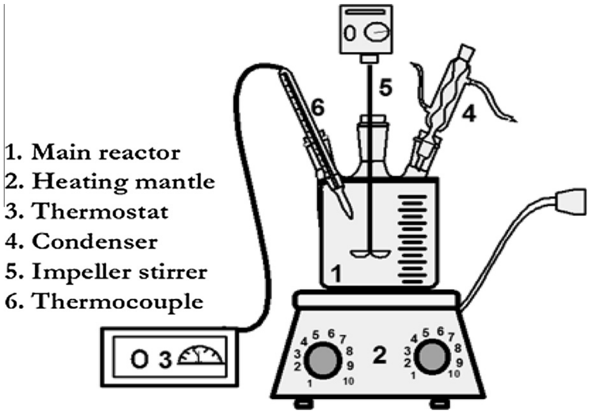

Fig. 1. Schematic for leaching reactor used for the leaching of indium from waste LCD glass.

2.3. Leaching procedure

All the leaching experiments were carried out using the reactor given in Fig. 1. The reflux condenser was used to avoid the vapor loss, heating was provided by an electrical mantle and temperature was controlled by a temperature monitoring apparatus. The required volume of HCl was poured into the reactor and allowed to reach thermal equilibrium, and then the weighted amount of waste LCD glass was added into the reactor. An agitation speed of 400 rpm was used throughout the studies. When required, the H_2O_2 solution was added into the reactor along with waste LCD glass. The 5 ml of the leach samples was drawn periodically at the desired time interval. Various process parameters such as; HCl concentration, H_2O_2 concentrations, pulp density and temperature were optimized. The solid and liquid was separated by filtration.

2.4. Analytical procedure

Concentrations of indium and tin after leaching were measured using ICP-AES (OPTIMA 4300DV, PerkinElmer, USA) after suitable dilution using 5 v/v% of HCl. The maximum deviations permitted were about ±3% in ICP-AES analysis, for temperature controlled processes the deviation were ±2 °C.

3. Results and discussion

3.1. Waste management strategies for waste LCD TVs

Closed loop, cradle-to-cradle processing of waste LCD TVs and develop a circular material flow is the primary management strategy getting developed in our current investigation. Briefly, the core waste management strategies for waste LCD TVs consist of following stages, (i) collection of EOL waste LCD TVs through various channels, (ii) characterization and classification of waste LCD TVs based on materials contents, (iii) disassembly and physical separation of various components, (iv) development of total recycling technology for each component. The EOL waste LCD TVs are collected through various establishments the different stakeholders. The establishment of characterization and classification process includes classification of the waste based on manufacturer and their material value content and create a database for the subsequent automated mechanical separation process. Environment-friendly, techno-economical, efficient disassembly and physical separation of various components followed by valorization process

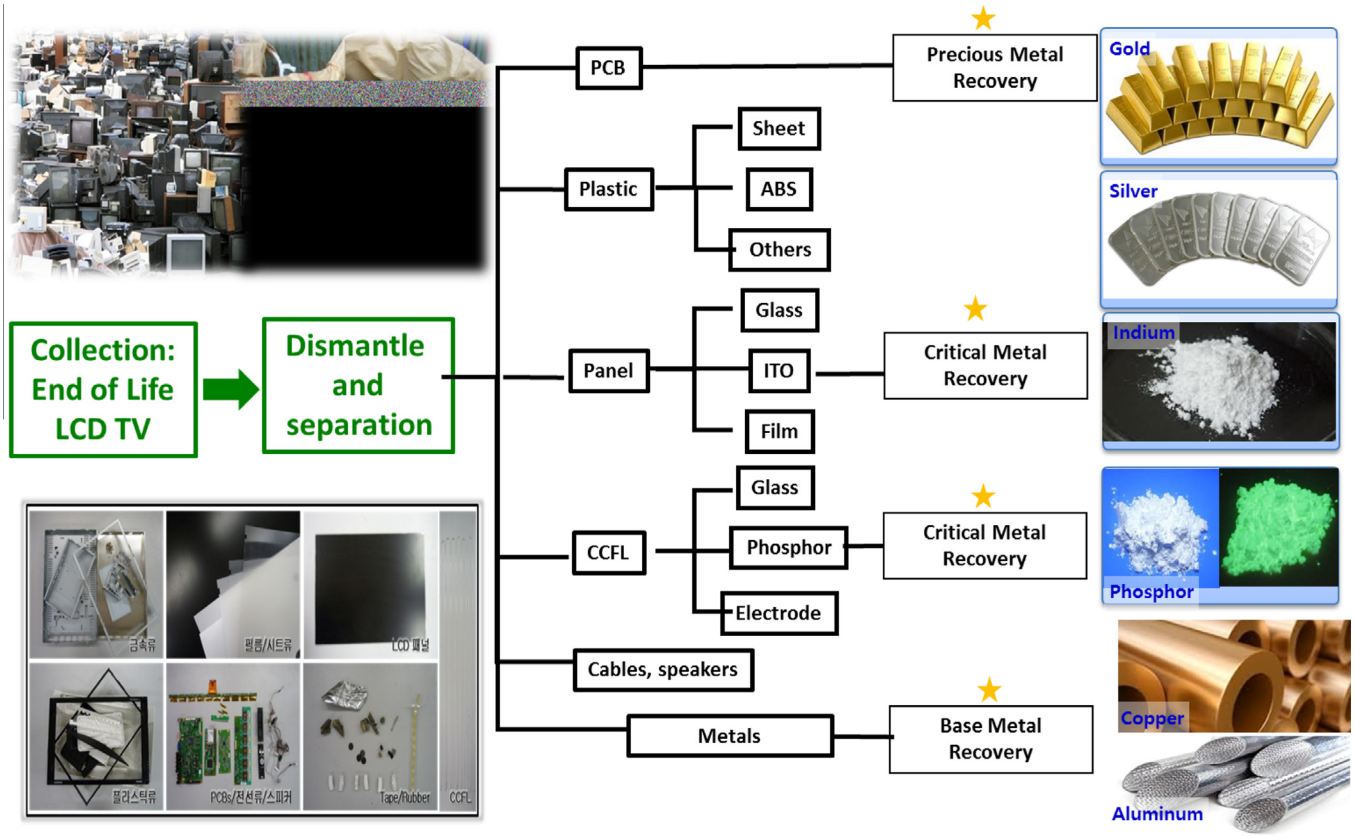

Fig. 2. Flow sheet for dismantling, beneficiation and total recovery process for waste LCD TV.

of each component being established at our institute, Institute for Advanced Engineering (IAE), the Republic of Korea. Fig. 2 shows a waste management strategy through the dismantling of waste LCD TVs in general and Fig. 3 shows waste LCD glass valorization strategy through the recovery of indium in particular. The current investigation is purely motivated for the recycling process development of indium. Hence, the dismantling of waste LCD panels and valorization of indium process has briefly been discussed and indium recovery process thoroughly investigated and reported.

3.2. Dismantling of the waste LCD panels and valorization of indium

In this process, LCD was mechanically separated along with other parts from EOL TVs through a smartly engineered state of the art mechanical process developed at our institute, Institute for Advanced Engineering (IAE), the Republic of Korea. Various parts from EOL TVs were separated individually. Fig. 2 shows flow sheet for dismantling and beneficiation strategy for waste LCD TVs. The same figure shows material and metal values those can be recovered, subsequently, can enter into the material flow stream. From the whole process explained in Fig. 2, the current research is focused on recovery of critical metal, i.e., indium from the ITO bearing LCD panel. The ITO bearing waste LCD glass panels (those were obtained from EOL TV after dismantling and separation of ITO bearing waste LCD glass material) were shredded for size reduction using the locally available shredder machine. Considering the content of indium in the panel hydrometallurgy should be a beneficial and versatile process for recovery of indium from waste LCD glass. For efficient leaching of indium, various leaching parameters have been optimized. The Fig. 3 shows the complete valorization process proposed for recovery of indium from waste LCD glass. The proposed process follows following stages; (i) collection and identification of ITO bearing LCD, (ii) mechanical separation of LCD glass panel from waste TV set, (iii) size reduction through mechanical shredding, (iii) leaching of indium and tin, (iv) indium purification by solvent extraction (SX), and (v) indium recovery or refining. This paper reports about leaching efficiency and optimization leaching parameters varying one parameter at a time. Based on indium and tin chemistry reported elsewhere, the HCl consider to be the best lixiviant for leaching of ITO (Swain et al., 2015a, 2015b, 2015c, 2015d).

3.3. Leaching kinetic

In the present work, we assumed that the indium rich waste ITO coating on the surface is of uniform homogenous surface and once inside the lixiviant the ITO is surrounded by the leaching active components. Different model equations, as explained by Cao et al. (2006) and House and House (2010), like the kinetic equations for the liquid–solid reaction were used for data analysis. A first order kinetics model was the best-fit among all possible models. The leaching efficiency of indium and tin exhibits an exponential growth to a maxima shaped trend as a function of time. A modified exponential equation is proposed to understand leaching kinetics, given in Eq. (1).

$$C_t = C_{max}(1 - exp^{-kt}) \qquad (1)$$

where C_t is the concentration of metal leached at time t, C_{max} is the concentration of metal leached at its maximum level (saturation

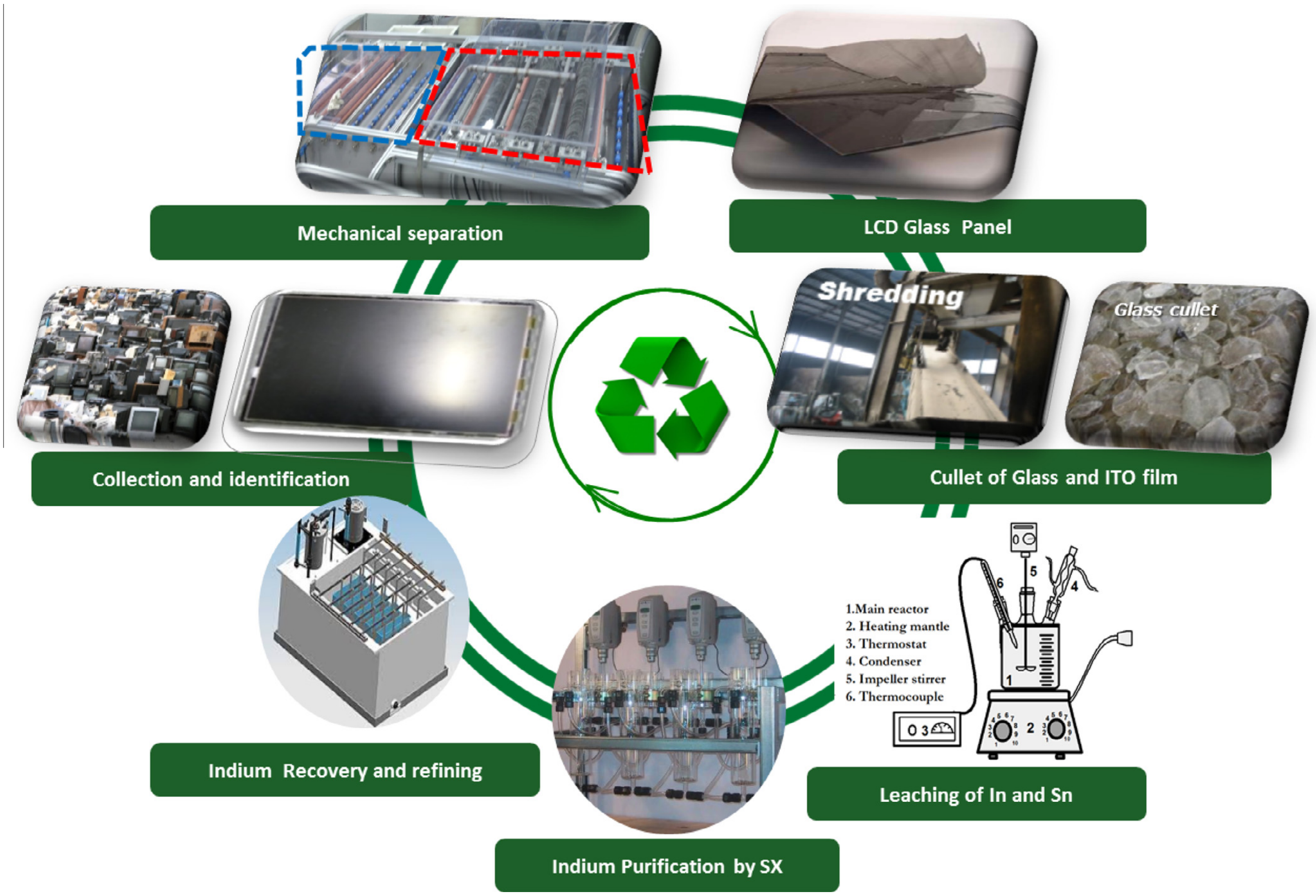

Fig. 3. The complete cycle of proposed process for recovery of indium from ITO bearing waste LCD glass.

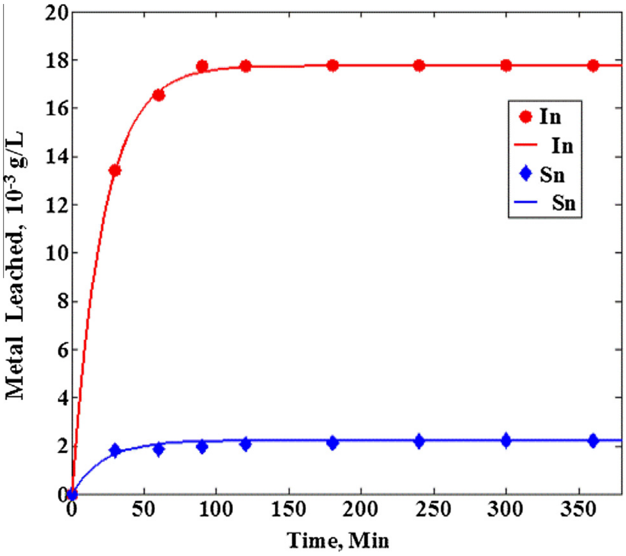

Fig. 4. Leaching of metal versus time, the plot of kinetic equation parameter versus leaching time for the leaching of indium and tin. Experimental condition: 25 °C, 5 M HCl, pulp density = 200 g/L, agitation speed = 400 rpm.

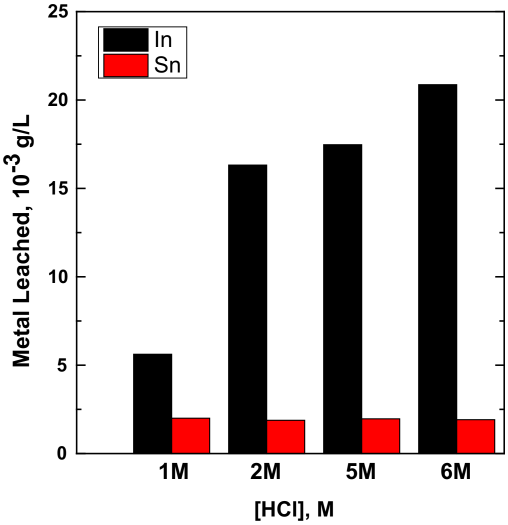

Fig. 5. Effect of HCl concentration on indium and tin leaching. Experimental condition: 25 °C, 120 min, pulp density = 200 g/L, agitation speed = 400 rpm.

point in Fig. 4), *k* is the first order rate constant and *t* is the time in min. As the only surface coated indium rich ITO is leached, but the solid glass remains unaffected, the conventional model of first order equation may be erroneous, hence, a modified rate equation has been used. As shown in Fig. 4, leaching of metal (g/L) versus time in min was fitted using MATLAB® 7.1.10 (2010a), The MathWorks, Inc. USA. The interactive curve fitting procedure was used to predict and understand the validity of the models. A set of best-fit parameters were estimated using the nonlinear least squares method, trust-region algorithms, and least absolute residual (LAR) robust method for performing the minimization of the objective function given by the sum of squares due to error (*SSE*) $\sum_i e_i^2$, for each model and individual curve of the respective model. The error (e) is the difference between the observed and predicted responses for g/L of metal leached as a function of time. The predicted responses are fitted values obtained by evaluating the best-fit equation at the observed values of the independent variable: i.e., concentration of metal leached (g/L). The asymptotic standard error values (SE) were also computed for each best-fit parameter. The coefficient of determination (*R*-square) and coefficient of determination adjusted for the number of coefficients (Adj *R*-square) values for the 95% confidence interval were also computed for each best-fit parameter of metal. In Fig. 4 symbols denote experimental points and line denotes fitted model when it is appropriate.

Fig. 4 shows, fitting of model Eq. (1) for the concentration of indium and tin leached (g/L) as a function of time. The goodness of fit for the leaching kinetics of indium were as such; *SSE* = 0.084, *RMSE* = 0.102, *R*-square = 0.999, and adjusted *R*-square = 0.999. The same figure shows that the goodness of fit for leaching kinetics of tin were as such; *SSE* = 0.144, *RMSE* = 0.134, *R*-square = 0.963, and adjusted *R*-square = 0.963. The statistical parameter values *SSE*, *RMSE*, *R*-square, and adjusted *R*-square values were accurate and desirable up to three significant numbers after the decimal. Hence, the validity of the model was good enough to conclude that the leaching kinetics follows the first order reaction kinetics. As the modified first order integrated form of the equation holds good for both the important element, i.e. indium and tin leached, is considered the leaching kinetics follow the first order reaction. The estimated first order rate constant for indium (k_{In}) is 0.047 ± 0.001 and the first order rate constant for tin (k_{Sn}) is 0.046 ± 0.016. Fig. 4 shows that, after 120 min of leaching, indium and tin concentration remains constant or the leaching kinetics curves have attended the saturation, hence, 120 min time is considered as the optimum condition and was used for further studies.

3.4. Effect of acid concentration on leaching

The effect of HCl concentration on the leaching efficiencies of ITO on the surface of waste LCD glass was studied. The concentration of HCl varied from 1 to 6 M, at a pulp density of 200 g/L, temperature 25 °C, and leaching time 120 min. Fig. 5 shows both indium and tin leaching was increased with the increase in the concentration of HCl. The indium leaching was increased from 5.62×10^{-3} g/L to 21.00×10^{-3} g/L as HCl concentration varied from 1 M to 6 M. The same figure shows that by increasing the HCl concentration, the tin leaching was not changed significantly because completion of the tin leaching at a minimum HCl concentration (Tin leached quantitatively). As an insignificant difference in indium leaching was observed using 5–6 M HCl, from the economy and minimal chemical investment perspective, 5 M HCl was considered for further studies. Although higher concentrations of HCl could achieve the better leaching efficiency, the higher HCl

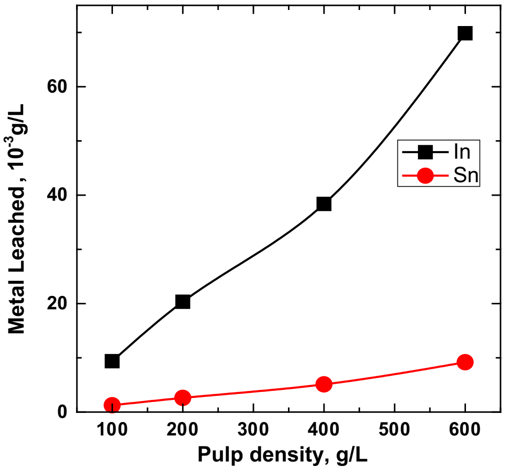

Fig. 6. Effect of pulp density on indium and tin leaching. Experimental condition: 25 °C, 120 min, HCl concentration = 5 M, agitation speed = 400 rpm.

concentration was not preferred because from sustainability, environment, and economy perspective. Considering all these factors, a minimum chemical was used in the process for optimization purpose.

3.5. Effect of pulp density

Effect of pulp density on the leaching efficiencies of indium and tin of waste LCD glass was studied. The experiments were conducted at 100 g/L, 200 g/L, 400 g/L, and 600 g/L at 25 °C and agitation speed of 400 rpm, lixiviant concentration 5 M HCl and time 120 min. Fig. 6 depicts that, with increasing pulp density, indium concentration increased from 9.4×10^{-3} g/L to 69.86×10^{-3} g/L as pulp density increased from 100 g/L to 600 g/L. Whereas tin extraction amount increased from 1.2×10^{-3} g/L to 9.20×10^{-3} g/L as a function pulp density increased from 100 g/L to 600 g/L. By increasing pulp density, metal leaching was increased approximately two fold, fourfold, and six fold, as a function of pulp density 100 g/L, 200 g/L, and 400 g/L, respectively. For pulp density of 600 g/L, the leaching efficiency was the most efficient considering indium leached per unit gram of waste used. Beyond pulp density of 600 g/L is not studied because, at higher pulp density, accommodating temperature control and the total volume of solid and liquid is not possible under the currently designed reactor. Though 600 g/L pulp density provided the best possible leaching considering the volume of waste versus volume of HCl, to provided sufficient surface area exposure into the HCl, the 500 g/L of pulp density is considered for further studies and optimum pulp density.

3.6. Effect of temperature

Effect of temperature on indium and tin leaching efficiency from ITO of waste LCD glass was studied using 5 M HCl, maintaining pulp density at 200 g/L for 120 min. Fig. 7 shows the leaching efficiency of metals increases with increase in leaching temperature. As the temperature was varied from 25 to 100 °C, the indium leaching was increased from 18.54×10^{-3} g/L to 29.50×10^{-3} g/L and tin leaching was increased from 2.27×10^{-3} g/L to 7.36×10^{-3} g/L. Leaching efficiencies of indium and tin at 75 °C is almost same as 100 °C. By increasing the temperature from 25 °C to 75 °C, the indium leaching increased up to 44% over the leaching efficiency that was achieved at 25 °C. However, tin leaching increased up to 182% over the leaching efficiency that was achieved at 25 °C. Higher temperature facilitates the leaching process for higher indium and tin leaching. Beyond the temperature of 75 °C, the leaching efficiency of indium and tin was increased marginally. Temperature beyond 75 °C has led no better selective leaching. Hence, 75 °C temperature can be considered as an optimized condition for carrying out the further experiment. Since leaching is only a part of the total recycling process (Fig. 3), considering the economic and environmental perspective 75 °C temperature should be an effective optimum condition, has considered for further studies.

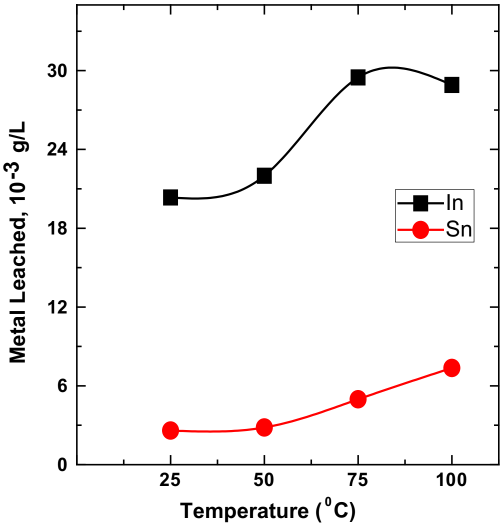

Fig. 7. Effect of temperature on indium and tin leaching. Experimental condition: 120 min, HCl concentration = 5 M, pulp density = 200 g/L, agitation speed = 400 rpm.

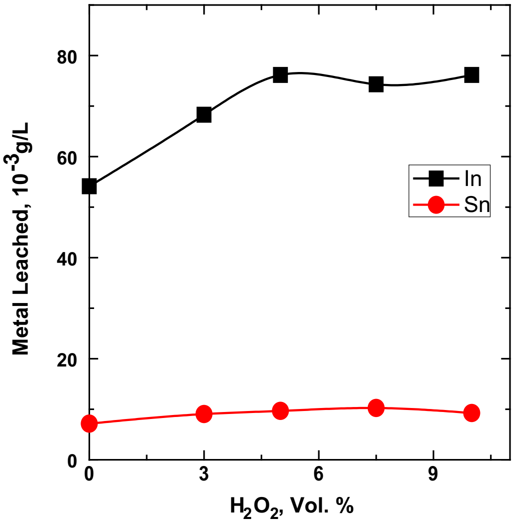

Fig. 8. Effect of oxidant concentration on indium and tin leaching. Experimental condition: 75 °C, 120 min, HCl concentration = 5 M, pulp density = 500 g/L, agitation speed = 400 rpm.

3.7. Effect of oxidant concentration

The leaching behavior of indium and tin from waste LCD glass was studied using H_2O_2 as an oxidant. Effect of H_2O_2 concentration (3 v/v%, 5 v/v%, 7.5 v/v%, and 10 v/v%) was investigated. Experiments are performed at 5 M HCl acid, pulp density 500 g/L, temperature 75 °C, and agitation speed 400 rpm. Fig. 8 shows that metal extractability increases with increase in oxidant concentration. Indium extraction increased from 54.11×10^{-3} g/L to 76.16×10^{-3} g/L as the volume of H_2O_2 increased from 0 v/v% to 10 v/v% and tin extraction increased from 7.14×10^{-3} g/L to 10.24×10^{-3} g/L. Leaching efficiency attains its maximum value at 10 v/v%. Hence, this value considered being the optimized value.

3.8. Waste ITO leaching chemistry and mechanism

As explained above, the ITO is a mixture of indium (III) and tin (IV) oxides, with a 90% of In_2O_3 and 10% of SnO_2 by weight. The ITO leaching chemistry using concentrated HCl can be explained as below using Eqs. (2)–(6). In the leaching process In_2O_3 is leached as $InCl_3$ and get soluble as a trivalent hexa-aquo-complex $[In(H_2O)_6]^{3+}$. Similarly, SnO_2 leached as $SnCl_4$ and soluble as divalent hexa-chloro-complex $[SnCl_6]^{2-}$.

$$In_2O_3 + 6HCl \xrightarrow{\text{Conc. HCl}} 2InCl_3 + 3H_2O \tag{2}$$

$$InCl_3 + 6H_2O \leftrightarrow [In(H_2O)_6]^{3+} + 3Cl^- \tag{3}$$

$$SnO_2 + 4HCl \xrightarrow{\text{Conc. HCl}} SnCl_4 + 2H_2O \tag{4}$$

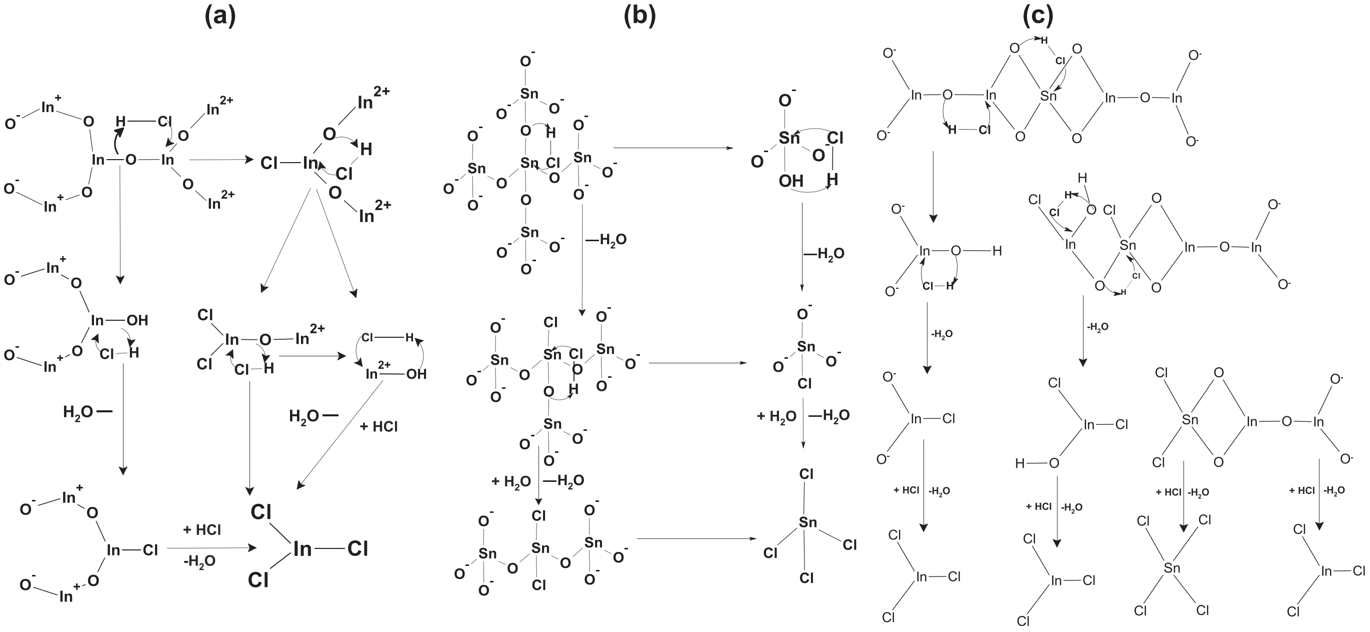

Fig. 9. Leaching Mechanism of (a) In_2O_3, (b) SnO_2, and (c) ITO in the concentrated HCl.

$$SnCl_4 + 2Cl^- \leftrightarrow [SnCl_6]^{2-} \tag{5}$$

$$In_2O_3SnO_2 + 10HCl \xrightarrow{\text{Conc. HCl}} 2InCl_3 + SnCl_4 + 5H_2O \tag{6}$$

Fig. 9 shows the leaching mechanism of the ITO coating from the surface of waste LCD. Fig. 9(a) shows a leaching mechanism for In_2O_3. The leaching process is initiated with an attack of HCl on the surface of ITO coating. The HCl dissociate as Cl^- and H^+, the Cl^- form a bond with indium moiety (In–Cl) and triggers In-O bond dissociation by forming an intermediate In–O–H bonding. Finally, from In–OH the OH^- substituted by Cl^- and form an In–Cl bond. The reaction continues until $InCl_3$ formation in the leach liquor. Fig. 9(b) shows the leaching mechanism for SnO_2. Fig. 9(c) shows the leaching mechanism for $In_2O_3SnO_2$ (ITO) from a representative molecule. The leaching mechanism in general and the substitution, association, and dissociation reaction for SnO_2 and $In_2O_3SnO_2$ are very similar to In_2O_3. As In_2O_3 to $InCl_3$ leaching reaction, the SnO_2 reaction continues until $SnCl_4$ dissolve into leach liquor.

4. Conclusions

The indium rich ITO bearing waste LCD glass can be leached easily by a cost effective method using HCl as lixiviant. Indium (76.16×10^{-3} g/L) and tin (10.24×10^{-3} g/L) leaching was achieved at their optimum condition, i.e., lixiviant of 5 M HCl, a pulp density of 500 g/L, temperature 75 °C, H_2O_2 of 10 v/v%, agitation speed of 400 rpm and time for 120 min. Indium rich LCD waste glass can be leached quantitatively. A cost effective, environment friendly hydrometallurgy process can be developed for the recycling of the indium rich ITO bearing waste LCD glass. It was observed from the experiments and kinetic analysis that, the kinetic model: $C_t = C_{max}(1 - exp^{-kt})$ was the most suitable to describe the leaching process of the indium rich ITO bearing waste LCD glass in the HCl solution. Integrating current leaching process with our reported commercial indium recovery process can be a sustainable and practical application of cradle to cradle technology management and circular economy. The proposed leaching process is a sustainable and clean technology, as minimum energy and no hazardous chemicals were used for processing.

Acknowledgements

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project No.: GT-11-C-01-020-0), Republic of Korea.

Appendix

Goodness-of-Fit Statistics was concluded by the following assumption, when

The sum of squares due to error (SSE) $\xrightarrow{\lim} 0$
R-square $\xrightarrow{\lim} 1$
Adjusted *R*-square $\xrightarrow{\lim} 1$
Root mean squared error (*RMSE*) $\xrightarrow{\lim} 0$
least absolute residual (LAR)

$$SSE = \sum_{i=1}^{n} w_i (y_i - \hat{y}_i)^2$$

Given these definitions, *R*-square is expressed as

$$R\text{-square} = \frac{SSR}{SST} = 1 - \frac{SSE}{SST} \tag{7}$$

The sum of squares of the regression (*SSR*) is defined as

$$SSR = \sum_{i=1}^{n} w_i (\hat{y}_i - \bar{y})^2 \tag{8}$$

SST is also called the sum of squares about the mean and is defined as

$$SST = \sum_{i=1}^{n} w_i (y_i - \bar{y})^2 \tag{9}$$

where $SST = SSR + SSE$. Given these definitions, R-square is expressed as

$$R\text{-square} = \frac{SSR}{SST} = 1 - \frac{SSE}{SST}$$

$$\text{adjusted } R\text{-square} = 1 - \frac{SSE(n-1)}{SST(v)}$$

Degrees of freedom adjusted R-square

This statistic used for the R-square statistic defined above and adjusts it based on the residual degrees of freedom. The residual degrees of freedom are defined as the number of response values n minus the number of fitted coefficients m estimated from the response values. $v = n - m$, v: indicates the number of independent pieces of information involving the n data points that are required to calculate the sum of squares.

Root Mean Squared Error is defined as

$$RMSE = s = \sqrt{MSE}$$

where MSE is the mean square error or the residual mean square

$$MSE = \frac{SSE}{v}$$

References

Alfantazi, A.M., Moskalyk, R.R., 2003. Processing of indium: a review. Minerals Eng. 16, 687–694.

Bauer, D., Diamond, D., Li, J., Sandalow, D., Telleen, P., Wanner, B., 2010. U.S. Department of Energy (DOE) Critical Materials Strategy. U.S. Department of Energy (DOE).

Buchert, M., Schüler, D., Bleher, D., 2009. Sustainable innovation and technology transfer industrial sector studies, Critical Metals For Future Sustainable Technologies And Their Recycling Potentia. Öko-Institut e.V, Darmstadt, Germany.

Cao, Yucai, Harjanto, Sri, Shibayama, Atsushi, Naitoh, Isao, Nanami, Toshiyuki, Kasahara, Koichi, Okumura, Yoshiharu, Fujita, T., 2006. Kinetic study on the leaching of Pt, Pd and Rh from automotive catalyst residue by using chloride solutions. Mater. Trans. 47, 2015–2024.

Charles Gibson, T.H., 2011. Indium and gallium overview. In: Limited, E.I.R. (Ed.), Edison Investment Research. Lincoln House, High Holborn, London, WC1V 7JH, pp. 296–302, <http://www.edisoninvestmentresearch.com/sectorreports/IndiumGalliumOverview071011.pdf>.

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

Eggert, Roderick G., Carpenter, A.S., Freiman, Stephen W., Graedel, Thomas E., Meyer, Drew A., McNulty, Terrence P., Moudgil, B.M., Poulton, Mary M., Surges, Leonard J., Eide, Elizabeth A., Rogers, Nicholas D., 2007. Minerals, Critical Minerals, and the U.S. Economy. The National Research Council, The National Academy of Sciences, Washington, D.C.

European-Union, 2011. THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION, Directive 2011/65/EU of the European Parliament and of the Council of 8 June 2011 on the restriction of the use of certain hazardous substances in electrical and electronic equipment Text with EEA relevance. Off. J. Eur. Union OJ L 174 (1.7.2011), 88–110.

European-Union, 2012. THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION, Directive 2012/19/EU of the European parliament and of the council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Off. J. Eur. Union 55, 38.

European-Union, The European Commision, May 2014. Report on critical raw materials for the EU. In: Materials, Members of the EU Ad-Hoc Working Group on Raw Materials (Eds.), Report of the Ad hoc Working Group on Defining Critical Raw Materials. European Commission, DG Internal Market, Industry, Entrepreneurship and SMEs Communication, Brussels (Belgium).

European-Union, The European Commision, 2015. Report on critical raw materials for the EU, CRITICAL RAW MATERIALS PROFILES Ref. Ares (2015) 1819595–29/04/2015.

Fontana, D., Forte, F., De Carolis, R., Grosso, M., 2015. Materials recovery from waste liquid crystal displays: a focus on indium. Waste Manage. 45, 325–333.

Graedel, T.E., 2015. Recycling rates of metals, a status report. In: International Resources Panel, Working group on the Global Metal Flows (Eds.), International Resources Panel, United Nation Environment Programme, <http://www.unep.org/resourcepanel/Portals/24102/PDFs/Metals_Recycling_Rates_110412-1.pdf>.

Graedel, T.E., Allwood, J., Birat, J.-P., Buchert, M., Hagelüken, C., Reck, B.K., Sibley, S.F., Sonnemann, G., 2011. What do we know about metal recycling rates? J. Ind. Ecol. 15, 355–366.

Hong, H., Jung, H., Hong, S.-J., 2010. Recycling of the indium scrap from ITO sputtering waste. Res. Chem. Intermed. 36, 761–766.

House, J., House, J.E., 2010. Inorganic Chemistry. Elsevier Science.

Hsieh, S.-J., Chen, C.-C., Say, W.C., 2009. Process for recovery of indium from ITO scraps and metallurgic microstructures. Mater. Sci. Eng.: B 158, 82–87.

Jaffe, Robert, Price, Jonathan, Ceder, Gerbrand, Eggert, Rod, Graedel, Tom, Gschneidner, Karl, Hitzman, Murray, Houle, Frances, Hurd, Alan, Kelley, Ron, King, Alex, Milliron, Delia, Skinner, Brian, Slakey, Francis, 2011. Energy Critical Elements, Securing Materials for Emerging Technologies. American Physical Society, Washington, DC.

Jewell, Sally, Kimball, S.M., 2014. USGS Mineral Commodities Summaries: 2014. U.S. Geological Survey, Reston, Virginia, <http://minerals.usgs.gov/minerals/pubs/mcs/2014/mcs2014.pdf>.

Kang, H.N., Lee, J.-Y., Kim, J.-Y., 2011. Recovery of indium from etching waste by solvent extraction and electrolytic refining. Hydrometallurgy 110, 120–127.

Kolias, K., Hahladakis, J.N., Gidarakos, E., 2014. Assessment of toxic metals in waste personal computers. Waste Manage. 34, 1480–1487.

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

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

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

Liu, H.-M., Wu, C.-C., Lin, Y.-H., Chiang, C.-K., 2009. Recovery of indium from etching wastewater using supercritical carbon dioxide extraction. J. Hazard. Mater. 172, 744–748.

Ma, E., Xu, Z., 2013. Technological process and optimum design of organic materials vacuum pyrolysis and indium chlorinated separation from waste liquid crystal display panels. J. Hazard. Mater. 263 (Part 2), 610–617.

Park, J.-C., 2011. The recovery of indium metal from ITO-scrap using hydrothermal reaction in alkaline solution. Bull. Korean Chem. Soc. 32, 3796–3978.

Park, K.-S., Sato, W., Grause, G., Kameda, T., Yoshioka, T., 2009. Recovery of indium from In_2O_3 and liquid crystal display powder via a chloride volatilization process using polyvinyl chloride. Thermochim. Acta 493, 105–108.

Polinares, 2012. Fact Sheet: Indium. <http://www.polinares.eu/docs/d2-1/polinares_wp2_annex2_factsheet5_v1_10.pdf> (Access Date 08.12.2015).

Rocchetti, L., Vegliò, F., Kopacek, B., Beolchini, F., 2013. Environmental impact assessment of hydrometallurgical processes for metal recovery from WEEE residues using a portable prototype plant. Environ. Sci. Technol. 47, 1581–1588.

Rocchetti, L., Amato, A., Fonti, V., Ubaldini, S., De Michelis, I., Kopacek, B., Vegliò, F., Beolchini, F., 2015. Cross-current leaching of indium from end-of-life LCD panels. Waste Manage. 42, 180–187.

Savvilotidou, V., Hahladakis, J.N., Gidarakos, E., 2015. Leaching capacity of metals–metalloids and recovery of valuable materials from waste LCDs. Waste Manage. 45, 314–324.

Silveira, A.V.M., Fuchs, M.S., Pinheiro, D.K., Tanabe, E.H., Bertuol, D.A., 2015. Recovery of indium from LCD screens of discarded cell phones. Waste Manage. 45, 334–342.

Swain, B., Mishra, C., Hong, H.S., Cho, S.-S., 2015a. Treatment of indium–tin–oxide etching wastewater and recovery of In, Mo, Sn and Cu by liquid–liquid extraction and wet chemical reduction: a laboratory scale sustainable commercial green process. Green Chem. 17, 4418–4431.

Swain, B., Mishra, C., Hong, H.S., Cho, S.-S., Lee, S.k., 2015b. Commercial process for the recovery of metals from ITO etching industry wastewater by liquid–liquid extraction: simulation, analysis of mechanism, and mathematical model to predict optimum operational conditions. Green Chem. 17, 3979–3991.

Swain, B., Mishra, C., Kang, L., Park, K.-S., Lee, C.G., Hong, H.S., 2015c. Recycling process for recovery of gallium from GaN an e-waste of LED industry through ball milling, annealing and leaching. Environ. Res. 138, 401–408.

Swain, B., Mishra, C., Kang, L., Park, K.-S., Lee, C.G., Hong, H.S., Park, J.-J., 2015d. Recycling of metal–organic chemical vapor deposition waste of GaN based power device and LED industry by acidic leaching: process optimization and kinetics study. J. Power Sour. 281, 265–271.

Swain, B., Mishra, C., Lee, C.G., Park, K.-S., Lee, K.-J., 2015e. Valorization of GaN based metal–organic chemical vapor deposition dust a semiconductor power device industry waste through mechanochemical oxidation and leaching: a sustainable green process. Environ. Res. 140, 704–713.

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

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

Waste Management 57 (2016) 215–219

Contents lists available at ScienceDirect

Waste Management

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

Combined oxidative leaching and electrowinning process for mercury recovery from spent fluorescent lamps

Cihan Ozgur[a], Sezen Coskun[b,*], Ata Akcil[c], Mehmet Beyhan[a], Ismail Serkan Üncü[d], Gokhan Civelekoglu[a]

[a] Department of Environmental Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey
[b] Egirdir Vocational School, Suleyman Demirel University, TR32500 Egirdir, Isparta, Turkey
[c] Mineral-Metal Recovery and Recycling Research Group, Mineral Processing Division, Department of Mining Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey
[d] Department of Electrical and Electronic Engineering, Suleyman Demirel University, TR32260 Isparta, Turkey

ARTICLE INFO

Article history:
Received 30 September 2015
Revised 30 January 2016
Accepted 21 March 2016
Available online 31 March 2016

Keywords:
Mercury recovery
Electrowinning
Leaching
E-waste
Spent fluorescent lamps

ABSTRACT

In this paper, oxidative leaching and electrowinnig processes were performed to recovery of mercury from spent tubular fluorescent lamps. Hypochlorite was found to be effectively used for the leaching of mercury to the solution. Mercury could be leached with an efficiency of 96% using 0.5 M/0.2 M NaOCl/NaCl reagents at 50 °C and pH 7.5 for 2-h. Electrowinning process was conducted on the filtered leaching solutions and over the 81% of mercury was recovered at the graphite electrode using citric acid as a reducing agent. The optimal process conditions were observed as a 6 A current intensity, 30 g/L of reducing agent concentration, 120 min. electrolysis time and pH of 7 at the room temperature. It was found that current intensity and citric acid amount had positive effect for mercury reduction. Recovery of mercury in its elemental form was confirmed by SEM/EDX. Oxidative leaching with NaOCl/NaCl reagent was followed by electrowinning process can be effectively used for the recovery of mercury from spent fluorescent lamps.

1. Introduction

Waste of electrical and electronic equipment commonly known as e-waste includes various forms of all electric and electronic apparatus which are at the end of its life. Some e-wastes such as televisions, computer monitors and fluorescent lamps contain Hg (mercury) (Bhutta et al., 2011; Garlapati, 2016). Due to the toxic effect of mercury, the disposal of e-wastes together with municipal wastes causes environmental problems in the landfill areas. Mercury is essential to the operation of fluorescent lamps. Distribution of electrical and electronic waste was determined in EU Directive 2002/96. Spent lamps were calculated 1.7% of total electrical and electronic wastes as the 5B lighting equipment e-waste group by European Union in 2005 (Erust et al., 2013; EU Directive 2002/96). E-waste stream is very fast growing in the modern world (Huang et al., 2009; Behnamfard et al., 2013) and these wastes should to be designed considering their recycle and reuse potential (Petter et al., 2014; Sahin et al., 2015). Though the lighting industry has achieved significant reductions in mercury content, the mercury is still an important component for the working of fluorescent lamps (NEMA, 2002; Tunsu et al., 2015). When the spent fluorescent lamps are improperly discarded, mercury may contaminate soil and water resources and it can be harmful to the humans and other organisms. Therefore, the recovery of mercury from spent fluorescent lamps would reduce the amount of waste, thus reducing the potential environmental risks (Durão et al., 2008; Coskun and Civelekoglu, 2014, 2015).

Hydrometallurgy process called as leaching had been widely applied for metal recovery from electronic wastes because of its' flexible and energy-saving characteristics (Kinoshita et al., 2003; Lai et al., 2008). However, acidic-leaching was usually applied to obtain high mercury yields in the studies (Rey-Raap and Gallardo, 2013; Tunsu et al., 2014), potential health risks and environmental impacts of using acidic reagents should be considered. In addition, acidic reagents used in the process caused to extraction of other metals (e.g., Al, Mn, Cu, Zn and Cd) solution and it may lead to reduce the efficiency of mercury leaching (Kalb et al., 1999; Coskun and Civelekoglu, 2014, 2015). Therefore, oxidative sodium hypochlorite (NaOCl)/sodium chloride (NaCl) was selected and conducted as oxidative leaching solution to extract mercury as Hg(II) complex as mercury tetra chloride, $HgCl_4^{2-}$ according to Eq. (1) (Twidwell and Thompson, 2001).

$$Hg_{(solid)} + HOCl + 3Cl^- \rightarrow HgCl_4^{2-}{}_{(aqueous)} + OH^- \quad K_f = 5.0 \times 10^{15} \qquad (1)$$

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* Corresponding author.
E-mail address: sezencoskun@sdu.edu.tr (S. Coskun).

http://dx.doi.org/10.1016/j.wasman.2016.03.039

In order to recovery of mercury from the leaching solution, it needs to be reduced to its elemental state (Hg^0). After oxidative leaching, mercury can be recovered as a Hg^0 from the leachate by suitable separation processes such as cementation, ion exchange, solvent extraction, biodegradation/bioreduction, heterogeneous photocatalysis, electrowinning and hybrid use of these processes (Cui and Zhang, 2008; Bussi et al., 2010; Chaturabul et al., 2015). The electrowinning technology was successfully applied electroplating process to recover heavy metals from concentrated leaching solutions (Vegliò et al., 2003). This process is attractive due to its versatility, energy efficiency, simple equipment, easy operation, and low operation cost (Jüttner et al., 2000; Meunier et al., 2006; Lai et al., 2008). However, little information is available about recovery of mercury using electrowinning from spent fluorescent lamps. The dissolved mercury in leachate can be recovered by cathodic reduction according to Eq. (2). On the other hand, mercury agglomerating may occur at the electrode surfaces. This may lead to Hg_2Cl_2 precipitation according to Eq. (3). When the solution pH goes down below 4, Hg_2Cl_2 is formed (Hummer et al., 2006). Therefore, neutral pH (pH of 7) condition was provided for electrowinning experiments in the current study

$$HgCl_{4\ (aqueous)}^{2-} + 2e^- \rightarrow Hg^0 + 4Cl^- \tag{2}$$

$$Hg^0 + Hg^{2+} + 2Cl^- \rightarrow Hg_2Cl_{2(s)} \tag{3}$$

In the present study, electrowinning process was applied for convert mercury to its metallic state after oxidative (hypochlorite) leaching of mercury from spent tubular fluorescent lamps. The optimal process conditions for high efficiency of recovery were identified.

2. Material and methods

2.1. Sample preparation and oxidative leaching tests

Spent fluorescent lamps were collected from hospitals, schools and factories in the city center of Isparta, Turkey. T8 and T12 linear (tubular) types of spent fluorescent lamps were selected for study owing to their high rate of consumption around the world (Coskun and Civelekoglu, 2015). These lamps also have higher mercury content than the other mercury-containing lamps such as T2, T5 and compact fluorescent lamps (CFLs) (Hu and Cheng, 2012). Each spent fluorescent lamp was manually dismantled under vacuum in laboratory. The oxidative leaching experiments were conducted on pulverized mixture samples of lamps (50–50% mixture of the T8 and T12 lamps) to simulate a realistic situation. Sample preparation method was described in detail by Coskun and Civelekoglu (2015).

To determine the initial mercury concentration of lamps, 20 g pulverized samples were extracted with 25 mL water and 25 mL aqua regia (HCl/HNO_3, v/v - 3/1) in polypropylene flasks using a magnetic stirrer at 200 rpm (Heidolph MR Hei-Tec 3001) at room temperature for 18 ± 2 h. Each sample was filtered through funnels using following the mixing stage. The initial mercury concentrations were determined using atomic absorption spectrophotometer (AAS) (PerkinElmer-FIMS 400, attached with flow injection automated system). NaOCl (6–14% active chlorine, Merck 105614) and NaCl (extra pure, Merck 106400) were used as chemical (oxidative) leaching reagents to extract mercury from pulverized lamp samples. The leaching tests were performed in 250 mL polypropylene flasks placed in temperature-controlled water baths (GFL 1086) with mechanical stirrers. During the leaching tests, the pH of the solutions was monitored using a digital pH meter (WTW multi, 340i). The solutions were filtered (20 μm, pure cellulose filter papers), and analyzed for their mercury content to quantify leaching efficiency. Each sample was diluted by a factor of 1:10 using nitric acid solution (pH = 2) to avoid the precipitation of metals and then stored at 4 °C for further analysis using AAS. Quantification of leaching efficiency was determined by comparing initial mercury concentration in extracted lamp sample solutions and final mercury concentration in filtered leaching solutions. All mercury analysis were based on Method 7471B (Mercury in solid or semisolid waste-manual cold vapor technique) from USEPA's "Test methods for evaluating solid waste-physical/chemical method" (SW-846) (USEPA, 1998).

2.2. Electrowinning tests

Leaching process was followed by electrowinning and oxidative leaching solution was used as electrolyte in this process. The reaction system was comprised of a 150 mL glass reactor with one graphite electrode (0.5 cm diameter, 6 cm length), acting as the cathode, one dimensionally stable anode (DSA®) (2 cm width, 5 cm length), which is made of titanium substrate with a thin layer of iridium oxide (IrO_2) acting as the anode of the electrolytic cell. A power supply (GW Instek GPR-1820 HD) that provides electric current (0–10 A and 0–18 V) was used to provide electric current. While the applied current was constant (e.g., 2, 4 or 6 A), the voltage value was varied from 7 to 12 V between the two electrodes during the experiments. All electrowinning tests were carried at room temperature and pH of 7. The pH values were adjusted using reagent grade NaOH and/or HCl solutions with different molar concentrations (0.2 M–0.5 M–1 M). The electrodes were connected parallel to the power supply and the mercury was analyzed with AAS.

Citric acid ($C_6H_8O_6$, Merck-818707) was added into filtered leaching solution as a reducing agent. The effects of the current intensity (A), citric acid amount (g/L), electrolysis time (min.) on process yield were evaluated on basis of 2^3 full factorial designs (Table 1) at 25 °C of temperature. The central point tests were used to evaluate the experimental error of electrowinnig process and therefore the SE (standard error) for the effects. The experimental matrix was designed according to Yates Algorithm (Montgomery, 1991).

The graphite electrodes were analyzed before and after of electrowinnig process by scanning electron microscope coupled with an energy-dispersive X-ray spectrophotometer (SEM/EDX) (FEI Quanta250 FEG) to investigate the elemental compositions.

3. Results and discussion

3.1. Leaching tests

Oxidative leaching tests were carried out to determine the optimal leaching conditions in terms of simultaneous mercury extractions. Mercury could be leached by NaOCl/NaCl reagent with an efficiency of 96% from real spent fluorescent lamps at 2-h contact time, 50 °C of temperature, pH 7.5 and 120 rpm agitation speed (Coskun and Civelekoglu, 2015). The addition of chloride ions

Table 1
Factors and levels investigated in electrowinning tests.

Code	Factor (variable)	Level		
		−1	0	+1
A	Current intensity (A[a])	2	4	6
B	Citric acid amount (g/L)	5	15	30
C	Electrolysis time (min)	30	60	120

[a] Ampère (A).

provided to increase the solubility of mercury through forming the soluble and stable complex of $HgCl_4^{2-}$ at neutral conditions. This process was found to be more environmental friendly than the acidic leaching of mercury. All leaching tests were carried out using this combination, prior to conducting the electrowinning tests.

3.2. Electrowinning tests

Complex of $HgCl_4^{2-}$ which was present in leaching solution transferred to the elemental mercury during electrowinning process. Electrowinning efficiencies were displayed in Fig. 1a. As seen from this figure, recovery efficiency of factor 1 (minimum current intensity, citric acid amount and electrolysis time) was found lower than the central point tests. When all of these factors increased to the average value (factor 0: A, current intensity 4 A; B, citric acid amount 15 g/L; and C, time 60 min.), the recovery efficiency also increased from a rate of 27–62% (Fig 1a). Citric acid was used as the reductant agent for the conversion of Hg (II) to Hg (0). Efficiency of factor A (maximum current intensity 6 A; minimum citric acid amount 5 g/L; and minimum electrolysis time 30 min.) and factor C (minimum current intensity 2 A; minimum citric acid amount 5 g/L; and maximum electrolysis time 120 min.) was measured low (Fig. 1a). However, factor B was found higher recovery yield than the factor A and C. According to these results, citric acid amount was more effective than current intensity and electrolysis time in the process. In addition, AB and ABC factors had high recovery efficiencies (about 77% and 81%, respectively). Therefore, the recovery efficiency was increased by the increasing current intensity and citric acid amount. The maximum electrowinning efficiency was calculated as 81% (Fig. 1a, ABC). Efficiency of mercury recovery was slightly increased with maximum of all factors (current intensity: A, citric acid amount: B and electrolysis time: C).

ANOVA method was used to evaluate the effect of the main factors on the process of electrowinning and the results were summarized in Fig. 1b. F test statistics was used to evaluate factor coefficients for significance at 95% ($p = 0.05$) confidence level. The calculated SE value using central point experiment of electrowinning was 6.76. The factors “C, “AC” and “ABC” were determined to be statistically insignificant ($p > 0.05$) and these factors were excluded from the figure (Fig. 1b).

It was found that current intensity (A) and citric acid amount (B) had positive effect for mercury reduction (Fig 1b, A; +19% and B; +28%). Furthermore, interaction effects of these variables (AB)

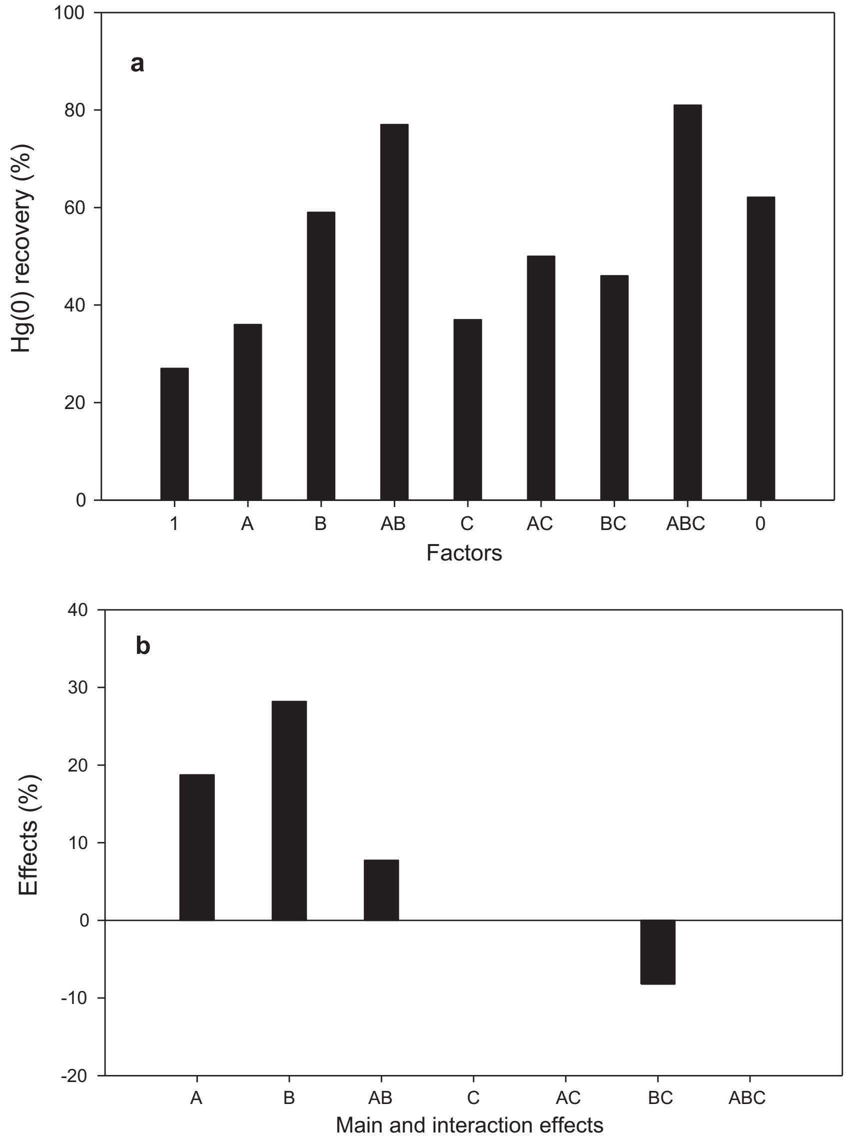

Fig. 1. Electrowinning process mercury extraction yield (a) and extraction effects (b).

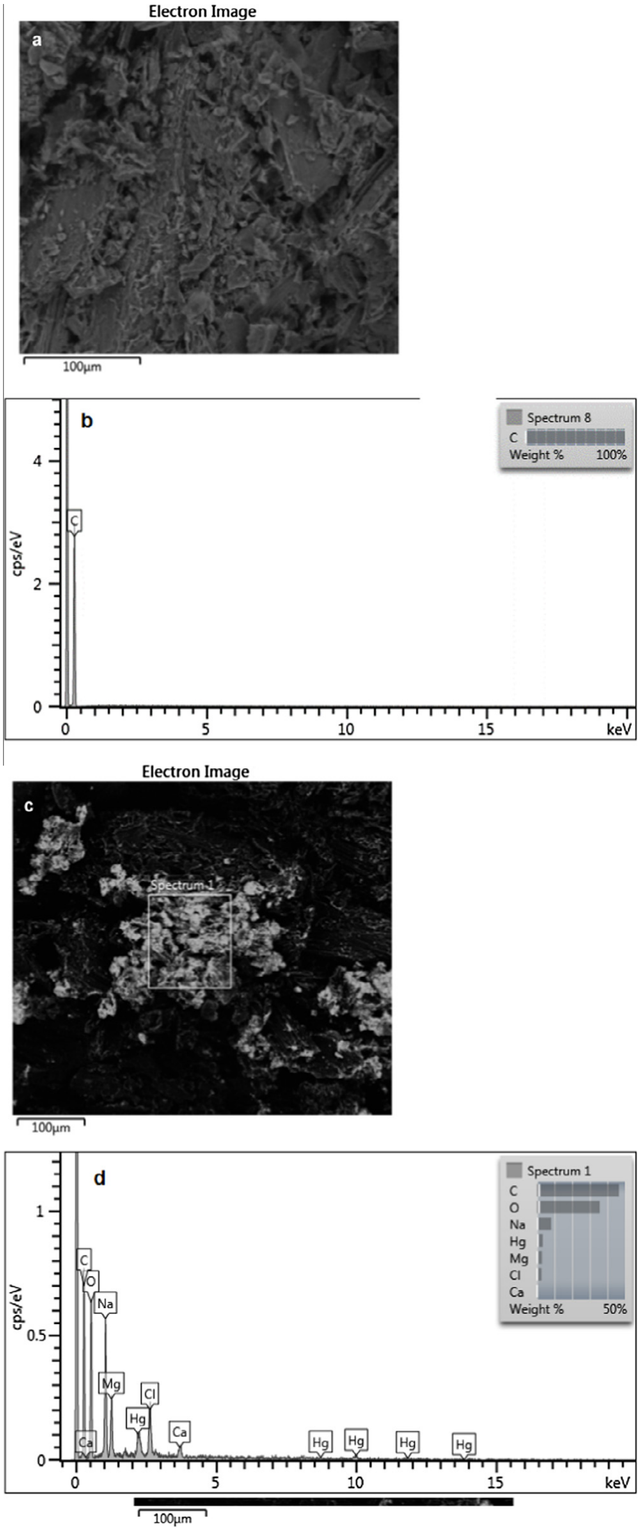

Fig. 2. Pure graphite electrode SEM image (a) EDX analysis (b) and graphite electrode - Hg SEM image (c) EDX analysis (d).

had positive effect to electrowinning process (+7.8%). Nanseu-Njiki et al. (2009) observed that an increase in current intensity also increases the rate of anode dissolution. The higher current intensity may play a role more turbid the solution, and consequently favors recovering. Citrate ions (Cit^{3-}) formed to a complex with Hg^{2+} was reduced to Hg^0 as shown in Eq. (4) (Kabra et al., 2004).

$$[Hg^{2+}nCit^{3n-} + (3n-2)H^{+} + (18n-2)OH^{*} \rightarrow 6nCO_2 + (13n-2)H_2O + Hg^{0} \qquad (4)$$

On the other hand, the main effect of electrolysis time (factor C) did not significantly influence mercury reduction. Interaction effects of citric acid amount and electrolysis time (BC) had little negative influence (−8.2%) on mercury recovery (Fig 1b). It means there was no advantage in working at high electrolysis time because of increasing the energy consumption and process costs as reported in Hummer et al., 2006.

Overall the results indicated that higher mercury recovery efficiencies could be reached with electrowinning experiments. The optimal process conditions were observed to be 6 A current intensity, 30 g/L of reducing agent concentration and 120 min. electrolysis time. Similarly, Hummer et al. (2006) reported high mercury recovery efficiency with a current intensity of 6 A, electrolysis time of 240 min. at the end of electroleaching process. As seen from the results, electrolysis time was reduced by half in our study. While white phosphor powders of fluorescent lamps were used as samples and NaCl was chosen as leaching solution in aforementioned study, we used pulverized glass and phosphor powder mixture samples of T8 and T12 lamps to simulate a more realistic situation. Furthermore, NaOCl and NaCl mixture reagent was used as leaching solution as distinct from Hummer et al. (2006).

3.3. Elemental composition experiments

SEM/EDX analyses of graphite electrode were obtained before and after the electrowinning process. Fig. 2a shows a SEM/EDX image including elemental analysis of pure graphite electrode. According to this analysis, 100% C of total weight was measured elemental composition of graphite electrode (Fig. 2b). After electrowinning test, approximately 46.65% C, 35.61% O, 8.25% Na, 3. 26% Hg, 2.83% Mg, 2.55% Cl and 0.85% Ca was measured on graphite electrode (Fig. 2d). Elemental mercury was detected in the SEM/EDX image in Fig. 2c.

4. Conclusions

The oxidative leaching and electrowinning processes were performed to recovery of mercury from spent tubular fluorescent lamps. The experiments were conducted on pulverized mixture samples of T8 and T12 lamp types. Mercury could be leached with an efficiency of 96% using NaOCl/NaCl reagent. The maximum electrowinning efficiency was calculated as 81%. It was found that current intensity and citric acid amount had positive effect for mercury reduction. Electrolysis time did not significantly influence the efficiency of electrowinning process. Recovery of mercury in its elemental form was confirmed by SEM/EDX. The oxidative leaching with NaOCl/NaCl reagent was followed by electrowinning process approach appears to be technical feasibility of the mercury from spent fluorescent lamps. In the future studies, the researchers can focus on using of different types, materials and numbers of electrodes in the process to improve the mercury recovery. Furthermore, the economical evaluations should be conducted prior to each specific application.

Acknowledgements

The authors would like to thank to Erik Zimmerman from Permascand AB for providing the DSA Anodes. This work was supported by research grants from Scientific and Technical Research Council of Turkey (TUBITAK) (project no. 110Y264).

References

Behnamfard, A., Salarirad, M.M., Veglio, F., 2013. Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation. Waste Manage. 33, 2354–2363.

Bussi, J., Cabrera, M.N., Chiazzaro, J., Canel, C., Veiga, S., Florencio, C., Dalchiele, E.A., Belluzzi, M., 2010. The recovery and recycling of mercury from fluorescent lamps using photocatalytic techniques. J. Chem. Technol. Biotechnol. 85 (4), 478–484.

Bhutta, M.K.S., Omar, A., Yang, X., 2011. Electronic waste: a growing concern in today's environment. Electrical and electronic equipment waste commonly known as e-waste. Econ. Res. Int. 2011, 1–9.

Chaturabul, S., Srirachat, W., Wannachod, T., Ramakul, P., Pancharoen, U., Kheawhom, S., 2015. Separation of mercury(II) from petroleum produced water via hollow fiber supported liquid membrane and mass transfer modeling. Chem. Eng. J. 265, 34–36.

Coskun, S., Civelekoglu, G., 2014. Characterization of waste fluorescent lamps to investigate their potential recovery in Turkey. Int. J. Global Warm. 6, 140–148.

Coskun, S., Civelekoglu, G., 2015. Recovery of mercury from spent fluorescent lamps via oxidative leaching and cementation. Water Air Soil Poll. 226 (6), 196–208.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: a review. J. Hazard. Mater. 158, 228–256.

Durão, W.A., de Castro, C.A., Windmöller, C.C., 2008. Mercury reduction studies to facilitate the thermal decontamination of phosphor powder residues from spent fluorescent lamps. Waste Manage. 28, 2311–2319.

Erust, C., Akcil, A., Gahan, C.S., Tuncuk, A., Deveci, H., 2013. Biohydrometallurgy of secondary metal resources: a potential alternative approach for metal recovery. J. Chem. Technol. Biot. 88, 2115–2132.

EU Directive 2002/96, 2008. Review of Directive on waste electrical and electronic equipment. Study No. 07010401/2006/442493/ETU/G4. <http://ec.europa.eu/environment/waste/weee/pdf/final_rep_unu.pdf> (29.09.2015).

Garlapati, V.K., 2016. E-waste in India and developed countries: management, recycling, business and biotechnological initiatives. Renew. Sust. Energ. Rev. 54, 874–881.

Hu, Y., Cheng, H., 2012. Mercury risk from fluorescent lamps in China: current status and future perspective. Environ. Int. 44, 141–150.

Huang, K., Guo, J., Xu, Z., 2009. Recycling of waste printed circuit boards: a review of current technologies and treatment status in China. J. Hazard. Mater. 164, 399–408.

Hummer, H., Sobral, L.G.S., Fernandes, A.L.V., Yallouz, A.V., 2006. Treatment of Mercury Bearing Fluorescent Lamps by Using an Electrochemical Process. CETEM – Centre for Mineral Technology.

Jüttner, K., Galla, U., Schmieder, H., 2000. Electrochemical approaches to environmental problems in the process industry. Electrochim. Acta 45, 2575–2594.

Kabra, K., Chaudhary, R., Sawhney, R.L., 2004. Treatment of hazardous organic and inorganic compounds through aqueous-phase photocatalysis: a review. Ind. Eng. Chem. Res. 43, 7683–7696.

Kalb, P.D., Adams, J.W., Milian, L.W., Penny, G., Brower, J., Lockwood, A., 1999. Mercury Bakeoff: Technology Comparison for the Treatment of Mixed Waste Mercury Contaminated Soils at BNL. Waste Management Congress, Tucson.

Kinoshita, T., Akita, S., Kobayashi, N., Nii, S., Kawaizumi, F., Takahashi, K., 2003. Metal recovery from non-mounted printed wiring boards via hydrometallurgical processing. Hydrometallurgy 69, 73–79.

Lai, Y.C., Lee, W.J., Huang, K.L., Wu, C.M., 2008. Metal recovery from spent hydrodesulfurization catalysts using a combined acid-leaching and electrolysis process. J. Hazard. Mater. 154, 588–594.

Meunier, N., Drogui, P., Montane, C., Hausler, R., Mercier, G., Blais, J.F., 2006. Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. J. Hazard. Mater. B 137, 581–590.

Montgomery, D.C., 1991. Design and Analysis of Experiments, third ed. Wiley, New York.

Nanseu-Njiki, C.P., Tchamango, S.R., Ngom, P.C., Darchen, A., Ngameni, E., 2009. Mercury (II) removal from water by electrocoagulation using aluminium and iron electrodes. J. Hazard. Mater. 168, 1430–1436.

National Electric Manufacturers Association, 2002. NEMA Lamp Manufacturers Reduce Use of Mercury by 67 Percent, press release, May 28, Available at www.nema.org.

Petter, P.M.H., Veit, H.M., Bernardes, A.M., 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Manage. 34, 475–482.

Rey-Raap, N., Gallardo, A., 2013. Removal of mercury bonded in residual glass from spent fluorescent lamps. J. Environ. Manage. 115, 175–178.

Sahin, M., Akcil, A., Erust, C., Altynbek, S., Gahan, C.S., Tuncuk, A., 2015. Potential alternative for precious metal recovery from E-waste: iodine leaching. Separ. Sci. Technol. http://dx.doi.org/10.1080/01496395.2015.1061005 (in press).

Tunsu, C., Ekberg, C., Retegan, T., 2014. Characterization and leaching of real fluorescent lamp waste for the recovery of rare earth metals and mercury. Hydrometallurgy 144–145, 91–98.

Tunsu, C., Ekberg, C., Foreman, M., Retegan, T., 2015. Investigations regarding the wet decontamination of fluorescent lamp waste using iodine in potassium iodide solutions. Waste Manage. 36, 289–296.

Twidwell, L.G., Thompson, R.J., 2001. Recovering and recycling hg from chlor-alkali plant wastewater sludge. JOM 53, 15–17.

US EPA, 1998. Mercury Emissions From the Disposal of Fluorescent Lamps, Final Report. U.S. Environmental Protection Agency, Washington, DC.

Vegliò, F., Quaresima, R., Fornari, R., Ubaldini, S., 2003. Recovery of valuable metals from electronic and galvanic industrial wastes by leaching and electrowinning. Waste Manage. 23, 245–252.

Waste Management 57 (2016) 198–206

Contents lists available at ScienceDirect

Waste Management

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

Feasibility of lead extraction from waste Cathode-Ray-Tubes (CRT) funnel glass through a lead smelting process

Jianfang Lv, Hongying Yang, Zhenan Jin *, Zhiyuan Ma, Yan Song

School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, China

ARTICLE INFO

Article history:
Received 24 February 2016
Revised 14 April 2016
Accepted 10 May 2016
Available online 7 July 2016

Keywords:
Cathode ray tube
Funnel glass
Lead recovery
Lead smelting

ABSTRACT

A novel and effective process for extracting lead from the hazardous waste Cathode Ray Tubes (CRT) funnel glass is presented. The technological breakthrough of this process is introducing the discarded CRT funnel glass to traditional lead smelting. In this study, the influences of amount of carbon addition, calcium-silicate ratio, temperature, holding time and funnel glass addition on lead extraction efficiency were investigated to determine the optimal operational parameters. With a glass addition of less than 30 wt%, a high extraction yield of 97.5% of lead from the mixture of funnel glass and lead slag was successfully obtained by controlling the C/PbO molar ratio, CaO/SiO_2 ratio, temperature, treatment time at 0.9, 0.8, 1200 °C, 60 min, respectively. The main crystalline phases of the residues were calcium silicate slag, and an amorphous glass phase appears at a glass addition more than 30 wt%. Thermodynamic calculation shows that the proportion of liquid phase in the slag first increased and then decreased, when the addition of glass is increased, while the viscosity of the slag exhibited a continuous decrease. Thus, based on all the results, it is concluded that the process proposed in this paper is an effective and promising approach for reutilization of obsolete CRT funnel glass.

1. Introduction

With the rapid advances in display technology, CRTs were replaced by advanced display products such as liquid crystal, plasma, or OLED (organic light emitting diode) displays (Gregory et al., 2009), resulting in a vast number of obsolete CRTs to dispose. It is estimated that approximately 6 million wasted TVs and 10 million computers are stockpiled each year in China (Xu et al., 2012), which has plagued landfills, electronics recyclers and governments for decades. CRTs are made of different glasses each with a different chemical composition and varying properties: (1) panel, a barium-strontium glass free of lead; (2) funnel, a lead glass with 20 wt% of PbO, accounting for about a third of a CRT's total weight; (3) neck, a lead-rich silicate glass containing more than 25 wt% PbO, which envelopes the electron gun; (4) frit, a lead-rich solder glass joining the three parts together (Gregory et al., 2009; Mear et al., 2006a). Previous studies have demonstrated that the lead-containing CRT funnel glasses must be considered as hazardous waste, due to the presence of lead in high levels, which could be leached steadily from broken lead glass, when mixed with acidic ground water in landfills (Chen et al., 2009; Lee et al., 2004; Yamashita et al., 2010; Yot and Mear, 2009a, 2011). Currently, most of the discarded CRTs end up in landfills or incinerators, and only a small part is recycled, resulting in secondary pollution to the environment. The CRT funnel glasses may seriously contaminate the environment and endanger human health, if not properly disposed of.

Generally, there are two principal ways of recycling CRT glass: closed loop recycling and open loop recycling. In closed loop recycling waste CRT glasses are used for manufacturing new CRT (Mostaghel and Samuelsson, 2010; Xu et al., 2012). However, the feasibility of relying mainly on the closed loop recycling to handle the abandoned CRTs reduced sharply, due to the rapid shrinkage of new CRT monitor demand. Accordingly, much attention has been drawn to the open loop recycling to utilize the increasing amount of waste CRTs. In recent years, many scholars have focused on recycling CRT glass as a secondary raw material, e.g., foam glass (Bernardo et al., 2007; Matamoros-Veloza et al., 2008; Mear et al., 2005, 2006b; F. Mear et al., 2007), glass ceramic (Andreola et al., 2005; Bernardo, 2007), ceramic glazes (Andreola et al., 2007), cement mortar (Ling and Poon, 2011, 2013). Nevertheless, these methods are quite problematic from the point of view of environmental security, because the prepared products still contain risky heavy metal that should be removed or separated, resulting in a potential threat to the environment and human health that precludes above-mentioned recycling. It is difficult to use conventional technologies to extract the lead from the lead glass because

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* Corresponding author.
E-mail address: jinzn@smm.neu.edu.cn (Z. Jin).

http://dx.doi.org/10.1016/j.wasman.2016.05.010

of its special structure, i.e., $xPbO(1-x)SiO_2$, where lead atoms are tightly entangled in the glass network (F.O. Mear et al., 2007; Wang and Zhang, 1996; Witkowska et al., 2005). Hence, techniques for extracting lead from discarded funnel glass through pretreatment to break the glass' stable structure, such as ultrasonically enhanced lead leaching (Saterlay et al., 2001), chemical-electrochemical method (Pruksathorn and Damronglerd, 2005), subcritical hydrothermal treatment followed by acid leaching (Miyoshi et al., 2004), mechanical activation (Yuan et al., 2012), chlorinating volatilization (Erzat and Zhang, 2014a,b; Grause et al., 2014), mechanochemical process using the chelate reagent Na_2EDTA (Sasai et al., 2008), were proposed. These technologies are less attractive, however, due to long-process time, complicated equipment and low-lead recovery. Moreover, pyrometallurgy technology has also been developed and employed for the recovery of lead from obsolete CRTs. Lu et al. (2013) extracted lead from funnel glass by thermal reduction with metallic iron, but the consumption of iron will definitely increase the treatment cost that limits its application. Yot and Mear (2009b) successfully extracted 40 wt% of lead from waste CRTs by reacting it with SiC after 60 min at 950 °C under atmospheric pressure, while Xing and Zhang (2011) and Chen et al. (2009) recovered more than 90 wt% of lead via vacuum carbon-thermal reduction at 1000 °C. However, there were still some disadvantages among these methods, e.g., long treatment time (1–4 h), high-energy consumption (>1000 °C) and harsh reaction conditions (vacuum atmosphere). All of these factors limit the common application of these methods. In addition, a recent research led by Okada and Yonezawa (2013) demonstrated that 92% of lead in the funnel glass can be recovered in 60 min via reduction-melting methods. However, this method required a large quantity of flux (Na_2CO_3) to promote the lead recovery, which increases the treatment cost. More importantly, further lead recovery was difficult for this reducing-melting method unless combined with the hydrochloric acid leaching. Thus, it is urgent to develop an alternative management method, which is environmental benign, cost-efficient and easier to implement, for CRT glass treatment and reutilization.

Lead and copper smelting operations use a great amount of silica flux, and discarded CRT glass can potentially be used to replace silica (Mostaghel and Samuelsson, 2010). Thus, the effect of using waste CRT glass as additional silica flux on the properties of slag in copper smelting has been investigated in a previous study. As to our best knowledge, little research has been conducted on the feasibility of extracting lead from discarded CRT funnel glass through lead smelting technology. In the present paper a novel process, namely reduction smelting for the mixtures of high lead slag and CRT funnel glass with carbon as reducing agent, was developed. Samples with different funnel glass addition were prepared and subjected to reduction smelting. The influences of the amount of carbon addition, calcium-silicate ratio, smelting temperature and treatment time on lead extraction efficiency and zinc recovery were investigated to determine the optimal operational parameters. The characterisation of the residues obtained with different funnel glass addition were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. In addition, the thermodynamic equilibrium calculation software FactSage 6.4 was also employed to calculate the proportion of liquid phase and the variation of viscosity depending on the funnel glass addition.

2. Materials and methods

2.1. Materials

The CRT funnel glass was obtained from an appliances dismantling enterprise in Liaoning province, China. High lead slag and anthracite were supplied by a metallurgical plant in China. The chemical composition of the high lead slag and the glass powder were determined by X-ray Fluorescence (XRF) analysis, and the results are presented in Table 1. Prior to use the samples were crushed, milled and dried at 105 °C for 24 h, then mixed to gain the desired proportions. For this work, three different mixtures, 90 wt% slag-10 wt% glass, 80 wt% slag-20 wt% glass and 70 wt% slag-30 wt% glass, were prepared. Each sample was placed in an alumina crucible.

2.2. Experimental procedure

The crucible was transferred into a silicon carbide bar heating furnace preheated to the target temperatures (1150–1250 °C) and thermally treated for a given time ranging from 30 min to 120 min in air. After thermal treatment, the crucible was removed from the furnace and allowed to reach room temperature by air-cooling. Then the crucible was broken and the metallic lead was separated from the residue. The residues were weight and ground into powder for analysis.

In the melting experiment the effects of the amount of carbon addition, the calcium-silicate ratio, the heating temperature and the treatment time on the lead extraction efficiency and the zinc recovery were investigated using the following equations:

$$R_{Pb} = \left(1 - \frac{m_{slag} \times C_{Pb}}{m_{mix} \times C^0_{Pb}}\right) \times 100\% \tag{1}$$

$$R_{Zn} = \frac{m_{slag} \times C_{Zn}}{m_{mix} \times C^0_{Zn}} \times 100\% \tag{2}$$

where m_{slag} is the mass of slag after the reduction melting, C_{Pb} is the lead concentration in the residue, m_{mix} is the mass of the mixture before smelting, $C^0{}_{Pb}$ is the lead concentration in the mixture, C_{Zn} is the zinc concentration in the residue, and $C^0{}_{Zn}$ is the zinc concentration in the mixture.

2.3. Analysis

The variation of the lead and zinc contents in the samples was measured using atomic absorption spectroscopy (AAS). X-ray diffraction analysis was carried out for the samples with various funnel glass additions. The XRD patterns of the samples were collected for 2θ from 10° to 80° using CuK radiation on a PANalytical B.V./X'Pert Pro diffractometer. A ZEISS Ultra Plus with accelerating voltage of 15 kV, equipped with an energy dispersive X-ray spectroscopy (EDS) detector, was employed to obtain the morphological information of the residues.

Table 1
Chemical composition of high lead slag and funnel glass used for experiments.

Components	Concentration (wt%)	
	Lead slag	Funnel glass
SiO_2	10.7	53.4
PbO	54.5	20.3
CaO	4.4	4.5
ZnO	9.3	0.1
Fe_2O_3	11.6	0.3
K_2O	0.8	9.9
Al_2O_3	0.8	3.7
MgO	1.3	1.7
Na_2O	–	4.4

3. Results and discussion

3.1. Effect of reducing agent content

It can be calculated that under atmospheric condition, according to the carbon-thermal reduction of lead oxide (Liang and Che, 1994), PbO can be reduced to Pb by carbon, when the temperature is higher than 580 °C. Therefore, PbO in the mixtures was considered to be reduced to metallic Pb, because the treatment temperatures were well far above 580 °C.

To obtain the influence of the amount of carbon addition (molar ratio of carbon to PbO) on the lead and zinc recovery, samples with different funnel glass addition were tested at a constant temperature of 1200 °C with a reaction time of 60 min and a calcium-silicate ratio of 1.0. Fig. 1(a) shows that for all systems, the lead recovery initially increased significantly as the amount of carbon addition increased and then held on a steady level, reaching its maximum at a C/PbO molar ratio of 1.2. When the C/PbO molar ratio was up to or more than 0.9, the lead recovery exceeded 95% regardless of funnel glass addition. This indicates that lead could be effectively extracted from the mixture of high lead slag with funnel glass via this reduction-melting process. More importantly, the lead content in the residues obtained with an addition of funnel glass were all below 2%, when the C/PbO molar ratio was more than 0.9. This value is much lower than that of high lead slag, which is preferably used in industrial operations. It could also be found that in the case of 10 and 20 wt% funnel glass addition the lead recovery was higher than that of the sample without glass employed at all ranges tested. Particularly, when the C/PbO molar ratio is 0.6, the lead recovery was 86% for the sample with 10 wt% funnel glass addition, while only 79% recovery for a pure slag sample was achieved, indicating that lead recovery could be enhanced by adding funnel glass. This observation might be attributed to the presence of potassium oxide and sodium oxide contained in the glass, which can reduce the melting temperature and promote the reaction rate. However, further funnel glass addition has an inhibiting effect on the lead extraction, as indicated by the slight decrease in the recovery of the sample with 30 wt% funnel glass addition, when compared with the case of 10 and 20 wt% glass addition. This is probably due to the excessive silica that may lead to an increase of viscosity, thereby hindering the sedimentation of the metallic lead particles. It should be pointed out that the higher addition of funnel glass in the high lead slag will produce a lower production efficiency, and a deeper influence on the process parameters will be. Thus, addition of funnel glass should be limited to a certain value to obtain a high production efficiency as well as to reduce the influence on the process parameters caused by glass addition as much as possible.

Conversely, the zinc recovery exhibited a continuous decrease with increasing the C/PbO molar ratio for all systems (Fig. 1b). It can be predicted that along with further increase of C/PbO molar ratio, ZnO can be completely reduced to zinc and then evaporate into the gas phase. Thus, it is necessary to obtain a relative high zinc recovery rate, since this zinc-containing slag was used for extracting the valuable metal zinc in the subsequent process. Furthermore, it is worth to notice that the introduction of funnel glass has an inhibitory effect on the zinc extraction efficiency, resulting in a high zinc content in the residue. For example, the zinc recoveries for the samples with 10, 20 and 30 wt% glass addition are 91%, 93% and 95%, respectively, while only 88% for the sample without glass. Based on these results, a C/PbO molar ratio of 0.9 was selected as an optimal value for carbon adding amount to obtain an optimal lead and zinc recovery rate.

3.2. Effect of calcium-silicate ratio

The effect of the calcium-silicate ratio was investigated using a fixed C/PbO molar ratio of 0.9 and a reaction time of 60 min, and a constant temperature of 1200 °C. Fig. 2(a) shows the dependence of the lead recovery on the CaO/SiO_2 ratio with funnel glass addition in the range from 0 up to 30 wt%. For all systems the trends are quite similar. The lead recovery rate first exhibited a significant increase concomitant with the increase of CaO/SiO_2 ratio and reached its maximum. Afterwards it dropped down with a further increasing CaO/SiO_2 ratio. This tendency was more pronounced in the sample prepared with 30 wt% funnel glass addition, for which an increase from 92% to 98% and a decrease from 98% to 92% were observed. This might be attributed to the important role of the slag viscosity caused by CaO. It is well-known that silicates slag has a network structure made of SiO_4^{4-} units, and Si tetrahedral ions are combined through bridging oxygen O^0. The availability of free oxygen ions (O^{2-}) increased, when adding basic oxides like CaO. This results in the progressive breaking of the Si—O bonds in the network structure of Si tetrahedral to form non-bridging oxygen (O^-). The non-bridging oxygen ions have a larger mobility than the bridging oxygen in the network structure (Nakamoto et al., 2007; Tang et al., 2011). Thus, the polymerization degree of complex viscous units was reduced and, thereby, the viscosity of slag decreased.

Generally, in the melting process the metallic lead particles generated by reduction-melting move in the molten slag, collide with each other, aggregate and finally settle at the bottom of the reactor (Okada and Yonezawa, 2013). A decrease in the viscosity of the slag can enhance the collision frequency between the lead particles and also promote the sedimentation of the metallic lead aggregate, resulting in a high lead separation efficiency, according to Stokes' law.

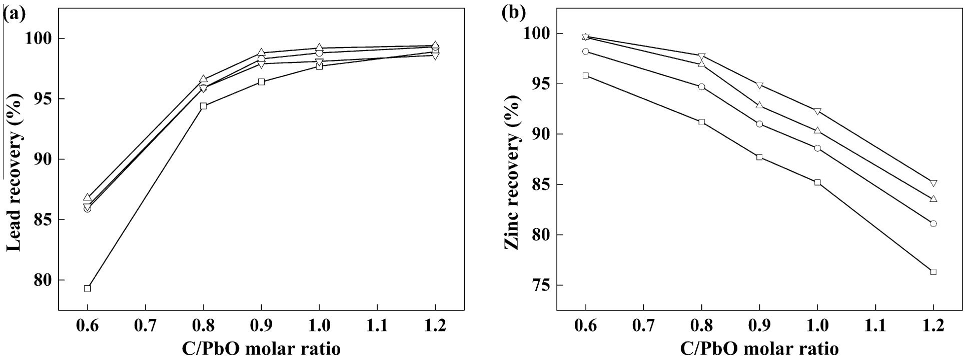

Fig. 1. Effect of C/PbO molar ratio on (a) lead recovery and (b) zinc recovery (CaO/SiO_2 ratio: 1.0, smelting temperature: 1200 °C, treatment time: 60 min, funnel glass addition: □ 0 wt%; ○ 10 wt%; △ 20 wt%; ▽ 30 wt%).

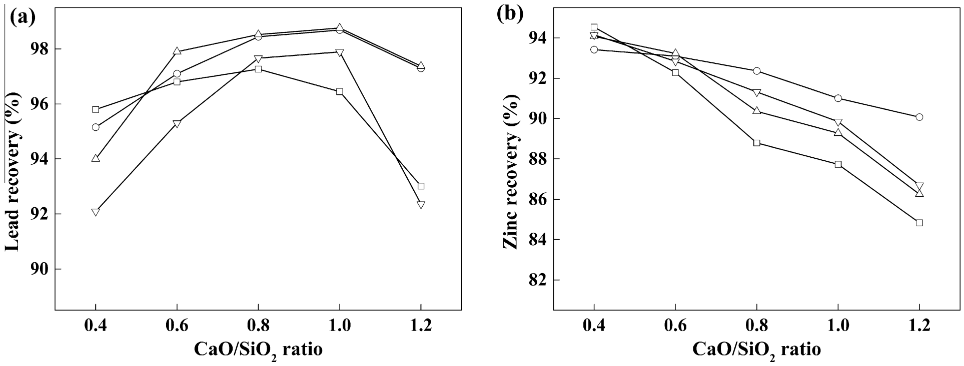

Fig. 2. Effect of CaO/SiO_2 ratio on (a) lead recovery and (b) zinc recovery (C/PbO molar ratio: 0.9, smelting temperature: 1200 °C, treatment time: 60 min, funnel glass addition: □ 0 wt%; ○ 10 wt%; △ 20 wt%; ▽ 30 wt%).

$$V = (\rho_s - \rho) g d_s^2 / 18\mu \quad (3)$$

where ρ_s is the density of metallic lead, ρ is the density of the slag, g is the gravitational acceleration, d_s is the diameter of the lead particles, and μ is the viscosity coefficient of the slag.

However, a further addition of CaO has an inhibiting effect on the lead recovery, as shown in Fig. 2(a), because the excessive CaO can increase the melting point of the slag. This reduces the phase separation between the molten metallic lead phase and the molten slag phase. The value of 0.8 was found to be a suitable CaO/SiO_2 ratio for lead extraction, since the lead recoveries were up to 96% under these conditions, regardless of the funnel glass addition.

Fig. 2(b) shows the zinc recovery rate as a function of the CaO/SiO_2 ratio. Similar to the results of amount of carbon addition (Fig. 1b), the zinc recovery exhibited a continuous decrease with an increase in the CaO/SiO_2 ratio for all systems. As mentioned before, CaO behaves as a network breaker to decrease the viscosity of the slag. As a result, zinc in the slag is readily to be reduced, causing a high zinc vaporization rate and a low zinc recovery. Meanwhile the results reveal that the zinc recovery can be enhanced by the introduction of funnel glass, and this enhancement was more pronounced at a higher CaO/SiO_2 ratio. This finding is in accordance with the observation mentioned in Section 3.1.

3.3. Effect of the temperature and the treatment time

To obtain the optimal parameters for the efficient recovery of lead, temperatures varying from 1150 °C up to 1250 °C were examined with a treatment time of 60 min, a C/PbO molar ratio of 0.9 and a CaO/SiO_2 ratio of 0.8. Fig. 3(a) shows the lead recovery rate as a function of the temperature. The four curves exhibited a similar trend, indicating that the lead recovery increased rapidly with the increase of temperature and then held on a steady level. This is especially valid for the samples with 0 or 30 wt% funnel glass addition. The marked increase in the lead extraction efficiency as a result of funnel glass addition at temperature below 1200 °C might be associated with the presence of potassium oxide and sodium oxide contained in the funnel glass, which can decrease the melting temperature of the slag (Li, 2005). Instead, the zinc recovery shows a reverse trend with an increase in the temperature, as illustrated in Fig. 3(b). The results further confirm that an addition of funnel glass can inhibit zinc oxide reduction and hence a high zinc content in the residue. Note that once the operating temperature is decreased, not only the energy consumption could be greatly reduced, but the zinc recovery enhanced because of the low vaporization rate, which is preferable in industrial operations. However, further study is needed to know the feasibility of employing lower operating temperature for the proposed technology, that is, lowering the smelting temperature should be on the premise that no significant effect occurs on the production flow and production efficiency, etc. Fig. 4(a) indicates that the lead recovery ratio of the samples prepared with 10 up to 30 wt% funnel glass addition had a maximum recovery (more than 95%), when the treatment time was 30 up to 60 min. It did not show any evident change when compared with the sample without glass addition, where the lead recovery increased rapidly with the increase of time. When the treatment time was more than 60 min, a slight decrease was observed for all systems. Similar results were previously obtained by Lu et al. (2013), who demonstrated the incorporation of lead into the glass matrix during a long treatment time, as defined by Eq. (4).

$$\equiv\text{Si—O} + \text{Pb}(0) \rightarrow \equiv\text{Si—O}^{-}\text{Pb}^{+} \quad (4)$$

It was noted that the lead in the samples prepared with 10 up to 30 wt% funnel glass addition can be more easily separated from the residue as compared with the raw material, where the residue contains some lead particles. This implies that the physical properties of molten slag can be improved by adding funnel glass to the original mixture. Fig. 4(b) summarizes the relationship between zinc recovery and smelting time. The results show that the zinc recovery ratio exhibited its maximum at 30 min, followed by a sharp decrease, and then became flat after 60 min. Therefore, the optimized operational parameters for lead extraction in the cases of 10 up to 30 wt% funnel glass addition are a C/PbO molar ratio of 0.9, a CaO/SiO_2 ratio of 0.8, a smelting temperature of 1200 °C and a treatment time of 60 min.

3.4. Properties of the residues

To further understand the effect of funnel glass addition on the properties of the residues, samples with 40 and 50 wt% funnel glass addition were tested and subjected to reduction smelting under optimum conditions (C/PbO molar ratio of 0.9, CaO/SiO_2 ratio of 0.8, 1200 °C, 60 min). The corresponding lead recovery rates are 95% and 93%, respectively. The chemical composition of the residues, obtained at the optimum conditions with different amount of glass addition, was determined. The results are presented in Table 2. It can be seen that the content of SiO_2, CaO and K_2O in the residues increased with the increase of funnel glass addition, whereas the amounts of Fe_2O_3, FeO and ZnO decreased. Moreover, most of the Fe in the residues is in bivalent state (Fe^{2+}) because of the reducing atmosphere. Only a small part is in trivalent state (Fe^{3+}) in spite of the funnel glass addition, which might generate from the oxidation of Fe^{2+} during the air-quenched process.

Fig. 5 presents the XRD patterns of the residues obtained at different amounts of funnel glass addition. No distinct differences

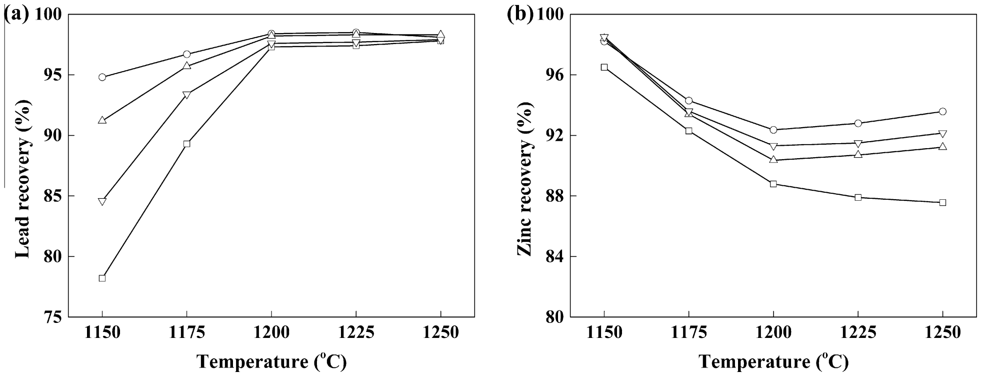

Fig. 3. Effect of temperature on (a) lead recovery and (b) zinc recovery (C/PbO molar ratio: 0.9, CaO/SiO_2 ratio: 0.8, treatment time: 60 min, funnel glass addition: □ 0 wt%; ○ 10 wt%; △ 20 wt%; ▽ 30 wt%).

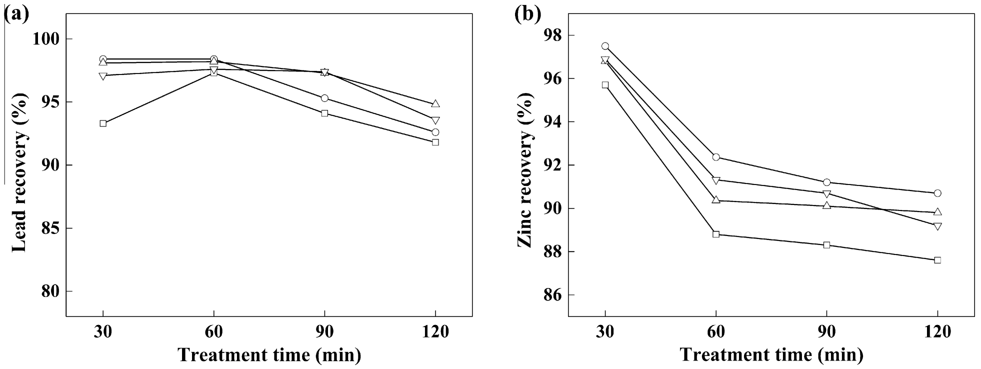

Fig. 4. Effect of treatment time on (a) lead recovery and (b) zinc recovery (C/PbO molar ratio: 0.9, CaO/SiO_2 ratio: 0.8, smelting temperature: 1200 °C, funnel glass addition: □ 0 wt%; ○ 10 wt%; △ 20 wt%; ▽ 30 wt%).

Table 2
Chemical composition of residues obtained under optimum conditions with funnel glass addition varying from 0 up to 50 wt%.

Materials	Concentration (wt%)								
	SiO_2	Fe_2O_3	FeO	CaO	ZnO	PbO	K_2O	Al_2O_3	MgO
Slag	22.7	7.5	21.4	21.2	16.4	3.0	1.3	3.0	2.1
Slag/glass-90/10 wt%	25.5	6.7	17.6	24.6	13.5	1.4	2.5	3.3	2.0
Slag/glass-80/20 wt%	27.6	5.3	12.8	27.6	10.9	1.4	3.9	3.7	1.9
Slag/glass-70/30 wt%	29.7	4.2	10.3	30.4	8.5	1.5	4.6	3.5	2.0
Slag/glass-60/40 wt%	32.1	2.4	8.8	33.5	7.4	2.6	5.0	3.1	1.9
Slag/glass-50/50 wt%	33.8	1.6	6.6	35.0	5.8	2.9	5.8	3.0	1.9

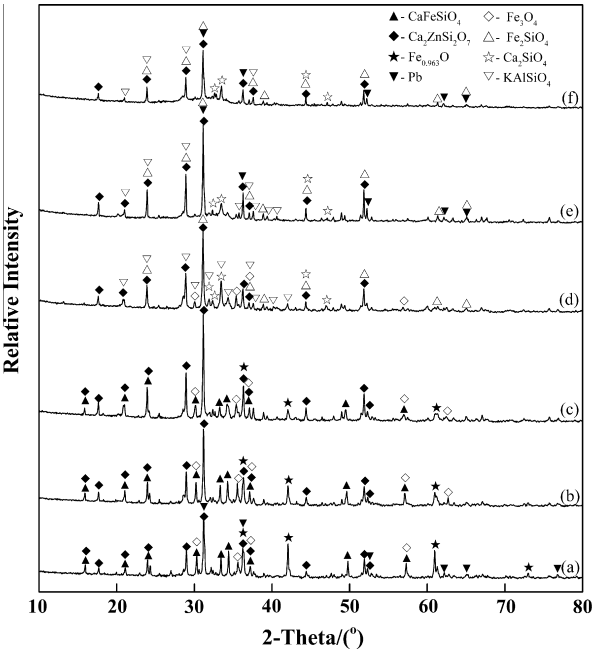

Fig. 5. XRD patterns of residues obtained with different funnel glass addition (C/PbO molar ratio: 0.9, CaO/SiO_2 ratio: 0.8, smelting temperature: 1200 °C, treatment time: 60 min, funnel glass addition: (a) 0 wt%; (b) 10 wt%; (c) 20 wt%; (d) 30 wt%; (e) 40 wt%; (f) 50 wt%).

were observed among the residues with 0, 10 and 20 wt% funnel glass addition, except for the peaks for the metallic lead observed in the sample without glass addition. The main crystalline phases are identified as kirschsteinite ($CaFeSiO_4$), hardystonite ($Ca_2ZnSi_2O_7$), wuestite ($Fe_{0.963}O$) and magnetite (Fe_3O_4). The peak intensity was found to decrease concomitant with the increase of the funnel glass addition. With the increased amount of glass, equal to or more than 30 wt%, the diffraction peaks for fayalite (Fe_2SiO_4), calcium silicate (Ca_2SiO_4) and potassium aluminum silicate ($KAlSiO_4$) became observable in the XRD patterns, while the peaks for $CaFeSiO_4$ and $Fe_{0.963}O$ disappeared. This observation is in agreement with the analysis data in Table 2. The transformation of the crystal structure of the residues is due to an increase of funnel glass addition. This addition results in a high CaO and SiO_2 content in the residue, which consequently, was prone to form silicate slag. Peaks attributable to metallic lead started to become noticeable when the glass addition increased to more than 30 wt%. This is in accordance with the chemical analysis results and suggests that a further increase of funnel glass addition can decrease the lead extraction efficiency. In addition, the amorphous glass phase appeared in the case of 40 and 50 wt% funnel glass addition, as demonstrated by the higher background signals from 20° to 40°.

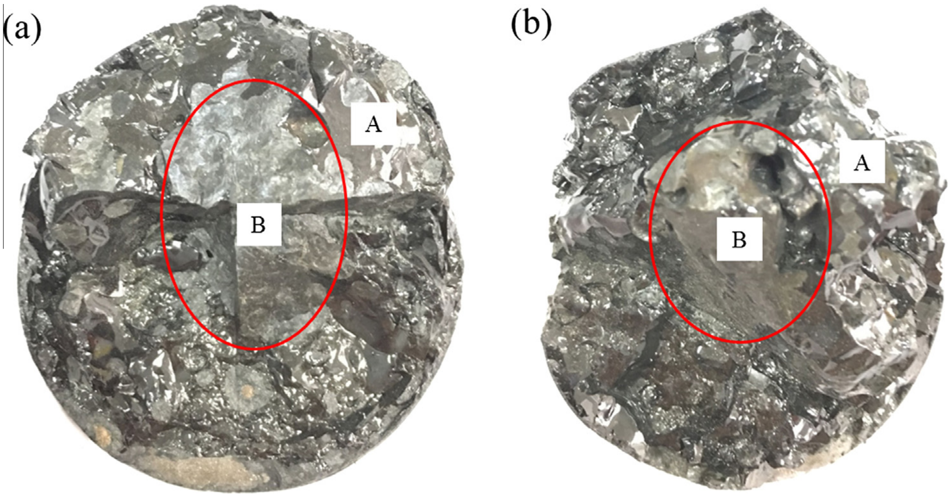

Fig. 6. Photograph of the residues obtained with different funnel glass addition (C/PbO molar ratio: 0.9, CaO/SiO_2 ratio: 0.8, smelting temperature: 1200 °C, treatment time: 60 min, funnel glass addition: (a) 40 wt%; (b) 50 wt%).

These findings could also be confirmed by the photograph of the residues, as shown in Fig. 6. Obviously, both residues are inhomogeneous, where the part A presents a typical amorphous glass phase, while the part B presents a crystalline phase.

In order to confirm the results of the XRD analysis, a SEM study of the six samples was carried out and a number of points were chosen for elemental analysis. Fig. 7 shows back scattering images of the residue powder for the samples with different funnel glass

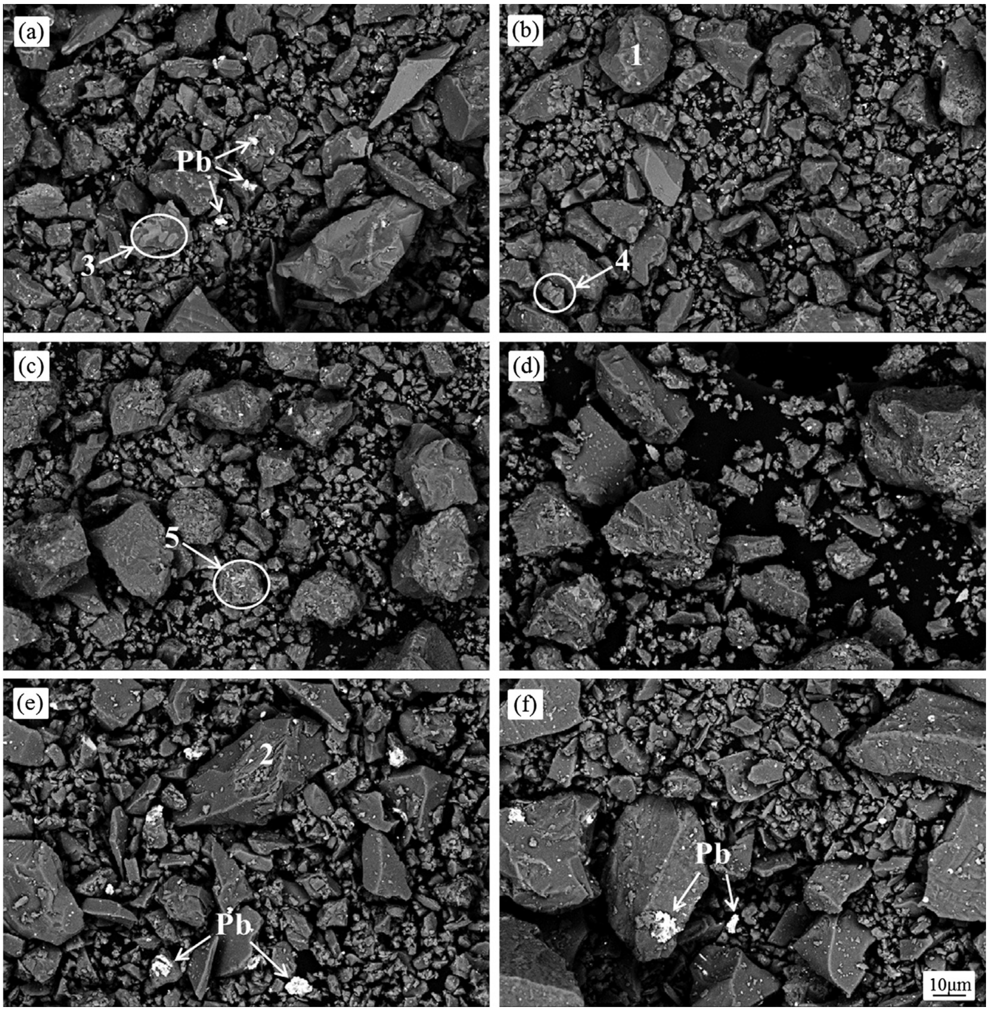

Fig. 7. Back scattering images of residue powders for samples with different funnel glass addition treated at the optimum conditions (C/PbO molar ratio: 0.9, CaO/SiO_2 ratio: 0.8, smelting temperature: 1200 °C, treatment time: 60 min, funnel glass addition: (a) 0 wt%; (b) 10 wt%; (c) 20 wt%; (d) 30 wt%; (e) 40 wt%; (f) 50 wt%).

Table 3
Proportions of liquid and their compositions of samples with various funnel glass addition at different temperature predicted by the thermodynamic calculations using the software FactSage.

Samples (wt%)	T (°C)	Liquid phase content (wt%)	Compositions (wt%)								
			K_2O	Al_2O_3	SiO_2	CaO	FeO	Fe_2O_3	MgO	PbO	ZnO
0	1000	3.5	37.4	14.8	34.9	4.6	0.1	2.7E−07	7.9E−03	8.1	0.1
	1100	4.2	32.7	13.9	34.7	6.6	0.3	4.9E−06	3.4E−02	11.5	0.4
	1200	26.9	4.9	4.7	24.3	18.3	16.5	3.4	1.4	10.0	16.6
	1300	100	1.3	3.1	23.0	21.5	21.7	7.6	2.1	3.0	16.6
10	1000	6.0	42.3	13.6	32.1	7.7	6.6E−02	6.7E−07	6.6E−03	4.0	9.8E−02
	1100	6.7	38.2	13.3	32.8	10.2	0.2	8.5E−06	2.8E−02	5.1	0.3
	1200	31.1	15.8	7.0	27.6	19.8	9.5	3.9	0.8	7.2	8.5
	1300	100	2.6	3.4	26.3	25.3	18.1	6.9	2.1	1.4	14.0
20	1000	9.5	43.4	13.7	32.5	8.5	6.6E−02	4.9E−07	5.2E−03	1.8	8.7E−02
	1100	10.4	39.7	13.6	33.4	10.9	0.2	5.8E−06	2.7E−02	2.0	0.2
	1200	41.6	9.9	4.8	28.3	27.8	12.6	3.6	1.1	3.3	8.7
	1300	100	4.1	3.8	29.0	29.1	13.5	5.6	2.0	1.4	11.4
30	1000	11.3	43.1	13.7	32.6	8.4	6.8E−02	5.9E−07	5.3E−03	2.1	7.8E−02
	1100	12.3	39.8	13.5	33.9	10.9	0.2	5.3E−06	2.8E−02	1.5	0.2
	1200	55.1	8.9	4.0	28.9	30.1	13.4	4.2	1.2	2.7	6.7
	1300	100	4.9	3.7	31.4	32.2	10.9	4.5	2.1	1.6	9.0
40	1000	12.0	42.8	13.6	32.6	8.1	7.4E−02	6.3E−07	5.3E−03	2.8	7.5E−02
	1100	13.1	39.4	13.3	34.0	10.6	0.3	4.8E−06	2.5E−02	2.2	0.2
	1200	52.2	9.9	4.2	30.0	29.1	13.2	2.9	1.1	4.1	5.7
	1300	100	5.1	3.2	33.2	34.7	9.1	2.4	2.0	2.7	7.6
50	1000	14.2	42.4	13.3	33.1	8.0	7.6E−02	6.7E−07	4.8E−03	3.1	5.2E−02
	1100	15.3	39.2	13.0	34.7	10.3	0.3	5.7E−06	2.0E−02	2.4	0.1
	1200	33.2	18.1	6.7	33.1	23.6	9.2	1.8	0.6	3.9	3.0
	1300	100	6.0	3.1	35.1	36.3	6.9	1.7	1.9	3.0	6.0

addition. Crystalline metallic lead was clearly observed in the samples with 0, 40 and 50 wt% funnel glass addition (Fig. 7a, e and f). The crystals are embedded in a dark matrix, indicating that a fraction of the metallic lead recovered by carbon has not settled to the bottom of the crucible during the melting process. The dark matrix consists mainly of glassy calcium silicate slag, containing Zn, Fe, K, Al, Mg, Na, Ca, Si and O in varying proportions. For example, point "1" in Fig. 7(b) is an analyzed point of this phase, which contains Fe, Ca, Si, O, while point "2" in Fig. 7(e) has a higher amount of Ca and Si, and contains K. The lighter-colored phases, characterized as oxidized Fe compounds, cf. point "3", "4" and "5", were observed in the samples with 0 up to 20 wt% funnel glass addition, and are less distinct with increasing glass addition.

The XRD and SEM results are in agreement with each other, confirming the relatively low lead extraction efficiency for the experiments with 0, 40 and 50 wt% funnel glass addition, the formation of calcium silicate slag in all systems, as well as the decrease of Fe oxides if the glass addition increased. These observations are also consistent with the chemical analysis listed in Table 2. Thus, we conclude that a funnel glass addition of 10 up to 30 wt% is the optimal addition for the lead recovery and the production efficiency.

3.5. Thermal calculation

The reaction between lead-rich slags and carbon is a complex process involving solid-liquid, solid-gas, liquid-gas and solid-solid reactions. Of these the solid-liquid reaction is the preferred one from chemical reaction viewpoint (Hou et al., 2013). In order to understand the function of the proportion of liquid phase in the reaction, the equilibrium module of the thermodynamic computer modeling package FactSage was employed to calculate the equilibrium state of the slag at 1000 °C, 1100 °C, 1200 °C and 1300 °C. Table 3 summarizes the results of the calculations, which indicates the followings: the proportion of the liquid phase increases with elevated temperature; it also increases with the increase of funnel glass addition and exhibits a maximum at 30 wt%; it decreases if more funnel glass is added, when temperature is fixed at 1200 °C. In addition, the viscosity of the slag was also predicted by FactSage and the results are shown in Fig. 8. It can be seen that the more funnel glass is added, the higher the viscosity of the slag will be. Thus, a possible mechanism for slag properties as a function of funnel glass addition was obtained: the introduction of funnel glass can improve the melting performance of slag as indicated by the proportion of liquid phase, and this is more pronounced at reduced temperature. For example, the liquid phase content in the case of 0 wt% funnel glass addition is only 4.2 wt%, while it is up to 12.3 wt% with a glass addition of 30 wt

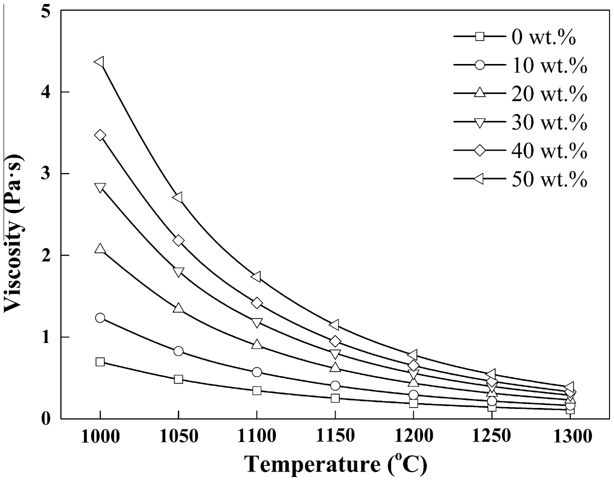

Fig. 8. Calculated viscosities of the slags as a function of temperature using FactSage 6.4.

Table 4
Comparison of the key operational parameters and extraction efficiencies of the methods used for extracting lead from CRT funnel glass.

Method	Reagents	Temperature	Pressure	Time	Extraction ratio (%)	Products
Mechanochemical process (Sasai et al., 2008)	Na_2EDTA	Room temperature	1 atm	20 h	99	Lead-EDTA
Subcritical hydrothermal treatment (Miyoshi et al., 2004)	Water, nitric acid	355 °C	237 atm	18–22 h	93	Orthoclase, alkaline-earth lead silicate
Power ultrasound (Saterlay et al., 2001)	Nitric acid	Room temperature	1 atm	1 h	>90	N.A.
Thermal reduction (Lu et al., 2013)	Fe	700 °C	1 atm	30 min	58	Metallic lead, glass
Pyrometallurgy (Okada and	SiC/TiN	950 °C	1 atm	1 h	40	Metallic lead, foam glass
Yonezawa, 2013; Yot and Mear, 2009b)	C, Na_2CO_3	1000 °C	1 atm	1 h	92	Metallic lead
Pyrovacuum (Chen et al., 2009;	C	1000 °C	500–2000 Pa	2–4 h	96.8	Nano-lead
Xing and Zhang, 2011)	C	1000 °C	1000 Pa	4 h	98.6	Metallic lead, foam glass
Reduction-melting (this work)	C	1200 °C	1 atm	0.5–1 h	>97.5	Metallic lead

N.A.: not available.

% at 1100 °C. These conditions lead to an increased reaction rate and result in a high lead extraction efficiency, as confirmed by the data in Figs. 2 and 3. With further addition of glass to 40 or 50 wt%, calcium silicate phase like Ca_2SiO_4 formed and, thus, melting temperature of the slag increased, which is in accordance with the thermodynamic calculation results. Additionally, an addition of glass also can increase the viscosity of the slag, thereby hindering the sedimentation of lead particles generated by reduction smelting. Based on the above-mentioned results, it is easy to understand the fact that lead contents in the residue obtained with 40 and 50 wt% funnel glass addition are higher than that with 10 up to 30 wt% glass addition.

4. Conclusion and recommendation

A lead extraction technology from waste cathode-ray-tubes (CRT) funnels glass in a lead smelting furnace was proposed based on the carbon-thermal reduction process. The results of main smelting parameters with different funnel glass addition show that the optimum operational parameters are C/PbO molar ratio of 0.9, CaO/SiO_2 ratio of 0.8, 1200 °C, 60 min and glass addition of 10 up to 30 wt%. Under these conditions, the Pb recovery rate is more than 97% in a shorter smelting time. When the glass addition is below than 10 wt% or more than 30 wt%, the Pb recovery decreased and more lead particles were observed in the residues. Meanwhile, XRD and SEM results indicate that the residues present as calcium silicate slag in all systems.

A comparison of the key operational parameters and extraction efficiencies of the methods used for extracting lead from CRT funnel glass is presented in Table 4. The results suggest that this method has such advantages as high efficiency, low energy consumption and high economic efficiency, because this method has a potential for implementation as a practical, industrial process for utilization of the waste funnel glass without the need for expensive processing equipment. What's important, this technology proposes a treatment and utilization method of the funnel glass in Waste Electrical and Electronic Equipment (WEEE), which remove the direct pollution of these lead-containing glasses. It is worth mentioning that the primary application of this technology to a lead smelter which we cooperate with has been carried out. With 10 up to 20 wt% funnel glass addition, not only a high extraction yield of lead 96% was successfully obtained, but the profit of the enterprise was improved by introducing the low-cost funnel glass to high lead slag. However, scarce of information about effect on the physical properties of slag and the corrosion behavior on refractory caused possibly by the addition of funnel glass, which is of vital importance to practical production, can retard the applications and popularize of this technology. It is therefore desirable to further study for the optimization and improvement of this waste CRT funnel glass processing technology.

Acknowledgements

The authors acknowledge the financial support of the National Key Technology R&D Program (2014BAC03B07). The authors also wish to express gratitude to Prof. Wolfgang Sand, University of Duisburg-Essen, Germany, for his assistance with writing and proof reading the article.

References

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., Falcone, R., Hreglich, S., 2005. Glass-ceramics obtained by the recycling of end of life cathode ray tubes glasses. Waste Manage. 25, 183–189.

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., 2007. CRT glass state of the art – a case study: recycling in ceramic glazes. J. Eur. Ceram. Soc. 27, 1623–1629.

Bernardo, E., 2007. Micro- and macro-cellular sintered glass-ceramics from wastes. J. Eur. Ceram. Soc. 27, 2415–2422.

Bernardo, E., Cedro, R., Florean, M., Hreglich, S., 2007. Reutilization and stabilization of wastes by the production of glass foams. Ceram. Int. 33, 963–968.

Chen, M.J., Zhang, F.S., Zhu, J.X., 2009. Lead recovery and the feasibility of foam glass production from funnel glass of dismantled cathode ray tube through pyrovacuum process. J. Hazard. Mater. 161, 1109–1113.

Erzat, A., Zhang, F.S., 2014a. Detoxification effect of chlorination procedure on waste lead glass. J. Mater. Cycles Waste 16, 623–628.

Erzat, A., Zhang, F.S., 2014b. Evaluation of lead recovery efficiency from waste CRT funnel glass by chlorinating volatilization process. Environ. Technol. 35, 2774–2780.

Grause, G., Yamamoto, N., Kameda, T., Yoshioka, T., 2014. Removal of lead from cathode ray tube funnel glass by chloride volatilization. Int. J. Environ. Sci. Technol. 11, 959–966.

Gregory, J.R., Nadeau, M.C., Kirchain, R.E., 2009. Evaluating the economic viability of a material recovery system: the case of cathode ray tube glass. Environ. Sci. Technol. 43, 9245–9251.

Hou, X., Chou, K.C., Zhao, B., 2013. Reduction kinetics of lead-rich slag with carbon in the temperature range of 1073–1473 K. J. Min. Metall. B 49, 201–206.

Lee, C.H., Chang, C.T., Fan, K.S., Chang, T.C., 2004. An overview of recycling and treatment of scrap computers. J. Hazard. Mater. 114, 93–100.

Li, H.G., 2005. Metallurgical Principle. Science Press, Beijing (in Chinese).

Liang, Y.J., Che, Y.C., 1994. Inorganics Thermodynamics Manual. Northeastern University Press, Shenyang (in Chinese).

Ling, T.C., Poon, C.S., 2011. Utilization of recycled glass derived from cathode ray tube glass as fine aggregate in cement mortar. J. Hazard. Mater. 192, 451–456.

Ling, T.C., Poon, C.S., 2013. Effects of particle size of treated CRT funnel glass on properties of cement mortar. Mater. Struct. 46, 25–34.

Lu, X.W., Shih, K.M., Liu, C.S., Wang, F., 2013. Extraction of metallic lead from cathode ray tube (CRT) funnel glass by thermal reduction with metallic iron. Environ. Sci. Technol. 47, 9972–9978.

Matamoros-Veloza, Z., Rendon-Angeles, J.C., Yanagisawa, K., Cisneros-Guerrero, M. A., Cisneros-Guerrero, M.M., Aguirre, L., 2008. Preparation of foamed glasses from CRT TV glass by means of hydrothermal hot-pressing technique. J. Eur. Ceram. Soc. 28, 739–745.

Mear, F., Yot, P., Cambon, M., Ribes, M., 2005. The changes in lead silicate glasses induced by the addition of a reducing agent (TiN or SiC). J. Non-Cryst. Solids 351, 3314–3319.

Mear, F., Yot, P., Cambon, M., Ribes, M., 2006a. The characterization of waste cathode-ray tube glass. Waste Manage. 26, 1468–1476.

Mear, F., Yot, P., Ribes, M., 2006b. Effects of temperature, reaction time and reducing agent content on the synthesis of macroporous foam glasses from waste funnel glasses. Mater. Lett. 60, 929–934.

Mear, F., Yot, P., Viennois, R., Ribes, M., 2007. Mechanical behaviour and thermal and electrical properties of foam glass. Ceram. Int. 33, 543–550.

Mear, F.O., Yot, P.G., Kolobov, A.V., Ribes, M., Guimon, M.F., Gonbeau, D., 2007. Local structure around lead, barium and strontium in waste cathode-ray tube glasses. J. Non-Cryst. Solids 353, 4640–4646.

Miyoshi, H., Chen, D.P., Akai, T., 2004. A novel process utilizing subcritical water to remove lead from wasted lead silicate glass. Chem. Lett. 33, 956–957.

Mostaghel, S., Samuelsson, C., 2010. Metallurgical use of glass fractions from waste electric and electronic equipment (WEEE). Waste Manage. 30, 140–144.

Nakamoto, M., Miyabayashi, Y., Holappa, L., Tanaka, T., 2007. A model for estimating viscosities of aluminosilicate melts containing alkali oxides. ISIJ Int. 47, 1409–1415.

Okada, T., Yonezawa, S., 2013. Energy-efficient modification of reduction-melting for lead recovery from cathode ray tube funnel glass. Waste Manage. 33, 1758–1763.

Pruksathorn, K., Damronglerd, S., 2005. Lead recovery from waste frit glass residue of electronic plant by chemical-electrochemical methods. Korean J. Chem. Eng. 22, 873–876.

Sasai, R., Kubo, H., Kamiya, M., Itoh, H., 2008. Development of an eco-friendly material recycling process for spent lead glass using a mechanochemical process and Na(2)EDTA reagent. Environ. Sci. Technol. 42, 4159–4164.

Saterlay, A.J., Wilkins, S.J., Compton, R.G., 2001. Towards greener disposal of waste cathode ray tubes via ultrasonically enhanced lead leaching. Green Chem. 3, 149–155.

Tang, X.L., Zhang, Z.T., Guo, M., Zhang, M., Wang, X.D., 2011. Viscosities behavior of CaO–SiO_2–MgO–Al_2O_3 slag with low mass ratio of CaO to SiO_2 and wide range of Al_2O_3 content. J. Iron Steel Res. Int. 18, 1–17.

Wang, P.W., Zhang, L.P., 1996. Structural role of lead in lead silicate glasses derived from XPS spectra. J. Non-Cryst. Solids 194, 129–134.

Witkowska, A., Rybicki, J., Di Cicco, A., 2005. Structure of partially reduced xPbO $(1-x)SiO_2$ glasses: combined EXAFS and MD study. J. Non-Cryst. Solids 351, 380–393.

Xing, M.F., Zhang, F.S., 2011. Nano-lead particle synthesis from waste cathode ray-tube funnel glass. J. Hazard. Mater. 194, 407–413.

Xu, Q.B., Li, G.M., He, W.Z., Huang, J.W., Shi, X., 2012. Cathode ray tube (CRT) recycling: current capabilities in China and research progress. Waste Manage. 32, 1566–1574.

Yamashita, M., Wannagon, A., Matsumoto, S., Akai, T., Sugita, H., Imoto, Y., Komai, T., Sakanakura, H., 2010. Leaching behavior of CRT funnel glass. J. Hazard. Mater. 184, 58–64.

Yot, P.G., Mear, F.O., 2009a. Lead extraction from waste funnel cathode-ray tubes glasses by reaction with silicon carbide and titanium nitride. J. Hazard. Mater. 172, 117–123.

Yot, P.G., Mear, F.O., 2011. Characterization of lead, barium and strontium leachability from foam glasses elaborated using waste cathode ray-tube glasses. J. Hazard. Mater. 185, 236–241.

Yuan, W.Y., Li, J.H., Zhang, Q.W., Saito, F., 2012. Innovated application of mechanical activation to separate lead from scrap cathode ray tube funnel glass. Environ. Sci. Technol. 46, 4109–4114.

Waste Management 57 (2016) 187–197

Contents lists available at ScienceDirect

Waste Management

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

Review

Global responses for recycling waste CRTs in e-waste

Narendra Singh, Jinhui Li *, Xianlai Zeng

State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 17 September 2015
Revised 3 February 2016
Accepted 6 March 2016
Available online 9 April 2016

Keywords:
E-waste
Waste CRT
Trans-boundary movement
Solution

ABSTRACT

The management of used cathode ray tube (CRT) devices is a major problem worldwide due to rapid uptake of the technology and early obsolescence of CRT devices, which is considered an environment hazard if disposed improperly. Previously, their production has grown in step with computer and television demand but later on with rapid technological innovation; TVs and computer screens has been replaced by new products such as Liquid Crystal Displays (LCDs) and Plasma Display Panel (PDPs). This change creates a large volume of waste stream of obsolete CRTs waste in developed countries and developing countries will be becoming major CRTs waste producers in the upcoming years. We studied that there is also high level of trans-boundary movement of these devices as second-hand electronic equipment into developing countries in an attempt to bridge the 'digital divide'. Moreover, the current global production of e-waste is estimated to be '41 million tonnes per year' where a major part of the e-waste stream consists of CRT devices. This review article provides a concise overview of world's current CRTs waste scenario, namely magnitude of the demand and processing, current disposal and recycling operations.

1. Introduction

The electronics industry is one of the most important industries in the world. It has grown steadily in recent decades, created a great number of jobs, promoted technological development and, at the same time, fueled a high generation of electronic waste (e-waste) after the end of the electronic products life (Veit and Bernardes, 2015). E-waste is one of the fastest growing solid waste streams around the world today. The continuous growth of e-waste is as a result of the rising demand for information technology and the advent of attractive new design of electronic products, which have today caused the early obsolescence of many electronic gadgets used across the world (Lundgren, 2012). According to the estimation by United Nation University that e-waste will rise from the 41 million tonnes currently produced each year to 47 million tonnes in 2017 (Baldé et al., 2015). In the European Union (EU), e-waste is growing at a rate of 3–5% per annum which is about three times faster than other individual waste streams in the solid waste sector (Schwarzer et al., 2005; Savage et al., 2006). It is estimated that in 2009 around 5 million tonnes of e-waste were in storage and 2.37 million tonnes of e-waste were ready for disposal, which represents an increase of around 120% from 1999 levels (US EPA, 2011; Perez-Belis et al., 2015).

CRTs may have disappeared from the shops of the developed nations, but the number entering the waste stream is yet to peak in Europe, while demand for the leaded glass they contain has faded (Messenger, 2015). Since the 1950s, CRTs have been used in television and computer screens (Rocchetti and Beolchini, 2014). Historically, their production has grown in step with Television and computer demand. For instance, the global CRT monitor industry was valued at US $19.5 billion, producing 108 million units in 2001 (Kuehr and Williams, 2003). However, at present, CRT technology for televisions and computers is obsolete, the market for new CRTs is dwindling and with almost no CRT manufacturers left to turn glass from end-of-life screens back into new televisions and monitors, and huge volumes of obsolete units entering the waste stream, around the world the hazardous leaded glass was piling up (Shaw Environmental Inc., 2013) because it is being replaced mainly by flat panel technologies for video displays.

Moreover, CRTs devices, such as televisions and computer monitors, have been considered an environmental hazard if disposed improperly because they contain large amounts of leaded glass, which is considered toxic (Jang and Townsend, 2003; Nnorom et al., 2011). The disposal of television and computers is a unique issue due to the fact that most television and computers are often disposed of before they truly become useless. In fact, the main reason for purchasing a new computer is not to replace a non-functioning system, but to keep up with rapidly changing technologies (Adamson et al., 2005). Moreover, the progressive replacement of old CRT TV and PC screen with LCD or PDPs has

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* Corresponding author.
E-mail address: jinhui@tsinghua.edu.cn (J. Li).

http://dx.doi.org/10.1016/j.wasman.2016.03.013
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creates a large volume of waste stream of obsolete CRTs waste in developed countries and developing countries will become major CRTs waste producers in the upcoming years, which may be going to be cause huge amounts of glasses to be landfilled (Bernardo et al., 2009).

Various reports within the past year have been indicated that some processors are stockpiling CRTs specifically in the developed countries due to a lack of market capacity or affordable access to market capacity (Schluep et al., 2009; Bhutta et al., 2011; Shaw Environmental Inc., 2013). Other processors are reporting concerns about the ability to continue securing markets for CRT glass. These market constraints are a concern given the high levels of lead in CRT glass and the continued interest in ensuring the viability of the e-waste recycling industry (Shaw Environmental Inc., 2013). This review article provides a concise overview of world's current CRTs waste scenario, namely magnitude of production and processing, environmental and health hazards, current disposal and recycling operations.

2. Generation and characteristics of waste CRT

2.1. Generation of waste CRT

The worldwide market for CRT has been downgraded to 32 million units on declining demand and waning supply of core components. This is evidenced by the market figures presented in Table 1, which shows the worldwide market for CRT and LCD television displays in 1998, 2002 and 2010–2016 (Socolof et al., 2005; Statica, 2015).

According to DisplaySearch, a market research company, three million CRT sets are expected to be shipped in 2014 to the Asia-Pacific region, which includes Southeast Asia and India, compared with 28.4 million LCD sets. According to the United Nation University (UNU), the global quantity of CRT screen waste generation of in 2014 was around 6.3 Mt. (Baldé et al., 2015). Most of the screen waste was generated in Asia: 2.5 Mt in 2014, followed by the highest screen waste generation in absolute quantities are Europe (1.7 Mt), America (1.7 Mt), Africa (0.3) and Oceania (0.1 Mt).

However, there still in developing countries demand for CRT TVs and monitors by low-income consumers because CRT sets are the cheapest option and often they cannot afford more expensive LCD TV sets (IHS, 2013). Meanwhile, It is also clear that, even for those markets, CRTs will eventually be supplanted (Gregory et al., 2009a,b). According to iSupply an industry-based statistical organization production of CRTs was not surpassed by LCDs until the fourth quarter of 2007, due largely to CRT production at factories in developing countries. As shown in Fig. 2, CRT has fallen from 77% of global TV shipments in Q1′06 to 46% in Q4′07, DisplaySearch reported that LCD TV shipments worldwide overtook CRT TV shipments for the first time, after rising 56% year over year to a record of more than 28.5 million units or 47% of the world TV market (IHS, 2013).

In case of developed nations, at least, it is now impossible to find a CRT computer monitor or television in electronic shops. However, they are still present in the houses of many people, and gradually being replaced by new flat screens (Rocchetti and Beolchini, 2014). According to WEEE collection and pre-treatment market, about 50,000–150,000 tons/year of end of life CRTs are currently collected within Europe and this flux is not expected to decrease in the upcoming years (Andreola et al., 2007). Besides, an analysis discovered the CRT replacement and the amount of waste generated for the whole EU market between 1996 and 2015. From the year 1996, CRT sales were at a level of 20 million units, and increased slightly from 1996 to 2005. From 2006 sales fell steeply to less than 10 million and continues to decline to about zero pieces in 2011. Simultaneously, the number of CRT in the waste stream rose gradually from 15 million pieces in 1996 to 20 million pieces in 2009 and declined gradually after 2009. Given the technology shift and introduction of flat panel displays, flat panel display sales increased dramatically from 10 million pieces in 2005 to 55 million pieces in 2012. It is predicted that there will be a gradual decline in sales after 2012 (Fakhredin and Huisman, 2013).

Table 1
Television displays in the worldwide market (millions unit).

Type	1998	2002	2010	2011	2012	2013	2014	2015	2016
CRT	80.7	83.3	36	21	18	12	7	5	5
LCD	1.3	32.2	178	197	205	222	238	250	261
Total	82.0	115.5	214	218	223	234	245	255	266

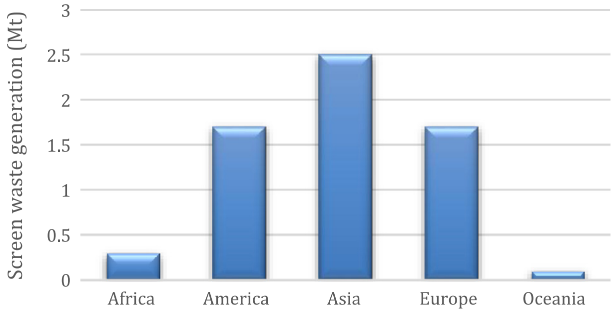

Fig. 1. Global monitor screen waste generated in 2014. Data source source from Baldé et al. (2015).

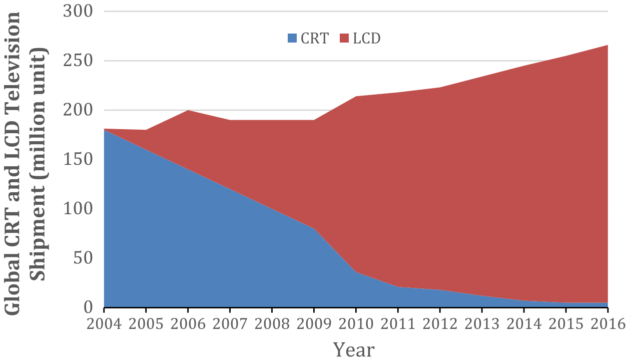

Fig. 2. The global CRT and LCD Television shipment. Data source from DisplaySearch report (2014).

Similarly, in the United State, an analysis of the demand for CRT glass has discovered that CRTs comprise the largest portion (estimated by U.S. EPA at 43%) of the current e-waste stream and significant quantities (6.9 million tons or 232 million units) of CRTs remain to be recovered from homes and businesses in the U.S. The vast majority of these CRTs (85%) are projected to be collected and require management over the next 10 years. Whilst an additional 330,000 tons (or 12,000,000 units) has reported to be currently stockpiled by processors (Shaw Environmental Inc., 2013).

According to the UNU report 2015, Japan produced 2.2 million tons of e-waste in 2014, ranking thereby third, behind the US (7.1 million) and China (6 million) who generated together around a third of the global total (32%) (Baldé et al., 2015). Additionally, approximately 1.87 million CRT TVs were collected in 2014. However, All the manufacturers and importers of e-waste successfully achieved recycling rates higher than the legal requirements. The recycling rates for the CRT TVs were 55% (METI, 2014; Yolin, 2015). Although, the millions of TVs and computers purchased around the world every year (183 million in 2004) become obsolete they leave behind lead, cadmium, mercury and other hazardous wastes. Over the past two decades, the global market of EEE continues to grow exponentially, while the lifespan of those products becomes shorter and shorter. In the United States (US) market, in 2006, more than 34 million TVs have been exposed in the market, and roughly 24 million PCs and 139 million portable communication devices have been produced. In the European Union, waste electrical and electronic equipment represents about 7.5 million tons each year, where computer monitors and TV sets containing CRTs represent about 80% of the total electronic waste (Andreola et al., 2005).

In China, approximately 48 million TVs were sold in 2001, and nearly 40 million PCs were sold in 2009. The situation is exacerbated by the rapid turnover of electronic devices. Because of the fast pace at which technology is evolving, most electronics have only a 2–3-year useful life (Xu et al., 2012; Yu et al., 2010). Countries in Asia have been at the forefront of the production of CRT-containing devices. For example, China manufactures approximately 90% of the global CRT production in 2005 (Widmer et al., 2005). The statistical data are presented in Fig. 3 (China Statistical Yearbooks 2013). The figure shows that the number of TV sets produced in China has grown rapidly since 2000–2012 and at present China is the largest producer and exporter of TV sets in the world. In 2010, the recycling and dismantling number of waste electrical appliances through “Old for new” policy is 56 million units, in which 80% are CRT monitor in China (Song et al., 2012). Similarly, the volume of waste CRT generation in India is typified by the study by Kumar and Shrihari (2007). This study used market supply method to estimate that about 132,000 kg of waste TVs will be generated in Mangalore city alone between 2007 and 2008. This will be expected to increase to 223,704 kg by 2009–2010. Waste PC generation is also expected to follow the same trend-218,742 for 2007/2008; 275,808 for 2008/2009 and 547,346 kg for 2009/2010. These categories are the leading contributors to WEEE generated in the city; waste TVs constituting 39% and waste PCs 55% (Kumar and Shrihari, 2007; Chatterjee, 2012).

Current e-waste flow in developing countries specially PCs and TVs waste has been estimated by Schluep et al. (2009), which were made mainly based on existing e-waste assessments or related reports, most of which were prepared by one or several partners of the Solving the E-waste Problem (StEP). Missing data of generated e-waste were calculated by applying average lifetime estimates with actual quantities put on the respective markets or the stock of specific product groups. Table 2, shows the quantities put on the market, stock or installed base and the quantities of PCs and TVs waste generated in 11 different countries, from the different product groups which were selected according to available country assessments.

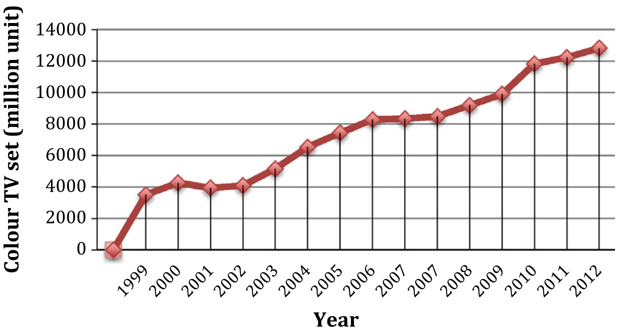

Fig. 3. Production of Color TV in China. Data source from (China Statistical Yearbooks, 2013, http://mcin.macrochina.com.cn/).

Similarly, (Gregory et al., 2009a,b) investigated the weight of CRT glass cullet generated and the amount of CRT glass collected in each region as it evolves over time. Figs. 1 and 2 show these amounts for the four regions in 2010 and 2020 (weights are in metric tons, as in all plots) (see Figs. 4–7).

2.2. Characteristics of waste CRT

A CRT is a specialized vacuum tube in which images are produced when an electron beam strikes a phosphorescent surface. Besides television sets, cathode ray tubes are used in computer monitors, automated teller machines, video game machines, video cameras, oscilloscopes and radar displays. The CRT is comprised mostly of glass, with some metals specially the lead. The concentration of lead in the glass depends on the size of the CRT glass, as shown in Table 3.

The CRT is a tube with a conical shape formed by three types of glass and the electron gun. It is the main component of the monitor because it is inside the CRT that the image formation process occurs. The cathode ray tube is also the heaviest component of the monitor, reaching 60% of its total weight (Veit and Bernardes, 2015).

Generally, there are two types of CRTs: black and white (monochrome) and color. In general CRT consists of a front panel used as the screen, a neck, which envelops the electron gun, and funnel, which connects the panel and the neck. It is estimated that CRT constitutes around 60% of the weight of a television or a computer monitor and is composed of 85% glass of which the front panel contributes 65%, funnel 30% and neck glass 5% (Andreola et al., 2007; Herat, 2008). Main raw material consists of silica, alumina, lime, magnesia, boric acid, etc., which are main component of the glass (Lee and Hsi, 2002). To compare with other wasted glass, the properties of panel CRT glass waste has low melting catalyst components like to K_2O, Na_2O and it contained about 10% BaO component. Funnel glass has some features that were excellent for index of refraction, dispensability and cutting because it contains 20% PbO (Lecler et al., 2015). To prevent the escape of radiation from the tube, lead is added to the composition of the glass. Lead has the ability to absorb the ionizing radiation (Parr and Davie, 1959). The addition of lead occurs in the funnel and neck glass. The panel glass has the addition of barium. Like lead, barium is capable of absorbing a certain amount of radiation because of its density.

3. Recycling and disposal of waste CRT

The recycling of CRT waste is a critical step in the recycling of electronic waste. The CRT monitor is the largest and heaviest component of a computer, it’s composition is basically Leaded glass and the fact that it is a hazardous residue makes the CRT monitor of low interest to the WEEE recycling companies (Lee and Hsi, 2002).

The recycling of CRTs is based on closed-loop and open-loop recycling systems. The closed-loop system refers to the recycling of CRTs in the manufacturing chain itself. Here, the end-of-life tubes are used in the manufacturing of new CRT tubes. The open-loop system involves the recycling of CRT glass in the manufacture of new products.

Although, currently both systems have difficulties/barriers. In the closed-loop system, the recycling of CRTs presents major logistical difficulties. The presence of manufacturers in the country is an important factor that makes this type of recycling logistically and economically feasible. However, many countries have no CRT manufacturers. Even if manufacturers of CRT are present in several countries, the recycling demands would be greater than the

Table 2
Quantity put on the market, Stock (Installed base) and quantity generated of PCs and TVs in metric tons/year Countries (Schluep et al., 2009).

Countries	Quantity put on the market		Stock (installed base)		Quantity of PCs & TVs generated	
	PCs	TVs	PCs	TVs	PCs	TVs
S. Africa	32,000	35,800	99,200	189,900	19,400	23,700
Kenya	5200	–	21,300	22,600	2500	2800
Uganda	700	–	7500	15,600	1300	1900
Morocco	15,100	16,800	67,500	151,000	13,500	15,100
Senegal	1100	4200	3100	15,000	900	1900
Peru	7000	–	70,000	92,300	6000	11,500
Colombia	13,600	–	57,300	146,400	6500	18,300
Mexico	63,700	224,100	300,000	750,000	47,500	166,500
Brazil	–	–	483,800	1,096,000	96,800	137,000
India	140,800	450,000	425,000	1904600	56,300	275,000
China	419,100	1,170,000	1,324,800	11,975,300	300,000	1,350,000

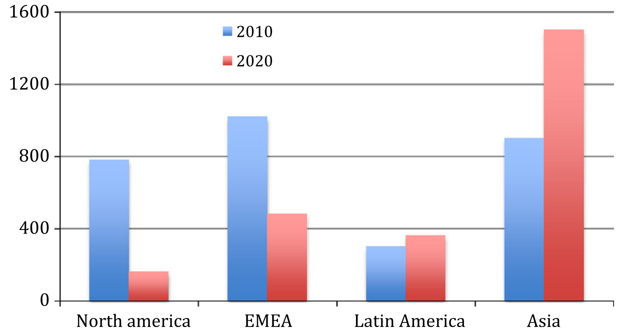

Fig. 4. Weight of CRT glass cullet generated in the four regions in 2010 and 2020 (weights are in metric tons, as in all plots, EMEA- Europe, the Middle East, and Africa) (Gregory et al., 2009a,b).

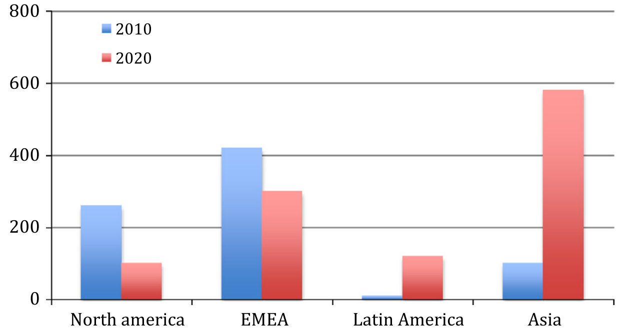

Fig. 5. Weight of CRT glass cullet collected in the four regions in 2010 and 2020 (weights are in metric tons, as in all plots, EMEA- Europe, the Middle East, and Africa) (Gregory et al., 2009a,b).

demand for new CRT tubes, mainly due to declining sales for new CRTs (Gregory et al., 2009a,b).

In Waste Electrical and Electronic Equipment (WEEE) recycling companies, the CRT recycling circuit starts with the collection, temporary storage and cleaning of monitors. The problem with collection and storage is that CRT monitors are considered hazardous residue, so its transportation and storage most comply with all the regulations of hazardous waste management. The dismantling of CRT components is the next step. The CRT monitor is manually opened and its components are removed one by one. The CRT is kept intact, without the metallic band and any polymeric adhesive on its surface. The other CRT components follow the conventional recycling systems. Polymers are crushed and sent to recycling companies, metals are sent to smelter companies and the printed circuit boards follow the viable recycling route. Fig. 8 shows the process flow diagram for the recycling of CRT monitors.

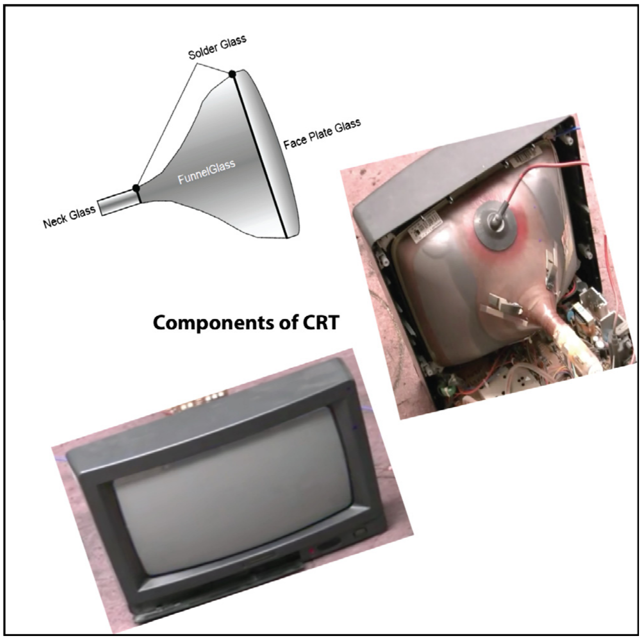

Fig. 6. A schematic view and Components of CRT.

The most important step in CRT recycling is the separation of the glass types. This separation is required because the three types of glass have different chemical compositions and, consequently, different methods of recycling. The depressurization is generally carried out by breaking the top of the neck glass or by electric wire heating method uses a special electrical wire (e. g. NiChrome wire) (Menad, 1999; Herat, 2008). The separation of the tube must be done mechanically because there is the risk of breaking the glass. The two most widely used methods for this purpose are the hot wire method and the diamond saw method. Both techniques are automated with little tube handling. Other technologies involve the laser cutting system, the wet jet separation method and the thermal-shock system method (Xu et al., 2012).

The hot wire system applies an electric current to a nickel-chromium wire that is coiled around the CRT at the interface between the funnel and the panel glasses. The heat wire melts the glass and an air flow cools down the wire. The thermal shock obtained from the heating and rapid cooling breaks the interface glass (Herat, 2008). Fig. 9, described the complete separation between the funnel and the faceplate glass in then completed manually by the operator.

The advantage of this method is its low cost and requirement for investment capital. The glass separation process should be

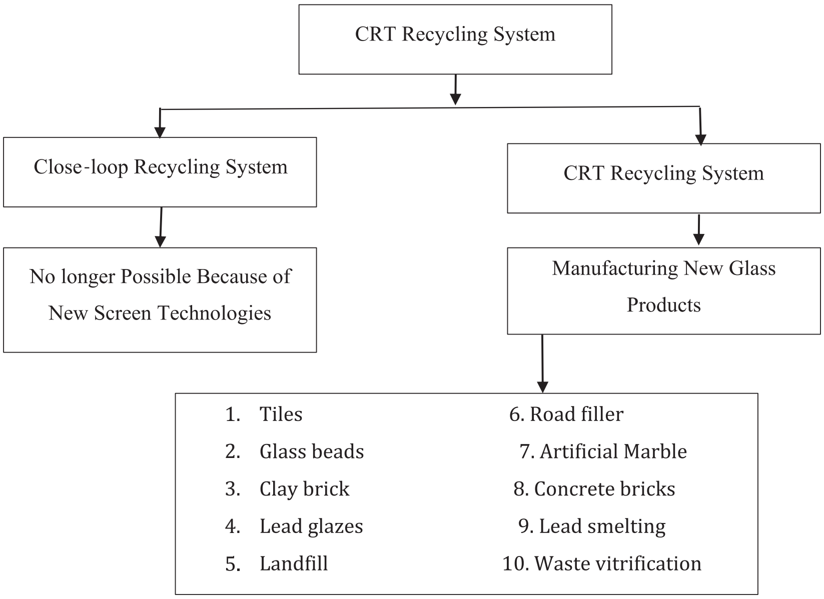

Fig. 7. A systematic overview of CRT recycling system.

Table 3
Lead content in different size of CRT devices (Karagiannidis et al., 2005; Iniaghe and Adie, 2015).

CRT size	Lead in (kg)	CRT size	Lead in (kg)
13-in.	0.5	27-in.	1.8
17-in.	0.7	32-in.	2.9

monitored to prevent possible contamination between the glass types. If the panel glass presents a certain amount of lead, it cannot be recycled directly. The funnel and electron gun glass can be recycled for products that use leaded glass, such as crystal glass, radioactive glass, optical dense barium crown glass or jewelry (Lee and Hsi, 2002). The addiction of lead in the glass varies from 1% in jewelry glass, to 65% in radio shielding glass. In general, because of the variation in glass composition in deferent CRTs proves to be a barrier in the recycling of leaded glass (Mear et al., 2006). It is also possible to recycle leaded glass for products that may contain certain amounts of lead in their composition, such as foam glass, bricks, clays, and piles. Many studies propose the recycling of CRT glass, especially leaded glass, in the ceramics industry (Bernardo et al., 2009; Guo et al., 2010).

3.1. Resource recycling and material flow of waste CRT treatment

The CRTs collected for recycling were recycled into new CRTs through glass-to-glass recycling, or else sent to secondary lead smelters to recover the lead. Glass-to-glass recycling has been the most common management method, but with the shift from CRT technology to flat panel technologies for video displays, the market for new CRTs is dwindling (Shaw Environmental Inc., 2013). Several reports in the past year have found that the amount of new glass required is decreasing, but is much greater than the amount of secondary glass collected, which is increasing

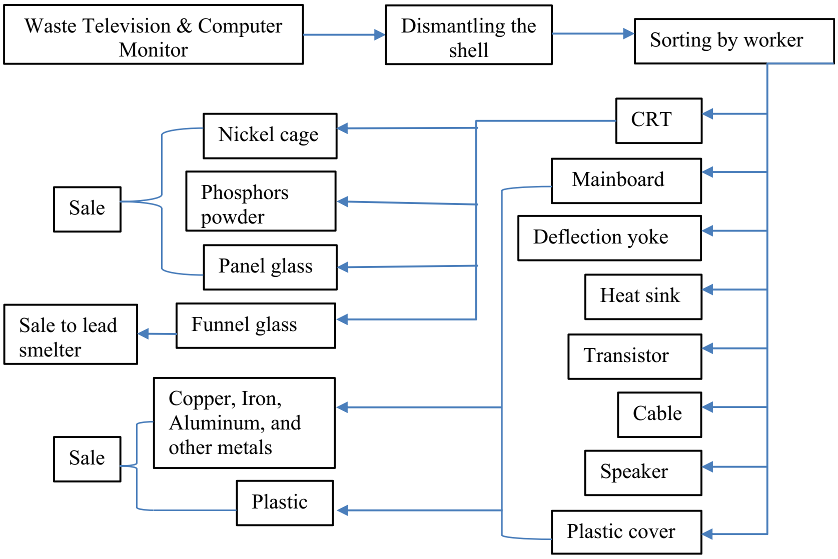

Fig. 8. Recycling processes and material flows of waste CRT monitors in China.

Fig. 9. Complete separation between funnel and panel glass by thermal-shock method.

(Gregory et al., 2009a,b). The glass in a monitor typically accounts for over half of the product weight and the panel glass accounts for over half the weight of the CRT (Andreola et al., 2006).

Owing to their different chemical compositions, CRT glass cullet must generally be separated into panel and funnel glass to be used extensively in the production of new CRTs (Dondi et al., 2009). Several barriers exist to increasing the recovery of CRT cullet. First, the lead in the glass precludes its use in high volume glass products such as containers or windows. The lead content can also lead to the glass being classified as a hazardous material; overall these factors mean that CRT glass has relatively low value. This creates situations where the materials in an End of Life TV or monitor are worth less than the cost to recover that material (Gregory et al., 2009a,b). In fact, depending on the degree to which the glass has been separated and cleaned, processors will often have to pay a downstream recipient to accept the cullet. Alternative applications for secondary CRT glass have been proposed including bricks, decorative tile, nuclear waste encapsulation, construction aggregates, fluxing agent, and sandblasting medium (Minay et al., 2003; Bernardo et al., 2009; Guo et al., 2010). Several projects are working to reduce the barriers to use in these applications, nevertheless, in all cases identified to-date secondary CRT glass substitutes only for other low cost materials (Gregory et al., 2009a).

Currently, the Nulife Glass Company and the Sweepkauusakoski Company extracting lead from the leaded glass. They use a furnace and chemicals to remove the lead from the glass. The process is based on the reduction of lead and its removal from the glass matrix. According to the company website, this unique CRT recycling furnace extracts the toxic lead from the glass in a safe and environmentally sustainable way. The process creates no waste and avoids export of hazardous material around the globe. Nulife Glass' CRT recycling furnace technology is capable of processing up to 10 tonnes of funnel glass per day, equivalent to the glass from approximately 60 tonnes of televisions (Nulife, 2013). SWEEEP Kuusakoski company stated that it is the first company in the world to have a genuine sustainable solution for CRT recycling (innovative CRT recycling furnace), which can extract lead from up to 10 tonnes of funnel glass per day, that's the glass from approximately 60 tonnes of televisions. The process has no emissions, creates no waste and avoids export of hazardous material from the UK. This unique CRT recycling furnace allows us to remove approximately 1 kg of lead per screen in a safe and environmentally sustainable way and create added value products from the remaining molten glass (Sweep Kuusakoski, 2014). Although few companies in the world use this technology, the process promises a new way to deal with waste CRT.

Smelting is a potentially important application for Pb-containing funnel glass for which other recycling options are limited and it does not require the removal of glass coatings before recycling can take place (ICER, 2004) Lead and copper smelters use large amounts of silica as flux to promote fluidity and to remove and transfer impurities to the process slag (USEPA, 1992; UK DOE, 1995; Mostaghel et al., 2011).The mass percentage of flux to concentrate feed in a copper furnace is less than 2% (Memary et al., 2012)

The technical feasibility of using mixed CRT funnel and panel glass as fluxing material in copper smelters has been investigated by Mostaghel et al. (2011). According to the authors, the mixed CRT glass could be an appropriate substitution of fluxing materials "as long as the mineralogy (physical properties, chemical composition and internal crystal structure) of the products (extracted metals) and by-products (mainly slag) remained the same". According to the results of the experiments, a replacement of 10% of the flux material with mixed CRT glass did not change the mineralogy of the slag. However, higher mass fractions of CRT glass changed the mineralogy and increased the lead leaching of the slag.

The global production of copper in 2012 was 17,000 kt (USGS, 2014; ILA, 2015). Assuming that it was produced from an ore concentrate of 30% Cu at a smelting efficiency of 98% (Yot and Méar, 2011), a total of 1180 kt of flux material would have been needed. If a replacement of 10% the flux material by CRT glass is possible, a total amount of 118 kt CRT glass (mixed funnel and panel; 35.40 kt funnel) would have been needed; the equivalent of 6 million CRT screens of 20 kg each.

3.1.1. Developing countries

The rapid development and new innovations give computers and televisions a very short life span and therefore create huge amounts of e-waste (Nnorom and Osibanjo, 2008). Apart from the domestic production of the CRT waste in developing countries, it is also having even Trans boundary movement of CRT waste from developed countries (INTERPOL, 2015). China is among the biggest receivers of E-waste sent by wealthier countries, along with countries such as Peru, Ghana, Nigeria, India and Pakistan (Li et al., 2008; Kahhat and Williams, 2009). Singapore is one of the known destination countries of E-waste in Southeast Asia, while neighboring countries such Malaysia, Vietnam, Philippines and Indonesia are suspected to receive a large share of this waste through illegal imports (Anderson, 2010).

For example, an independent enquiry carried out by a branch of the US government to find out the widespread distribution of CRTs to the black market by recycling companies. In addition to remote transactions via websites, buyers from developing countries, particularly African countries, are also known to travel to OECD countries as "waste tourists" to secure supplies of e-waste and arrange shipment (UNODC, 2015). The trans-boundary movement of WEEE has been particularly controversial when the waste has been exported from developed countries to developing countries. Basel Action Network (BAN) and Silicon Valley Toxics Coalition (SVTC), both active Non-Governmental Organizations (NGOs), warned that the main WEEE traffic routes directed toward Asia, and the primitive recycling systems often used there have caused significant environmental damage, partly due to the multitude of electronic products or parts containing hazardous materials (Widmer et al., 2005; Schwarzer et al., 2005; M.H. Wong et al., 2007).

Similarly, one of the most comprehensive insights into the illicit e-waste trade comes from the results of Project Sky-Hole Patching, initiated in Asia and the Pacific by the World Customs Organization and UNEP. This operation was carried out in 21 countries under the aegis of the WCO's Regional Intelligence Liaison Office for Asia-Pacific and instigated by China Customs. The first phase began in September 2006 and focused on ozone-depleting substances, with hazardous waste movements added from March 2007. The aim of the project was to foster regional cooperation between customs agencies through intelligence sharing and interception of illegal shipments. Over eight months (March-October 2007) Hong Kong Customs intercepted 98 illegal shipments of hazardous waste from 25 countries, predominantly the European Union, Japan and the United States (RILO-AP, 2007; UNODC, 2012).

But now a more complex picture is emerging: since 2013, the developing and transition countries have been producing more e-waste than the so called industrialized world. Latin America, for example, contributed approximately 3.95 million tonnes to the world's e-waste mountain last year (Baldé et al., 2015).

3.1.2. Industrial nations

At present, most of the developed countries focusing on management of CRT waste and it also has attracted considerable interest because it is strongly related to environmental protection and resource shortages. Waste CRT glass contains high content of lead in the funnel glass (15–25% PbO). It can be recovered by mechanical activation or hydro-metallurgical and pyro-metallurgy processes (Yuan et al., 2012). Discarded CRT glass can potentially be used to replace silica in Lead and copper smelting operations (Huisman, 2004) as silica flux required as a raw material. Although there are a limited number of smelters for CRT glass available in world, how to treat the slag in an environmentally friendly way is still a problem.

Disposal of CRTs in landfills and their incineration both are bans in the United State, which began in Massachusetts in 2000 and in California in 2001. Maine and Minnesota have also recently banned CRTs disposal. According to these bans, all CRTs must be recycled in these states. The State of California passed the 'California Electronics Waste Recycling Act' in 2010 stipulating that each manufacturer that sells electronic devices must either collect an equivalent to 90% of the number of devices they sell or they must pay the alternative fee for recycling the devices they sell. The U.S. Environmental Protection Agency (EPA) provides conditional exclusions from the federal hazardous waste management if CRTs glass destined for recycling. These safe, yet simplified standards aim to increase the collection and recycling of CRTs, and to reduce the amount of lead in landfills by allowing the lead to be reused to make new CRTs glass or sent to lead smelters (Li et al., 2015a,b).

An Analysis report based on US, Projected the future CRT glass quantities, if recovery rates of 50% and 100% to provide a lower-bound and upper-bound estimate of the amount of glass to be managed through recycling. At the lower-bound rate of 50%, 206,000 tons per year of CRT-glass will be recovered over the next 10 years. At the upper-bound rate of 100%, 392,000 tons per year of CRT-glass will be recovered (Shaw Environmental Inc., 2013).

3.2. Detoxification and environmental benefit of waste CRT treatment

The main environmental risk is associated with the possibility of the lead present in the CRT tube leaching. Several authors point out that the lead present in the glass can leach in various environments and in concentrations higher than the environmental standards (Jang and Townsend, 2003). There is also a leaching risk of other toxic metals present in the glass, such as barium and strontium, and of cadmium, which can be found in the phosphor layer. When considering the global environmental implications of end-of-life CRTs, the primary effects are generally thought to be the potential emission of toxic material from improper landfill disposal and the impact on humans and communities involved in informal recycling operations in the developing world. These environmental risks exist as long as the hazardous materials remain inside the CRT. The major and primary channel for the release of heavy metals are landfills which has specially been poorly designed, constructed, and operated landfills or in older unlined landfills (Williams et al., 2008) and recycling of lead- contaminated waste under primitive conditions can result in contamination of nearby waterways and ecosystems (Robinson, 2009).

Previous studies have shown that when CRTs are disposed of in landfill sites, lead can leach from the crushed glass and contaminate ground water. This is a major driver for CRT recycling. It is also important to reclaim the other materials, such as ferrous and non-ferrous metals and plastics, which are associated with CRTs. Lead is especially an issue in waste disposal because it becomes bioavailable in soils with increasing pH, and becomes available to animals and humans through the food chain and soil dust inhalation (Martinez-Villegas et al., 2004). Once in the body, it can attack proteins and DNA (Bechara, 2004) as well as interfere with the functions of the central and peripheral nervous systems. At high enough doses, it can result in brain edema and haemorrhage (Needleman, 2004).

Lead is toxic to the kidneys, accumulating in the body and eventually affecting the nervous and reproductive systems. Children's mental development can be impaired by low-level exposure to lead. According to UNEP in total about 40% lead in landfills come from electrical and electronic equipment (UNEP, 2014).

3.2.1. Developing countries

Dumping of CRT screens mostly occurs in developing countries. This is a big problem, since it is very common for homeless people, both adults and children, to live in, and around refuse dumps. These people are therefore very exposed to the lead that is leached from screens by the rainwater. The most common way for the exposed people to become lead poisoned is that they are drinking water with high content of lead. Lead can also be spread to lands through the air and by direct discharges in water and lands. It takes a very long time for lead to form harmless compounds in the nature.

A big problem is when lead is spread to farms and arable lands. When this happens, people are exposed to lead poisoning from eating the fruits and vegetables that are grown on these lands. Adults and children can also be affected when they eat meat from animals that has grazed on grounds exposed to lead, and also when they eat fish, which is affected by lead that comes from discharges from industries in seas and lakes, leachate from refuse dumps and landfills and outflow from sewages. According to UNEP report Lead poisoning is entirely preventable, yet lead exposure is estimated to account for 0.6% of the global burden of disease, with the highest burden in developing regions. Childhood lead exposure is estimated to contribute to about 600,000 new cases of children with intellectual disabilities every year (UNEP, 2013).

3.2.2. Industrial nations

In most industrialized countries, including all of the European Union, E-waste management is implemented quite effectively on the basis of Extended Producer Responsibility (EPR), to cope with the pollution and waste generated (Nnorom and Osibanjo, 2008). EPR is defined as "an environmental policy approach in which a producers' responsibility for a product is extended to the post-consumer stage of a products' life cycle including its final disposal" [OECD, 2014). Due to the high cost of recycling in an environmentally sound way in industrialized countries, much of the E-waste is sent to poorer countries, even though this practice is banned by the Basel Convention and the European directive on Waste for Electrical and Electronic Equipment (Robinson, 2009; Bisschop, 2012). It's well documented that used equipment is also shipped to developing countries for reuse, but much of it still ends up as e-waste. The unsophisticated, informal recycling common in many countries; such as China, India and African countries (Leung et al., 2006;

Deng et al., 2007; Lundgren, 2012; Garlapati, 2016) pollutes the environment and puts people's health at risk.

In the European Union (EU), the scarcity of landfill sites for solid waste drove technological innovation toward alternative waste treatment techniques and encouraged recycling and source reduction approaches. Although e-waste may account for only ~1% of landfilled waste, its content of hazardous materials necessitated the development of new regulatory approaches to deal with this category of solid waste (Castell et al., 2004). Therefore, in 1998, the European Commission published the *Directive on Waste Electrical and Electronic Equipment* (WEEE Directive) (The detailed legislation system and framework can be seen in SI Table S3(A)) (Dully et al., 2009) Similarly in Japan, the scarcity of land for solid waste disposal also motivated the development of special e-waste regulation, the *Home Appliance Recycling Law* (HARL) and *Small Appliance Recycling Law* were implemented to increase recycling rates by imposing responsibilities and costs on manufacturers, retailers and consumers (SI Table S3(B)) (Sawhney et al., 2008; Lee and Na, 2010; Yolin, 2015)

The United States (U.S.) has not ratified the Basel Convention, and only a small fraction of e-waste generated within the country is recycled whereas there is evidence of exportation to developing countries such as China and India (C.S. Wong et al., 2007). Transboundary movement of e-waste seems to have declined with enforcement of environmental and custom officials by developing countries and the joint effort of international society under Basel Convention. But in some cases, becoming a party of the Basel Convention and bilateral agreements were reached to continue the practice (Kahhat et al., 2008). The lack of federal regulation of e-waste has obliged many states within the U.S. to develop specific policies requiring higher volumes of e-waste to be collected and processed separately from the domestic waste stream. Until now, 25 states have similar e-waste regulations, although most do not provide sufficient infrastructure or dedicated revenue streams to enforce compliance and to promote public participation (The detailed legislation framework can be seen in SI Table S3(C)).

4. Gaps and challenges for sustainable waste CRT recycling

According to the European Union-funded project, Countering WEEE (waste electrical and electronic equipment) Illegal Trade (CWIT), 1.3 million tonnes of discarded electronics departed the EU in undocumented mixed exports, of which an estimated 30% (about 400,000 tonnes) was electronic waste; and 70% functioning equipment. More than 10 times the 400,000 tonnes of e-waste exported - some 4.7 million tonnes - was wrongfully mismanaged or illegally traded within Europe itself. And, the research found, even in the few EU member states with robust, effective reporting systems, monitoring of de-pollution efforts and up-to-standard treatment conditions are not always securely in place (CWIT, 2015). For solving the current problem, The dedicated roadmap developed for improving collection and treatment of e-waste in both develop and developing countries will be a valuable result for all parties involved and at the same time strong domestic laws needs to be enforced.

For trade control policies to mitigate the environmental impacts of informal recycling trade policies must be effectively enforced. There are clearly many challenges in developing countries to implementing trade controls, as evidenced by repeated failures in practice (Yu et al., 2010). And for trade bans to work properly they must effectively cut off the supply of e-waste to informal recyclers. This effectiveness is predicated on the assumption that the main source of e-waste is imports from the developed world. For example, only 60% of e-waste is recycled under existing national systems in Europe, and despite an export ban, it is thought that the remaining 40% is exported to Asia or Africa (Huisman et al., 2008).

On the other hand, informal recycling activities score worse for environmental impacts and economic gains compared with modern recycling practices. This is a challenge for waste management as many electronic products contain hazardous materials, as well as valuable elements. But there is a way to offer affordable and environmentally friendly recycling for developing countries: through cooperation between local dismantling operations and the global networks of infrastructure that can further refine materials.

This can be achieved through a global 'reverse supply chain', where treatment facilities in various locations work together to deliver recycling solutions for different materials and at different treatment stages. Such a concept has already been developed by the institutions involved in the Solving the E-waste Problem (StEP) Initiative coordinated by UNU. The concept, called Best-of-2-Worlds (Bo2W), aims to integrate technical and logistical aspects of best practices in advanced, international end-processing facilities (UNU, 2015).

But in the short term, the 'best-of-2-worlds' initiative can be a pragmatic solution until developing countries can establish full end-processing facilities. Its implementation should be flexible and adjusted to local conditions. This could, for example, decide the depth of dismantling and what fractions to send to global facilities. Experiences from pilot projects in China and India have also highlighted societal factors that influence successful implementation (Wang et al., 2012). For instance, the model would work well in a relatively small country generating limited amounts of e-waste because the domestic waste stream cannot justify building a full-scale refinery.

Zoeteman et al. (2010) take a closer look at existing disposal schemes and propose a future outlook on where the disposal of e-waste should be developing (Fig. 10): (1.) Local dumping: This scenario applies to large parts of the world where e-waste ends up in local landfills. (2.) Export and dump: In this scenario, e-waste is exported to developing countries and dumped there.

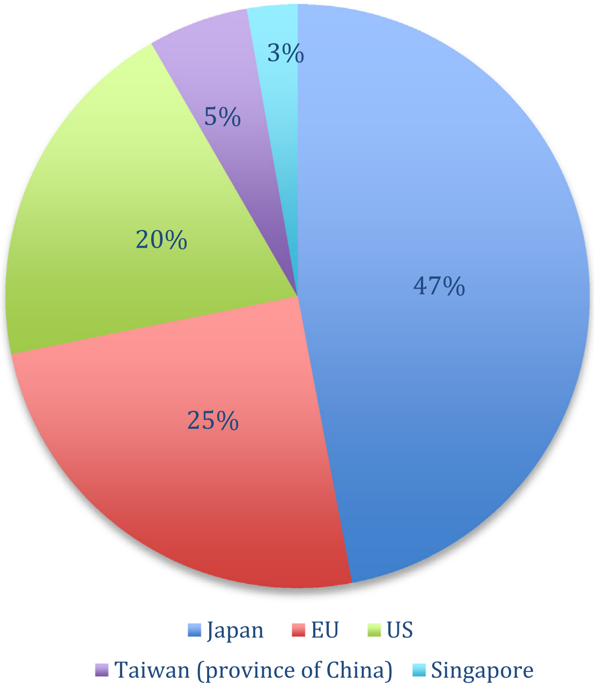

Fig. 10. Sources of seized CRT in Hong Kong (China), March – October 2007 (RILO-AP, 2007; UNODC, 2012).

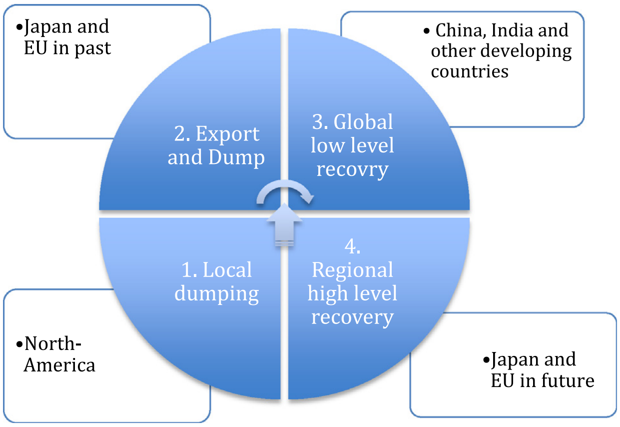

Fig. 11. Global scenarios in sustainable e-waste recovery and examples on regions representing such scenarios.

Waste brokers usually make money of the export and import countries for relieving developed countries of their waste and selling it as resources to developing countries. (3.) Global low-level recovery: A strong demand for materials, mainly in Asia, is the basis for trading recyclables in co-operation with companies employing EPR. This approach saves energy and raw materials. (4.) Regional high-level recovery: This approach also saves raw materials and energy. Additionally, it prevents illegal exports to developing nations and guarantees quality standards due to health, safety and environment standards not applied in Asia or Africa (see Fig. 11).

Apart from new materials and emerging technologies, legislation is also of necessity to smoothly assure and promote eco-friendly recycling of hazardous waste. The international community has established many standards, directives, or regulations related to hazardous waste including CRT, in order to improve its eco-efficiency throughout the life cycle. The International Organization for Standardization set up ISO/TR 14062 (2002) and ISO 14001 (2004) with assistance from the United Nations and The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal; these state that the integration of environmental aspects into the product design and development process should be completed as early as possible, to facilitate the flexibility to make changes and improvements to the product. In addition, these conventions specify many requirements for an environmentally sound management system, to enable organizations to develop and implement policies and objectives (Li et al., 2015a).

In addition to the global environmental agreement, regional and national directives or regulations have been set up as well since 2002. Almost all the regulations are based on extended producer responsibility, to solve the e-waste problem (Sander et al., 2007; Lundgren, 2012; Hotta et al., 2014) The European Union or the European Communities have established the *Directive on Waste Electrical and Electronic Equipment*, *Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment*, *Directive on Packaging and Packaging Waste*, *Directive on Energy-related Products*, and the *Integrated Pollution Prevention and Control Directive*. China, since 2003, has set up the *Cleaner Production Promotion Law*, *Ordinance on Management of Prevention and Control of Pollution from Electronic and Information Products*, *Circular Economy Promotion Law*, and *Administrative Regulation for the Collection and Treatment of Waste Electric and Electronic Products* (Zeng et al., 2013). Within the United States, 25 states have e-waste laws and 65% of the population is now covered by a state e-waste recycling law, although some do not provide sufficient infrastructure or dedicated revenue streams to enforce compliance or to promote public participation (USEPA, 2015).

Moreover, in 2014, Switzerland initiated a project sustainable Recycling Industries (SRI). SRI is an initiative funded by the Swiss State Secretariat for Economic Affairs. SRI develops basic life cycle inventory data for industrial, agricultural and other activities in Brazil, Egypt, India and South Africa. These will form a reliable pool of data for these countries and regions for use in LCA and environmental assessments. To support the component, expertise building and training events will also take place in these countries and the surrounding regions. SRI improves local capacity for sustainable recycling, especially of secondary metals, together with private and public institutions, as well as the informal sector in several developing and transition countries (SRI Project, 2014).

5. Conclusions and recommendations

CRTs waste is universal. Currently a large volume of waste stream of obsolete CRTs waste in developed countries and developing countries will be become major CRTs waste producers in the upcoming years. Comparing the current use of recycled cullet, the potential volume of recycled cullet, and the potential increase of available end-of-life recycled cullet, CRT glass manufacturers do not have the capacity to absorb the total amount of recycled cullet if the widespread collection of end-of-life CRT' were to begin.

CRT waste is chemically different from most other waste forms in that it contains hazardous materials, and special treatment and recycling techniques must be employed to avoid consequences such as environmental impact and damage to living organisms. Substantial amounts of CRT waste exported to developing countries are in fact illegal under the Basel Convention. Contamination associated with CRTs waste has already caused considerable environmental degradation in poor countries and negatively affected the health of the people who live there (Lundgren, 2012; Yoshida et al., 2016).

The data reported in this paper highlights the need for CRT glass manufacturers, recyclers, state and federal regulators and the public to work together to find a use for the increased volume of CRT cullet so it can be recycled into new products, including, but not limited to, new CRTs. Industry and government also need to find ways to promote the development of technology needed to allow recyclers to more accurately classify CRT cullet. With better classification and sorting technology, the amount of CRT cullet the CRT glass manufacturers could recycle could increase dramatically. Some ideas such as the Nulife Glass Company and the Sweep kauusakoski Company, for new technologies exist but a great deal of work needs to be done to develop new technologies that are environmentally and economically feasible and widely available.

Acknowledgements

The work was financially supported by National Nature Science Foundation of China (Grant No. 71373141), China Postdoctoral Science Foundation funded project (Grant No. 2015M571056), and National Key Technology R&D Program (Grant No. 2014BAC03B04).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.wasman.2016.03.013.

References

Adamson, M., Hamilton, R., Hutchison, K., Kazmierowski, K., Lau, J., Madejski, D., MacDonald, N., 2005. Environmental Impact of Computer Information Technology in an Institutional Setting: A Case Study at the University of Guelph. University of Guelph, p. 29.

Anderson, M., 2010. What an E-waste. IEEE Spectr. 47 (72-72).

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., Falcone, R., Hreglich, S., 2005. Glass–ceramics obtained by the recycling of end of life cathode ray tubes glasses. Waste Manage. 25, 183–189.

Andreola, F., Barbieri, L., Corradi, A., Ferrari, A.M., Lancellotti, I., Neri, P., 2006. Recycling of EOL CRT glass into ceramic glaze formulations and its environmental impact by LCA approach. Int. J. LCA 12, 448–454.

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., 2007. CRT glass state of the art. J. Eur. Ceram. Soc. 27, 1623–1629.

Baldé, C., Wang, F., Kuehr, R., Huisman, J., 2015. The Global E-Waste Monitor – 2014. United Nations University, IAS–SCYCLE, Bonn, Germany.

Bechara, A., 2004. The role of emotion in decision-making: evidence from neurological patients with orbitofrontal damage. Brain Cogn. 55, 30–40.

Bernardo, E., Esposito, L., Rambaldi, E., Tucci, A., 2009. 'Glass based stoneware' as a promising route for the recycling of waste glasses. Adv. Appl. Ceram. 108, 2–8.

Bhutta, M.K.S., Omar, A., Yang, X., 2011. Electronic Waste: A Growing Concern in Today's Environment. Economics Research International (2011).

Bisschop, L., 2012. Is it all going to waste? Illegal transports of e-waste in a European trade hub. Crime, Law Soc. Change 58, 221–249.

Wong, C.S., Duzgoren-Aydin, N.S., Aydin, A., Wong, M.H., 2007. Evidence of excessive releases of metals from primitive e-waste processing in Guiyu, China. Environ. Pollut. 148, 62–72.

Castell, A., Clift, R., Francae, C., 2004. Extended producer responsibility policy in the European Union: a horse or a camel? J. Ind. Ecol. 8, 4–7.

Chatterjee, S., 2012. Sustainable electronic waste management and recycling process. Am. J. Environ. Eng. 2, 23–33.

CWIT, 2015. Countering WEEE Illegal Trade, Report, <http://www.weee-forum.org/countering-weee-illegal-trade>.

Deng, W., Zheng, J., Bi, X., Fu, J., Wong, M., 2007. Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. Environ. Int. 33 (8), 1063–1106.

DisplaySearch report, 2014. LCD TV Growth Improving, As Plasma and CRT TV Disappear, According to NPD DisplaySearch Available at: <http://www.displaysearch.com/cps/rde/xchg/displaysearch/hs.xsl/140415_lcd_tv_growth_improving_as_plasma_and_crt_tv_disappear.asp>.

Dondi, M., Guarini, G., Raimondo, M., Zanelli, C., 2009. Recycling PC and TV waste glass in clay bricks and roof tiles. Waste Manage. 29, 1945–1951.

Dully, S., Westkèamper, E., Ulbricht, C., Lückefett, H.-J., 2009. National Registration for Producers of Electronic Waste. Springer.

Fakhredin, F., Huisman, J., 2013. Analyzing End of Life LCD TV WEEE Flows in Europe. Proceedings of Conference EcoDesign 2013.

Garlapati, V.K., 2016. E-waste in India and developed countries: Management, recycling, business and biotechnological initiatives. Renew. Sust. Energ. Revi. 54, 874–881.

Gregory, J., Nadeau, M.-C., Kirchain, R., 2009a. Supply and demand in the material recovery system for cathode ray tube glass. pp. 1–6.

Gregory, J.R., Nadeau, M.-C., Kirchain, R.E., 2009b. Evaluating the economic viability of a material recovery system: the case of cathode ray tube glass. Environ. Sci. Technol. 43, 9245–9251.

Guo, H., Gong, Y., Gao, S., 2010. Preparation of high strength foam glass–ceramics from waste cathode ray tube. Mater. Lett. 64, 997–999.

Herat, S., 2008. Recycling of cathode ray tubes (CRTs) in electronic waste. Clean – Soil Air Water 36, 19–24.

Hotta, Y., Santo, A., Tasaki, T., 2014. EPR-based Electronic Home Appliance Recycling System under Home Appliance Recycling Act of Japan.

Huisman, J., 2004. QWERTY and Eco-Efficiency analysis on treatment of CRT containing appliances at Metallo-Chimique NV. The Ecoefficiency of Treating CRT Glass Fractions Versus Stripped Appliances in a Secondary Copper–Tin–Lead Smelter, Report Written for Metallo-Chimique NV, Beerse, Belgium.

Huisman, J., Kuehr, F.M.R., Maurer, C., Ogilvie, S., Poll, J., Delgado, C., Artim, E., Szlezak, J., Stevels, A., 2008. Review of Directive 2002/96 on Waste Electrical and Electronic Equipment. ENV.G.4/ETU/2006/0032. United Nations University, Bonn, Germany.

ICER (Industry Council for Electronic Equipment Recycling), 2004. Materials Recovery from Waste Cathode Ray Tubes (CRTs). R&D Report: Glass. Waste and Resource Action Programme.

IHS Pressroom, 2013. IHS Pressroom, 2013, See more at: <http://press.ihs.com/press-release/design-supply-chain-media/tv-market-declines-again-2013-sales-both-developed-and-emerg-sthash.lS2hcnwn.dpuf>.

ILA, 2015. Lead Production & Statistics, <http://www.ila-lead.org/lead-facts/lead-production–statistics>.

Iniaghe, P.O., Adie, G.U., 2015. Management practices for end-of-life cathode ray tube glass: review of advances in recycling and best available technologies. Waste Manage. Res., 0734242X15604212

INTERPOL, 2015. Coordinated EU Project Outlines Roadmap Against Unregulated e-Waste, 31 August 2015, <http://www.interpol.int/News-and-media/News/2015/N2015-118>.

Jang, Y.-C., Townsend, T.G., 2003. Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates. Environ. Sci. Technol. 37, 4778–4784.

Kahhat, R., Williams, E., 2009. Product or waste? Importation and end-of-life processing of computers in Peru. Environ. Sci. Technol. 43, 6010–6016.

Kahhat, R., Kim, J., Xu, M., Allenby, B., Williams, E., Zhang, P., 2008. Exploring e-waste management systems in the United States. Resour. Conserv. Recycl. 52, 955–964.

Karagiannidis, A., Perkoulidis, G., Papadopoulos, A., Moussiopoulos, N., Tsatsarelis, T., 2005. Characteristics of wastes from electric and electronic equipment in Greece: results of a field survey. Waste Manage. Res. 23, 381–388.

Kuehr, R., Williams, E., 2003. Computers and the Environment: Understanding and Managing Their Impacts: Understanding and Managing Their Impacts. Springer.

Kumar, P., Shrihari, S., 2007. Estimation and material flow analysis of waste electrical and electronic equipment (WEEE) – a case study of Mangalore City, Karnataka, India. In: Proceedings of the International Conference on Sustainable Solid Waste Management, Chennai, India, pp. 5–7.

Lecler, M.T., Zimmermann, F., Silvente, E., Clerc, F., Chollot, A., Grosjean, J., 2015. Exposure to hazardous substances in Cathode Ray Tube (CRT) recycling sites in France. Waste Manage. 39, 226–235.

Lee, C.-H., Hsi, C.-S., 2002. Recycling of scrap cathode ray tubes. Environ. Sci. Technol. 36, 69–75.

Lee, S.-C., Na, S.-I., 2010. E-waste recycling systems and sound circulative economies in East Asia: a comparative analysis of systems in Japan, South Korea, China and Taiwan. Sustainability 2, 1632–1644.

Leung, A., Cai, Z.W., Wong, M.H., 2006. Environmental contamination from electronic-waste recycling at Guiyu, Southeast China. J. Mater. Cycl. Waste Manage. 8 (1), 21–33.

Li, Y., Xu, X., Liu, J., Wu, K., Gu, C., Shao, G., Chen, S., Chen, G., Huo, X., 2008. The hazard of chromium exposure to neonates in Guiyu of China. Sci. Total Environ. 403, 99–104.

Li, J., Zeng, X., Chen, M., Ogunseitan, O.A., Stevels, A., 2015a. "Control-Alt-Delete": rebooting solutions for the E-waste problem. Environ. Sci. Technol. 49, 7095–7108.

Li, J., Zeng, X., Stevels, A., 2015b. Ecodesign in consumer electronics: past, present, and future. Crit. Rev. Environ. Sci. Technol. 45, 840–860.

Lundgren, K., 2012. The Global Impact of e-waste: Addressing the Challenge; International Labour Office, Programme on Safety and Health at Work and the Environment (SafeWork), Sectoral Activities Department (SECTOR). Geneva: ILO.

Wong, M.H., Wu, S.C., Deng, W.J., Yu, X.Z., Luo, Q., Leung, A.O.W., Wong, C.S.C., Luksemburg, W.J., Wong, A.S., 2007. Export of toxic chemicals: a review of the case of uncontrolled electronic waste recycling. Environ. Pollut. 149, 131–140.

Martınez-Villegas, N., Flores-Vélez, L.M., Domınguez, O., 2004. Sorption of lead in soil as a function of pH: a study case in México. Chemosphere 57, 1537–1542.

Mear, F., Yot, P., Ribes, M., 2006. Effects of temperature, reaction time and reducing agent content on the synthesis of macroporous foam glasses from waste funnel glasses. Mater. Lett. 60, 929–934.

Memary, R., Giurco, D., Mudd, G., Mason, L., 2012. Life cycle assessment: a time-series analysis of copper. J. Clean Prod. 33, 97–108.

Menad, N., 1999. Cathode ray tube recycling. Resour. Conserv. Recycl. 26, 143–154.

Messenger, B., 2015. Ray of Light for CRT Recycling: Waste Management World Magazine, <http://www.waste-management-world.com/articles/print/volume-13/issue-2/features/ray-of-light-for-crt-recycling.html>.

METI, 2014. Enforcement Status of the Home Appliances Recycling Law and Recycling Statistics for Manufacturers and Importers, <http://www.meti.go.jp/english/press/2015/0623_01.html>.

Minay, E.J., Desbois, V., Boccaccini, A.R., 2003. Innovative manufacturing technique for glass matrix composites: extrusion of recycled TV set screen glass reinforced with Al_2O_3 platelets. J. Mater. Process. Technol. 142, 471–478.

Mostaghel, S., Yang, Q., Samuelsson, C., 2011. Recycling of cathode ray tube in metallurgical processes: influence on environmental properties of the slag. Glob. J. Environ. Sci. Technol 1, 19.

Needleman, H., 2004. Lead poisoning. Annu. Rev. Med. 55, 209–222.

Nnorom, I.C., Osibanjo, O., 2008. Overview of electronic waste (e-waste) management practices and legislations, and their poor applications in the developing countries. Resour. Conserv. Recycl. 52, 843–858.

Nnorom, I.C., Osibanjo, O., Ogwuegbu, M.O.C., 2011. Global disposal strategies for waste cathode ray tubes. Resour. Conserv. Recycl. 55, 275–290.

Nulife Glass, 2013. Recycling CRTs from Televisions & Computer Screens Available at: <http://www.nulifeglass.com/>.

OECD, 2014. Extended Producer Responsibility Available at: <http://www.oecd.org/env/tools-evaluation/extendedproducerresponsibility.htm>.

Parr, G., Davie, O.H., 1959. Cathode-ray Tube and its Applications.

Perez-Belis, V., Bovea, M., Ibanez-Fores, V., 2015. An in-depth literature review of the waste electrical and electronic equipment context: trends and evolution. Waste Manage. Res. 33, 3–29.

RILO-AP, 2007. <https://www.unodc.org/documents/toc/Reports/TOCTA-EA-Pacific/TOCTA_EAP_c10.pdf>.

Robinson, W.S., 2009. Ecological correlations and the behavior of individuals. Int. J. Epidemiol. 38, 337–341.

Rocchetti, L., Beolchini, F., 2014. Environmental burdens in the management of end-of-life cathode ray tubes. Waste Manage. 34, 468–474.

Sander, K., Tojo, N., Vernon, J., 2007. The Producer Responsibility Principle of the WEEE Directive.

Savage, M., Ogilvie, S., Slezak, J., Artim, E., Lindblom, J., Delgado, L., 2006. Implementation of Waste Electric and Electronic Equipment Directive in EU 25. European Commission, Brussels.

Sawhney, P., Henzler, M., Melnitzky, S., Lung, A., 2008. Best Practices for E-Waste Management in Developed Countries. Adelphi Research, Austria.

Schluep, M., Hagelueken, C., Kuehr, R., Magalini, F., Maurer, C., Meskers, C., Mueller, E., Wang, F., 2009. Sustainable Innovation and Technology Transfer Industrial Sector Studies: Recycling-From E-Waste to Resources. United Nations Environment Programme & United Nations University, Bonn, Germany.

Schwarzer, S., De Bono, A., Giuliani, G., Kluser, S., Peduzzi, P., 2005. E-waste, the Hidden Side of IT Equipment's Manufacturing and Use.

Shaw Environmental Inc., 2013. (Shaw), a CB&I Company, for Kuusakoski Recycling, LLC. White Paper: An Analysis of the Demand for CRT Glass Processing in the US.

Socolof, M.L., Overly, J.G., Geibig, J.R., 2005. Environmental life-cycle impacts of CRT and LCD desktop computer displays. J. Clean Prod. 13, 1281–1294.

Song, Q., Wang, Z., Li, J., Zeng, X., 2012. Life cycle assessment of TV sets in China: a case study of the impacts of CRT monitors. Waste Manage. 32, 1926–1936.

SRI Project, 2014. <http://www.ecoinvent.org/about/sri-project/sri-project.html>.

Statica, 2015. Global TV Shipments Forecast From 2009 to 2016, by Technology (in million units) Available at: <http://www.statista.com/statistics/260367/global-tv-shipments-forecast/)>.

Sweep Kuusakoski, 2014. Available at: <http://www.sweeepkuusakoski.co.uk/>.

UK Department of the Environment, 1995. Metal Manufacturing, Refining and Finishing Works: Lead Works. Department of the Environment (DOE), UK.

UNEP, 2013. International Lead Poisoning Awareness Week Available at: <http://www.unep.org/chemicalsandwaste/LeadCadmium/PrioritiesforAction/LeadPaints/FocalAreasofWork/GAELP/tabid/106381/Default.aspx>.

UNEP Blog, 2014. Electronic Waste, the Fastest Growing Waste Stream in the World Available at <http://www.unep.org/unea/e_waste.asp>.

UNODC, 2012. Illicit Trade in Electrical and Electronic Waste (e-waste) From the World to the Region, Chapter 9, <https://www.unodc.org/documents/toc/Reports/TOCTA-EAPacific/TOCTA_EAP_c09.pdf>.

UNODC, 2015. Illicit Trade in Electrical and Electronic Waste (e-waste) From the World to the Region, <http://www.unodc.org/toc/en/reports/TOCTA-EA-Pacific.html>.

UNU, 2015. Solving the E-waste Problem (StEP) Initiative Available at: <http://ias.unu.edu/en/research/solving-the-e-waste-problem-step-initiative.html#outline>.

United States Environmental Protection Agency, 2011. 'National Strategy for Electronics Stewardship', Strategy Report jointly prepared by US EPA, White House Council on Environment Quality and General Services Administration, 20 July 2011, pp. 32.

U.S. Environmental Protection Agency, 1992. Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste. U.S. Environmental Protection Agency, Cincinnati, OH.

USEPA, 2015. State Legislation: States Are Passing E-Waste Legislation Available at: <http://www.electronicstakeback.com/promote-good-laws/state-legislation/>.

USGS, 2014. Mineral Commodity Summaries 2014. U.S. Geological Survey, USA.

Veit, Hugo Marcelo, Bernardes, Andréa Moura, 2015. Electronic Waste. Springer.

Wang, F., Huisman, J., Meskers, C.E., Schluep, M., Stevels, A., Hagelüken, C., 2012. The Best-of-2-Worlds philosophy: developing local dismantling and global infrastructure network for sustainable e-waste treatment in emerging economies. Waste Manage. 32, 2134–2146.

Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M., Böni, H., 2005. Global perspectives on e-waste. Environ. Impact Assess. Rev. 25, 436–458.

Williams, E., Kahhat, R., Allenby, B., Kavazanjian, E., Kim, J., Xu, M., 2008. Environmental, social, and economic implications of global reuse and recycling of personal computers. Environ. Sci. Technol. 42, 6446–6454.

Xu, Q., Li, G., He, W., Huang, J., Shi, X., 2012. Cathode ray tube (CRT) recycling: current capabilities in China and research progress. Waste Manage. 32, 1566–1574.

Yolin, C., 2015. Waste Management and Recycling in Japan Opportunities for European Companies (SMEs Focus) Tokyo (September).

Yoshida, A., Terazono, A., Ballesteros, F.C., Nguyen, D.-Q., Sukandar, S., Kojima, M., Sakata, S., 2016. E-waste recycling processes in Indonesia, the Philippines, and Vietnam: A case study of cathode ray tube TVs and monitors. Resour. Conserv. Recy. 106, 48–58.

Yot, P.G., Méar, F.O., 2011. Characterization of lead, barium and strontium leachability from foam glasses elaborated using waste cathode ray-tube glasses. J. Hazard. Mater. 185, 236–241.

Yu, J., Williams, E., Ju, M., Yang, Y., 2010. Forecasting global generation of obsolete personal computers. Environ. Sci. Technol. 44, 3232–3237.

Yuan, W., Li, J., Zhang, Q., Saito, F., 2012. Innovated application of mechanical activation to separate lead from scrap cathode ray tube funnel glass. Environ. Sci. Technol. 46, 4109–4114.

Zeng, X.L., Li, J.H., Stevels, A., Liu, L.L., 2013. Perspective of electronic waste management in China based on a legislation comparison between China and the EU. J. Clean Prod. 51, 80–87.

Zoeteman, B.C., Krikke, H.R., Venselaar, J., 2010. Handling WEEE waste flows: on the effectiveness of producer responsibility in a globalizing world. Int. J. Adv. Manu. Technol. 47, 415–436.

Waste Management 57 (2016) 176–186

Contents lists available at ScienceDirect

Waste Management

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

Recent development of recycling lead from scrap CRTs: A technological review

Yu-Gong, Xiang-miao Tian, Yu-feng Wu *, Zhe-Tan, Lei-Lv

Institute of Recycling Economy, Beijing University of Technology, No. 100, Pingleyuan Street, Chaoyang District, Beijing 100124, PR China

ARTICLE INFO

Article history:
Received 8 July 2015
Revised 3 September 2015
Accepted 3 September 2015
Available online 11 September 2015

Keywords:
CRT
Lead
Funnel glass
Pyrometallurgical
Hydrometallurgical

ABSTRACT

Cathode ray tubes (CRTs) contain numerous harmful substances with different functions. Lead is found in the funnel glass of CRTs. Improperly treated toxic lead may pose significant risks to human health and the environment. This paper reviews and summarizes existing technological processes on the recycling of lead from waste CRTs, including pyrometallurgy, hydrometallurgy, and product-regeneration. The present situation, advantages, and disadvantages of these techniques are described in detail. Generally, pyrometallurgy shows better practicability in recovery lead from waste CRT than hydrometallurgy and hydrometallurgy, in view of environmental impact, energy-consumption, product formats and safety and maturity of technology. Moreover, the gaps in the existing technologies were identified and recommendations for future research were provided.

1. Introduction

Cathode ray tubes (CRTs) have been extensively used for more than 70 years. CRT has been the core unit for display in electrical and electronic equipment, such as TV, computer, and oscilloscope, because of its mature technology, high reliability, low price, and long lifespan (Lairaksa et al., 2013). Current annual CRT production has surpassed the global demand for CRTs, which has declined dramatically in recent years. The reduced demand is primarily due to the technical innovation of replacing CRTs by thinner and light-weight display such as plasma display panel and liquid crystal display (LCD) technology. In addition, the lifespan of a CRT is continuously decreasing. According to data from the United States Academic and Business Sectors, CRTs have a lifespan of six years from 1985 to 2000 and three years in 2007 (Babbitt et al., 2009). Consequently, numerous discarded CRTs account for over 70% of waste electrical and electronic equipment (WEEE) worldwide (Gable and Shireman, 2001; Xie et al., 2012). The EU (European Union) generates around 7.5 million tons of electrical waste yearly, which increases annually by approximately 3–5%. According to a white paper on WEEE Recycling Industry in China (CHEARI, 2013), more than 32 million units of waste televisions and 37 million units of waste computers are produced only in 2013, and 43.11 million tons of CRT glasses are generated in 2013. Approximately 20–50 million metric tons of WEEE are generated worldwide (Tuncuk et al., 2012). Thus, proper CRT disposal is a global concern.

CRTs are usually incinerated and dumped in landfills as municipal solid waste (MSW) in both developed and developing countries after extraction of precious metals from these materials. In the USA and Japan, WEEE is commonly managed in MSW treatment systems, and several types of electronics are covered in WEEE legislation (Oguchi et al., 2013). Developing countries, such as China and Thailand, also adopt similar treatment processes after recovering valuable components (Lairaksa et al., 2013). Proper disposal of CRTs is a main concern because CRTs contain a large amount of Pb, which is harmful to the environment (Chen et al., 2009a).

CRTs for television sets and computer monitors contain hazardous heavy metals, especially Pb, resulting in significant and ubiquitous concerns over the persisting toxicity of this equipment (Méar et al., 2007; Tsydenova and Bengtsson, 2011; Oguchi et al., 2013). Improperly disposed CRTs pose considerable threats to the environment and human beings. Soil, air, and water are subjected to considerable pollution, which may result in serious physical and mental health damages (Kiddee et al., 2013). The reason is that lead is released and dissolved from lead glass with improper treatment, which is verified by many leaching tests (Yamashita et al., 2008; Wadanambi et al., 2008). Numerous studies have verified that Pb can damage the human central and peripheral nerves, blood, kidney, and reproductive systems, as well as results in cognitive defects in children, among others (RIS et al., 2004; Birdsall et al., 2010; Xu et al., 2013; Fernandes et al., 2014; Konstantinos et al.,

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* Corresponding author at: Institute of Circular Economy of Beijing University of Technology, Beijing, China.

E-mail address: xunhuan3r@126.com (Y.-f. Wu).

http://dx.doi.org/10.1016/j.wasman.2015.09.004
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2014; Popovici et al., 2013). Thus, CRTs have attracted much attention because of their toxicity. For example, Guiyu of Guangdong province suffered from severe Pb pollution caused by improperly landfilled and illegally dumped funnel glass. In addition, laborers had been preoccupied in their careers, so nearby residents were subjected to serious damage (Liu et al., 2011; Xu et al., 2012).

Global prevention of Pb contamination by proper disposal of Pb-containing CRT wastes should be undertaken. Pb is vital in basic metal industry. This metal is extensively used in the production of ammunition, X-ray shielding, solder, and batteries considering its unique properties such as high density, softness, corrosion resistance, and malleability. The approximate annual Pb mining in major countries and globally according to the Mineral Commodity Summaries (2015) of the US Geological Survey (USGS, 2015) is shown in Fig. 1. Except for Australia, Mexico, and Canada, the product life in the majority of countries are less than 30 years based on the reserves and exploitation of Pb in various years. Tremendous resource and economic value are required for recovering elemental Pb from waste CRTs because of high demand for Pb.

Precious metals, such as Au, Cu, Y and Eu, have been recycled effectively from waste CRTs. However, Pb has not been recycled efficiently because this metal is not as valuable as the aforementioned metals (Dexpert-Ghys et al., 2009; Lee and Pandey, 2012; Pant et al., 2012; Rath et al., 2012; Innocenzi et al., 2013; Zhang et al., 2013; Wu et al., 2014; Resende and Morais, 2015). Pb, along with other heavy metals, from improperly treated waste CRTs remarkably pollutes the environment. Numerous studies on environmental pollution have resulted in remarkable developments. However, no mature and stable technology has been established to remedy Pb pollution in the commercial scale. In this paper, previous studies were reviewed, and relevant methods for disposing Pb-containing waste CRTs were summarized. The results are expected to facilitate subsequent research.

2. CRT structure

A personal CRT monitor typically weighs approximately 25 kg, and the CRT, which consists of 85% glass, accounts for two-thirds of this device (Berkhout and Hertin, 2004; Andreola et al., 2005, 2007). A typical structural diagram of a CRT is shown in Fig. 2. A CRT is primarily composed of a panel (faceplate), funnel, and neck (Lee and Hsi, 2002; Méar et al., 2006a,b; Xu et al., 2012; Lairaksa et al., 2013; Sua-iam and Makul, 2013). The panel is made of barium strontium glass, which accounts for 65% of the whole glass. The panel contains 14–22 wt% rare-earth phosphors Y_2O_2S or $Y_2O_2S:Eu^{3+}$. The efficient recycling of this part has been extensively investigated. The funnel accounts for 30% of the total glass in a CRT and contains Pb to prevent UV and X-ray radiation that causes severe human health damage. The neck contains a higher amount of Pb than the funnel (Lee and Hsi, 2002; Xu et al., 2012).

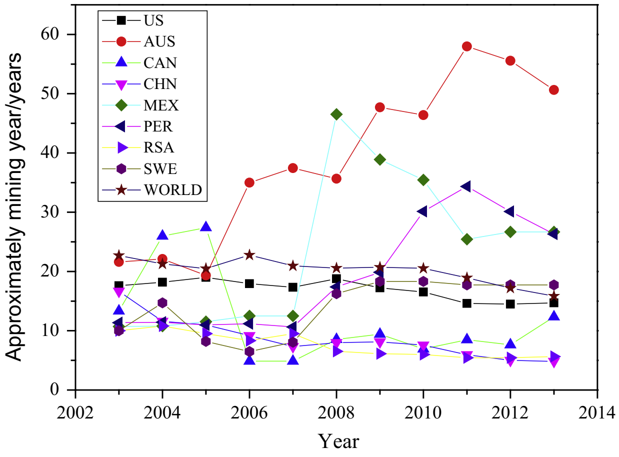

Fig. 1. Approximate lead mining years of major countries and globally.

Chemical compositions of the three parts vary slightly and depend on several parameters such as manufacturer, version, and time of production. Chemical compositions of monochromatic (black & white) and color CRT glasses are shown in Table 1.

The glass parts contain varying contents of lead oxide. The panel glass, which formerly contains a small quantity of lead oxide in earlier production, is currently frequently produced as non-leaded (Lee and Hsi, 2002). The funnel and neck have high lead oxide contents of 15–25% and approximately 30%, respectively (Méar et al., 2006a,b; Gregory et al., 2009; Tsydenova and Bengtsson, 2011; Ling et al., 2012). However, the total content of lead in the neck is too little compared to the funnel. The average Pb content is around 1.6–3.2 kg/CRT weight. Therefore, massive Pb is generated annually (Jang and Townsend, 2003; Lu et al., 2013). In China, 512.6 thousand metric tons of recyclable Pb are produced in 2013 (Fig. 3) (CHEARI, 2013).

Lead species encapsulated in tetrahedral silicate glass network are PbO_4, PbO_3, and PbO_6. Pb is difficult to treat because of the extremely complex network structure and strong binding energy between Pb and Si (Méar et al., 2007).

3. Panel and funnel separation

Waste CRT is first manually sorted before the panel and funnel are separated. The separation is a critical step in recycling the CRT, so efficient separation operation is beneficial to Pb recovery. Technical feasibility, operation cost, and environmental friendliness mainly determine the efficiency of a separation method. The current conventional separation methods are shown in Table 2.

3.1. Electric-wire heating method

A wire is heated by passing an electrical current through it. Then, the wire is wound around the interface between the panel and funnel glass. The glass surface is heated for a certain time before cool air is blown on the surface. The thermal shock generated by the cool air separates the panel and funnel along the interface. This method is characterized by fast isolation, high efficiency, easy operation, low cost, and absence of noise, which is suitable for mass production. Thus, electric-wire heating is frequently used in China. Nevertheless, irregular winding of the wire is detrimental to subsequent treatment (Lee et al., 2004).

3.2. Laser cutting method

Automatic laser cutting device is patented to Finland Preventia Company. This completely automatic facility uses laser to cut the panel and funnel. No leaded panel and lead-containing funnel are directly applied to new CRTs via washing, forming closed-loop recycling. No chemical substance and water are used in this process. Additionally, the quantity of this device was counted using a kinescope. However, the laser cutting method is extremely expensive for some recycling enterprises, because a set of this device costs 500,000 Euros and generates substantial dust particles (Yan et al., 2008).

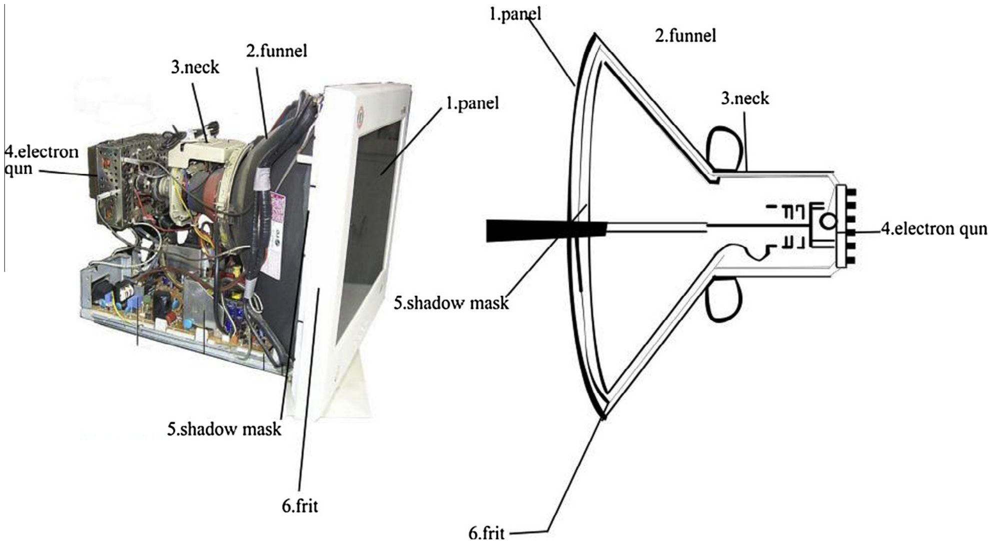

Fig. 2. Typical structure of a CRT (Sua-iam and Makul, 2013).

Table 1
General chemical composition of monochromatic (black & white) CRT and color CRT glasses (Shi et al., 2011).

Oxide	Monochromatic (black & white) CRT[a] (wt%)			Color CRT[a] (wt%)		
	Panel	Funnel	Neck	Panel	Funnel	Neck
SiO_2	66.05	65.49	56.50	61.23	56.72	50.00
Al_2O_3	4.36	4.38	1.00	2.56	3.42	1.00
K_2O	6.65	5.72	9.00	5.56	5.73	10.00
Na_2O	7.63	7.05	4.00	8.27	6.99	2.00
CaO	0.00	0.00	0.00	1.13	3.12	2.00
MgO	0.01	0.00	0.00	0.76	2.02	0.00
BaO	11.38	11.92	0.00	10.03	4.03	0.00
SrO	0.99	0.94	0.00	8.84	1.99	0.00
PbO	0.03	0.00	29.00	0.02	15.58	34.00

[a] Mass fractions of oxides less than 1% (wt%) are not listed above.

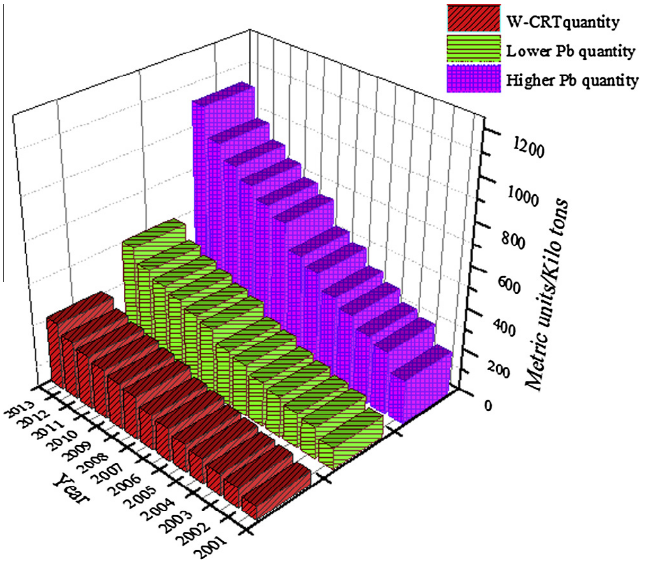

Fig. 3. Quantity of waste CRT and recyclable Pb in China from 2001 to 2013 (CHEARI, 2013).

3.3. Acid melting

Acid melting divides the panel and funnel with nitric acid by dissolving the interface using hot acid injection and hot acid bath. This technique is not efficient, and a large amount of wastewater and little contaminated leachates is generated resulting in high disposal cost after subsequent treatment process. Therefore, acid melting is best avoided because of its considerable unfavorable influence on the environment (Yan et al., 2008).

4. Recycling strategies for Pb from waste CRTs

Traditional disposal strategies for WEEE are landfilling and incineration. Scrap CRT funnel glasses had been regarded as MSWs and disposed by landfilling or incineration because of their low recyclable value in the earlier times worldwide. Typical MSW treatment process for Pb is described in Fig. 4 (Lee et al., 2000; Kang and Schoenung, 2005; Nnorom et al., 2011; Ling et al., 2012; Rath et al., 2012). Landfilling is generally considered as an unacceptable option, because landfills merely occupy massive lands, which lead to uncontrolled pollution via soil contamination and groundwater pollution (Cossu and Lai, 2012). Therefore, many countries have prohibited this method for leaded glass (Spalvins et al., 2008; Ongondo et al., 2011; Milovantseva and Saphores, 2013). Incineration is a good way to reduce volume to save space, but it poses serious threats of air pollution and problems similar to landfilling (Kuchar et al., 2007; Okada and Tomikawa, 2012; Zekkos et al., 2013; Liu et al., 2014; Song and Li, 2014). Consequently, landfilling and incineration are banned in an increasing number of countries because of their numerous anti-environmental effects (Kim et al., 2009). Thus, new and efficient methods should be proposed to remedy the problem of proper CRT disposal. Exploration of solutions to solve the serious disposal problem has been paid much attention. Two solutions, namely, closed-loop recycling (waste to new CRT) and open-loop recycling (waste CRT to new products such as foam glass), are proposed (Chen et al., 2009a; Nnorom et al., 2011; Xie et al., 2012). Closed-loop recycling was apparently preferred in its early application because this process led to considerable profit. However, open-loop recycling is currently attracting much attention because it results in the generation of a certain profit but is more focused on environmental protection.

Table 2
Comparison of different techniques for separating the panel and funnel.

Method	Mechanism	Advantages	Disadvantages	Acceptability
Electric-wire heating (Lee et al., 2004)	Expansion and contraction	High efficiency, easy operation, low cost, no noise	Wound irregularity	High
Laser cutting (Yan et al., 2008)	Mechanical	High efficiency, easy operation	Expensive, noise, fine dust	Low
Acid leaching (Lee et al., 2004)	Acid digestion	High efficiency	High cost, contaminated leachates	Low

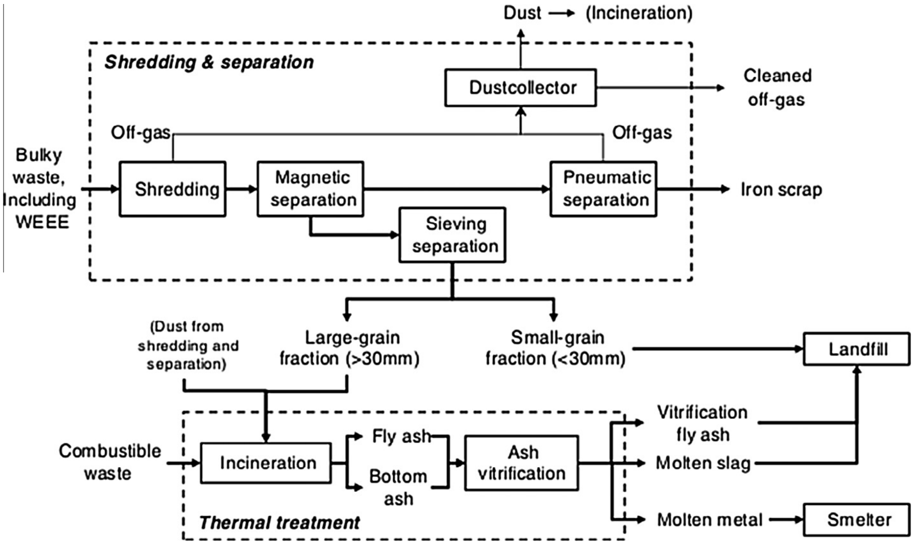

Fig. 4. Schematic diagram of material flow in the MSW treatment processes (Oguchi et al., 2013).

In 1998, Menand proposed industrial closed-loop glass recycling, which facilitated the industrial-scale recycling of waste CRTs into new CRTs (Menad, 1999). The recovered glass serves as a raw material for new CRTs. In this process, waste CRT glass is divided into non-leaded panel glass and Pb-containing funnel glass used in new CRT production after the old CRTs are disassembled manually or automatically. Separation of the panel and funnel glasses is achieved by utilizing sensor-guided automatic sorting system. Thus, high-quality glass cullet for new CRTs is produced. This option of recycling has shown great progress in managing CRTs. This technique is an environmentally and economically sound approach because, compared with landfilling and incineration, closed-loop glass recycling offers the potential in reducing lead without increasing massive Pb released into the environment. Additionally, this technique also greatly lessens waste management costs, reduces the demand for Pb in new CRT glass production, and saves energy for CRT glass manufacturing (Nnorom et al., 2011). Reapplying the majority of CRT glass directly into LCD or other monitors is undoubtedly unrealistic. World supply of CRTs has been predicted to have exceeded the demand by the end of 2014 (Gregory et al., 2009), which occurred earlier in the majority of developed countries. In the US, saturation point for CRTs has been surpassed in 2001 (Mueller et al., 2012). China faces a similar challenge on how to treat toxic waste (Xu et al., 2012). The potential application of open-loop recycling is currently explored worldwide.

Open-loop recycling is very attractive because of its economic and environmental value. This process basically refers to pyrometallurgical and hydrometallurgical processes for recovering lead element. New products are produced by adding lead oxide derived from the funnel glass of waste CRT (see Table 3).

4.1. Pyrometallurgical processes

Pyrometallurgy involves the addition of a reducing agent, such as carbon powder and metallic iron, replacing Pb via redox reaction. This process is shown in Fig. 5.

Chen et al. (2009a) recovered Pb from waste funnel glass through pyrovacuum process (Fig. 6). This process resulted in Pb recovery rate of 98.6% and purity of 99.3% under the following optimal conditions: temperature, 1000 °C; vacuum pressure, 1000 Pa; carbon content, 9%; and holding time, 4 h. The reduction reaction of the Pb–O tetrahedral is a redox reaction, as follows:

$$\mathrm{PbO(s) + C(s) \rightarrow CO(g) + Pb(g)} \tag{1}$$

The temperature should be lower than 1000 °C, which is close to the boiling point of Pb. Metallic Pb could immediately evaporate into gaseous state at temperatures >1000 °C. Moreover, the system pressure should not exceed its critical pressure. Additionally, the leaching experiment indicates the necessity of having relatively higher recovery rate of more than 96% for the safe treatment of funnel glass. Okada et al. have explored the relevant Pb recovery process (Okada et al., 2012; Okada and Yonezawa, 2013, 2014). They displaced Pb from the CRT funnel glass with carbon powder. Moreover, an amount of flux Na_2CO_3 was added to promote Pb recovery. The general process is shown in Fig. 7. Metallic Pb was removed after the mixture was heated under reductive atmosphere and cooled to room temperature. The residue was heated in oxidative atmosphere for the recovery of Na_2CO_3. Total recovery rate reached 96% after 1.5 h of reduction-melting at 1000 °C.

Yot and Méar (2009) recovered metallic Pb by adding silicon carbide (SiC) and titanium nitride (TiN) as reducing agents. $PbSiO_3$ consists of numerous metasilicate chains interconnected by Pb^{2+}

Table 3
key parameters for some typical Pyrometallurgy.

Agents (amounts wt%)	Temperature (°C)	Time	Extraction efficiency (%)	Advantages	Disadvantages
C (5%) (Chen et al., 2009a)	1000	4 h	98.6%	High recovery; High purity (99.3%)	Time-consuming Energy-consuming
SiC (5%) TiN (5%) (Yot and Méar, 2009)	950	1 h	40% 20%	Lower energy; Shorter time	Low recovery; High agent cost
Fe (50%) (Lu et al., 2013)	700	30 min	58%	Lower energy; Shorter time	Low recovery
$CaCl_2$ (Grause et al., 2014a,b)	1000	1 h	53%	Shorter time	Low recovery
$Ca(OH)_2$ (Cl/Pb = 16) + poly(vinyl chloride) (Ca/Si = 2) (Grause et al., 2014a,b)	1000	40–150 min	99.9% (volatilization)	High potentiality; Construction using; Waste using	Toxic gas
$Mg + Fe_2O_3$ (Chen et al., 2009b)	2000	–	–	No extra energy; Building materials	Extra agent
C (2.4%) + Na_2CO_3 (49%) (Okada and Yonezawa, 2014)	1000	1.5 h	96%	High recovery; Low time	Toxic gas; Extra agent; High energy consumption

ions. Pb–oxygen (O) coordination number dramatically fell from 3 to 1 for TiN instead of 3 to 2 for SiC. However, the recovery rate should be improved, considering the 40% Pb reduced at optimal conditions.

Lu et al. (2013) extracted metallic Pb from CRT funnel class by thermal reduction with metallic iron (Fe). The effects of temperature, reducing agent content, and holding time on Pb reduction were examined to determine the optimal extraction efficiency. A total of 58 wt% Pb was achieved at the optimized operational parameters. Furthermore, phase transformation was analyzed as follows:

$$\equiv Si—O—Pb^{+} + Fe(0) \rightarrow Pb(0) + Fe^{+}O^{-}—Si\equiv \quad (2)$$

However, prolonging the heating time decreased Pb extraction concentration, as follows:

$$\equiv Si—O + Pb(0) \rightarrow \equiv Si—O—Pb^{+} \quad (3)$$

Innovations to this method are the reduction in temperature to save energy and the use of inexpensive reagent to reduce cost.

Chlorination has been applied to remove Pb from MSW, such as molten slag, fly ash, and electric arc furnace dust (Chan and Kirk, 1999; Matsuno et al., 2003; Nowak et al., 2010; Kageyama et al., 2013). Grause et al. (2014a,b) developed chloride volatilization to remove Pb from CRT funnel glass through a horizontal quartz glass tube heated by an electric furnace (Fig. 8). The mixture of glass powder and chlorination agent (NaCl, $CaCl_2$, or PVC) reacted in the tube. Then, the residue gas was absorbed via HNO_3 and NaOH before the gas was released into the atmosphere.

The experimental results indicated that 80% of Pb was removed at a Cl/Pb ratio of 14.2 at 1000 °C. However, NaCl was not as efficient as $CaCl_2$, yielding only 53% of Pb under the same conditions. Furthermore, HCl released from the degradation of PVC has a substantial difficulty in recovering lead, because the reaction is limited to the surface of the glass melt which cannot sufficiently react with PbO. PVC is another waste that should be disposed of reasonably. Thus, this technique is novel and environmentally friendly. Further improvement of Pb recovery is required in future studies because of the moderate recovery rate in this study (Grause et al., 2014a,b).

Grause et al. further explored the combination of calcium hydroxide and poly (vinyl chloride) to recover Pb from CRT. Temperature, molar Cl/Pb ratio, and Ca/Cl ratio were considered for Pb volatilization in this experiment. Approximately 99.9% of Pb was volatilized at the following optimal conditions: molar Cl/Pb ratio, 16; Ca/Si ratio, 2; and 1000 °C. In this experiment, PVC was decomposed at 250 °C, and HCl was released. Then, HCl was

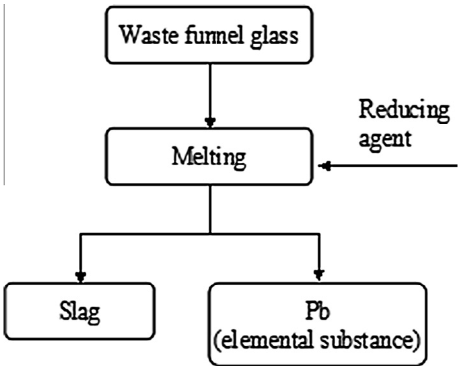

Fig. 5. Pyrometallurgical process.

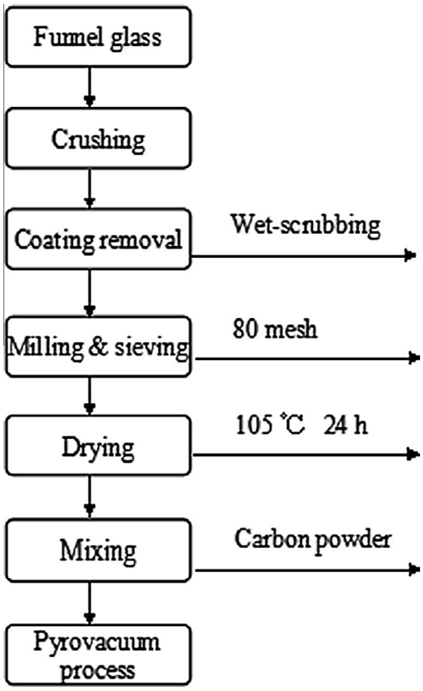

Fig. 6. Chen's diagram (Chen et al., 2009a).

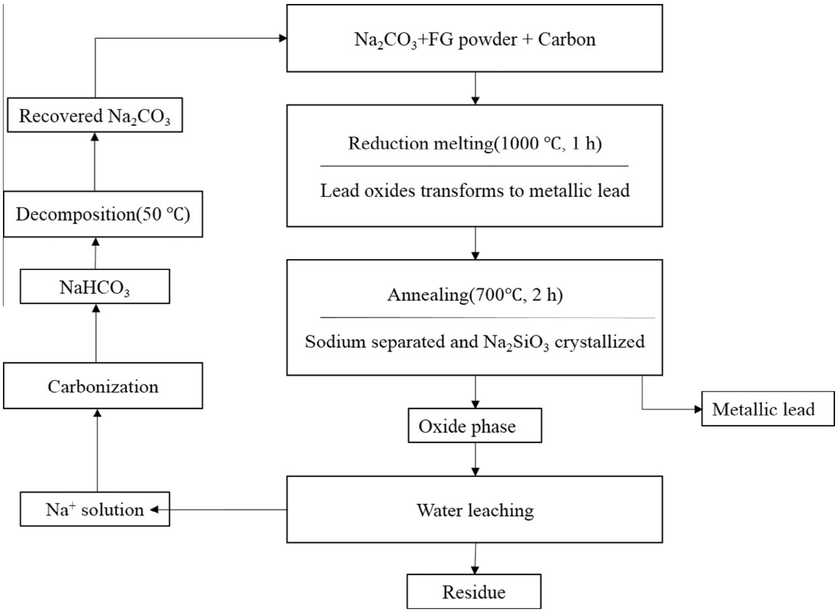

Fig. 7. Schematic diagram of Okada's experiment (Okada and Yonezawa, 2014).

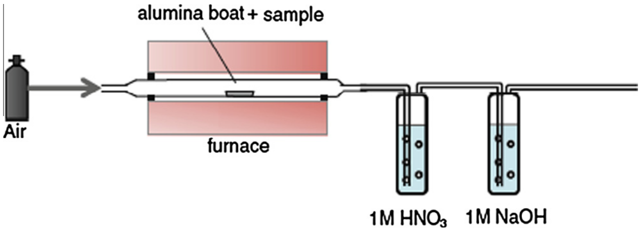

Fig. 8. Experimental apparatus for chloride volatilization (Grause et al., 2014a,b).

captured by $Ca(OH)_2$, and then $CaCl_2$ was formed. When the heating temperature was increased to 600 °C, CaO, which was derived from the dehydration of $Ca(OH)_2$, displaced Pb from the glass network to produce calcium silicate and lead oxide. PbO was chlorinated as the temperature approached the melting point (782 °C) of $CaCl_2$. The reaction formula is as follows:

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \qquad T = 250\,^\circ C \tag{4}$$

$$CaO(S) + PbSiO_{3(S)} \rightarrow CaSiO_{3(S)} + PbO_{(l)} \qquad T = 600\,^\circ C \tag{5}$$

$$CaCl_{2(g)} + PbO_{(s)} \rightarrow PbCl_{2(g)} + CaO_{(s)}$$
$$T = \text{melting point of } CaCl_2 \tag{6}$$

A very high Pb recovery rate was obtained, and calcium silicate-containing residues provided great potential for reuse as safe construction materials (Grause et al., 2014a,b).

Self-propagating high-temperature synthesis (SHS) is also favorable for the detoxification of Pb in discarded funnel glass. Waste powder is blended with suitable amount of metallic magnesium and ferric oxide for a self-propagating reaction after crushing, dry ball milling, and sieving. In this experiment, the primary reaction is as follows:

$$SiO_2 + 3Mg^0 + Fe_2O_3 \rightarrow Mg_2SiO_4 + MgO + 2Fe^0 \tag{7}$$

The emergence of forsterite demonstrates that some of the SiO_2 in the funnel glass are released from the glass network and transformed into forsterite (XRD results) during the self-propagating process. This effect could lead to the great increase in Si–O–Pb linkage. At the same time, heavy metals are stabilized by SHS. Results from sequential toxicity leaching tests show the successful detoxification of funnel glass using SHS. The experiment also indicates that the CRT glass content in the mixture is less than 60 wt%, and this process consumes much energy because the peak temperature is more than 2000 (Chen et al., 2009b).

A typical and complete pyrometallurgical process is shown in Fig. 9. Pre-treatment, such as dismantling, crushing, and physical process, can recover many kinds of relatively non-ferrous metals with high purity, and no hazardous is gas released into atmosphere producing sulfuric acid (Tuncuk et al., 2012).

Utilizing mechanochemical sulfidization to remove Pb from CRT funnel glass is a highly favorable process because this process does not need high-temperature conditions. CRT funnel glass is co-grinded with element sulfur in a planetary ball mill at nitrogen atmosphere. During the grinding process, Si–O–Pb is bonded in glass. S–S bond is broken and recombined into lead sulfide (PbS). When the co-grinding time is increased from 10 min to 120 min, the sulfidizing rate is rapidly improved from 16.6% to 96.7%. Contrary to pyrometallurgy, mechanochemical sulfidization does not consume much energy. Subsequent recovery for PbS is necessary using mineral processing technique such as flotation separation (Yuan et al., 2013). Moreover, PbS is also can changed into ion by acid leaching and reused in other fields rationally (Pashkov et al., 2002).

4.2. Hydrometallurgical processes

Yuan et al. recovered Pb from scrap CRT funnel class through mechanical activation–acid leaching–sulfur sulfidization. This process generally involves the mechanically activation by the glass powder using the ball-mill apparatus, subsequent acid leaching of samples by nitric acid, and sulfidization by adding sulfide of sodium and flotation. This method explores the mechanism of mechanical activation. The results indicate that mechanical activation produces substantial mechano-radicals to destroy the glass inner structure, facilitating the easy dissolution of increased amount of Pb. Thus, 92.5% yield is reached at the optimal conditions. The process is efficient and simple, with huge potential for detoxifying all types of leaded glass (Yuan et al., 2012). Tan and Li (2015) further employed this method by adding Fe powder to recover Pb, and the results show increased proportion to 96.7% after 120 min of grinding.

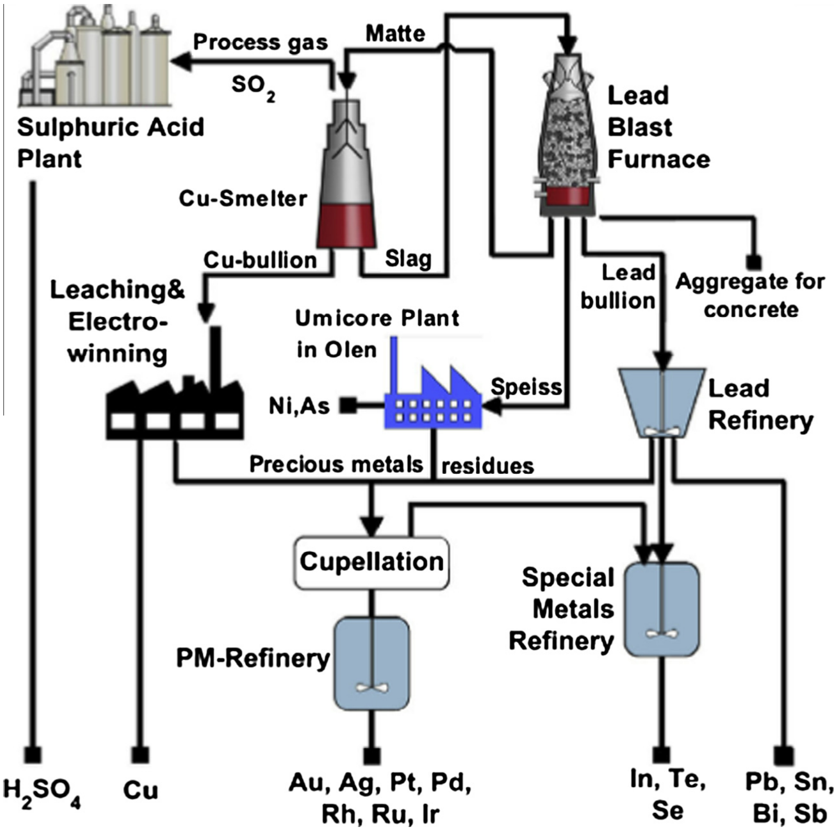

Fig. 9. Flow sheet of Hoboken integrated smelter and refinery plant of Umicore.

Ultrasonically enhanced-acid leaching-electrochemical recovery was also developed to recycle Pb from CRT funnel glass. Leaching experiments were implemented in a jacketed glass cell by strengthening with ultrasound. Then, the leachable Pb^{2+} was recovered with electrochemical methods for additional benefit. More than 90% of leachable Pb^{2+} was recovered after merely 1 h of sono-leaching in ultrasonically enhanced acid leaching. Thus, green disposal strategy is more ideal for glass recycling purposes (Saterlay et al., 2001).

The technique that uses mechanochemical process and Na_2EDTA reagent is eco-friendly for recycling Pb (Fig. 10). Adding Na_2EDTA forms highly stable Pb-EDTA after intense mechanical energy from the wet ball-milling treatment that weakened or broke the Pb–O–Pb bonds in the glass network. More than 99% of Pb was removed successfully from the special structure at room temperature. Afterward, 100 wt% of the Pb in Pb-EDTA was substituted chemically with ferric sulfate in terms of $PbSO_4$, and the EDTA reagent was recycled in the form of solution or solid reused in wet ball-milling treatment as chelate reagent. This method has several remarkable advantages such as low energy consumption, reuse of reagent, and silica powder for new glass production (Sasai et al., 2008).

Hydrometallurgy combined with bio-assisted process is also called a hybrid process that offers more extensive advantages on economic value, efficiency, and eco-friendliness when used for metal recovery (Pant et al., 2012).

4.3. Product-regeneration

4.3.1. Building applications

Encapsulation is a potential alternative for disposing PbO-containing funnel glass, because earlier efforts has indicated the potential of this process for encapsulating Pb as an ingredient in the crystal structure of cement clinker (Murata and Sorrentino, 1996). Romero et al. (2013) added CRT glass as a fine aggregate replacement in concrete. Compared with three different concrete mixtures (10%, 20%, 30% CRT glass), using more than 10% CRT glass in concrete may lead to deleterious expansions throughout the life of concrete. A cross-linked biopolymer has significant impact on reducing the content of Pb leaching from the samples. Approximately 20% CRT can be substituted into the concrete, and it remains below the threshold limits of drinking water. Ling et al. used recycled CRT glass in cement mortar for X-ray radiation shielding applications. A series of comparative experiments were conducted using CFG (crushed and without acid treatment), TFG (acid washed and crushed CRT funnel glass), and CBG (conventional crushed beverage glass) at different replacement levels. The results demonstrate substantially enhanced radiation-shielding properties because of the additive CFG and TFG as aggregates. Thus, CFG and TFG may be used as aggregates in mortar-based composites for various shielding applications, such as in diagnostic X-ray and CT scanning rooms. Therefore, CFG and TFG may also be applied in building materials because of their high flexural and compressive strength as well as hardened density (Ling et al., 2012). CRT glass with concrete has also been explored (Kim et al., 2009; Hui and Sun, 2011; Ling and Poon, 2011; Hui et al., 2013; Lairaksa et al., 2013; Sua-iam and Makul, 2013).

Waste CRT funnel glass is also used to produce other building products, such as clay bricks and roof tiles, as demonstrated by Dondi et al. (2009). Laboratory simulation depicts the technological feasibility of using CRT as building materials, and addition of 2–5 wt% does not remarkably alter the technological performances.

4.3.2. Glass products

Glass ceramic is attractive for solving waste CRT glasses. This ceramic has widely been used in heat insulation, sound absorption,

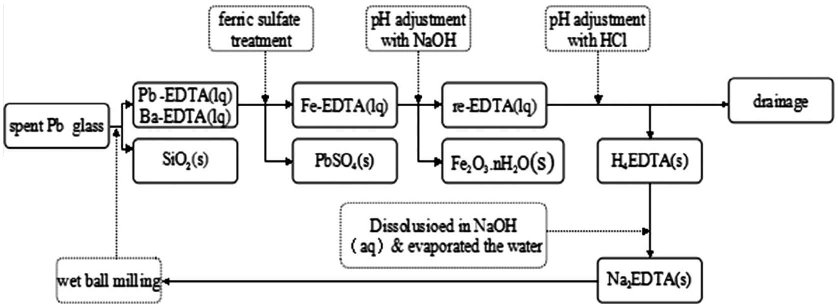

Fig. 10. Flowchart for a novel recycling system using mechanochemical process (Sasai et al., 2008).

moisture-proofing, fire-proofing, and absorption of shock waves from explosions and earthquake (Guo et al., 2010).

Pb-containing glass can form glass ceramics by mixing with suitable raw materials (dolomite and alumina) and subjecting the glass to adequate thermal treatment. Calcium and magnesium oxides facilitate the crystallization process because high field strength is necessary given that lead oxide has low tendency for crystallization. Andreola et al. (2005) showed that a high proportion of waste funnel glass (50–75%) can be introduced. However, no final products have been studied. Two different studies conducted by ISTEC-CNR and Modena University have verified the possibility of using CRT glass in porcelain stoneware bodies. The test results showed that 5 wt% do not convert the requirements of final products (Andreola et al., 2007). Sintering was adopted to fabricate foam glass ceramics from waste CRTs. The mechanical properties were investigated by changing the dosage of SiC at sintering temperatures of approximately 840–850 °C. The experimental results indicate that the variation trend of compressive and bending strengths decreased when the SiC content was lower than 4 wt%, but the strengths increased rapidly after this point. Conducive temperature of 780 °C applied to the mixture was also found to decrease the viscosity and intensify the reaction between PbO and SiC (Guo et al., 2010).

Foaming glass may be fabricated from glass with carbon-based foaming agents, such as graphite, coal, carbon black, and SiC, and decomposition of minerals, such as carbonates ($CaCO_3$, Na_2CO_3, etc.), or sulfates ($CaSO_4$, i.e., gypsum) through oxidation (Bernardo et al., 2007). Given its excellent mechanical, chemical, and thermal stability, foaming glass can be utilized for thermal and acoustic insulation, such as in inflammable retarding material for restraining fire (Bernardo et al., 2007).

Bernardo et al. manufactured foaming glasses from dismantled CRTs by adding $CaCO_3$ powder (Bernardo and Albertini, 2006; Méar et al., 2006a,b). Fernandes et al. (2013) produced foaming glass with egg shells as foaming agent. The results proved that egg shells can be a good alternative to conventional foaming agent, such as $CaCO_3$. This process is advantageous because it requires cost-free waste material, poses less threat to the environment, and needs relatively low temperature (about 700 °C) to release gas. The panel and funnel glass powders are converted to foaming glass using different foaming agents such as egg shells, calcite, and dolomite via direct heating. Funnel glass is more prone to foaming at low temperature (650–750 °C), which is due to the lower refraction index of funnel glass than that of panel glass. Moreover, rich PbO content and poor SiO_2 content in the funnel, as well as the high BaO content glass, indicate the aforementioned phenomena. However, the panel can enhance the compressive strength of foaming glass. Thus, foaming glass is an extraordinary alternative for separating funnel from panel glasses (Fernandes et al., 2014).

4.3.3. Adsorbent

Commercial sorbents, such as activated carbons, activated alumina, polymeric adsorbents, zeolites, and silica gel, has been applied in large-scale absorptive and separation processes. However, their potential application is limited by high cost. Waste CRT glass is also produced by adsorbent via chemical modification involving thermo-ionic treatment using fluoride reagent and calcinations at 600 °C. This method not only converts lead oxide into Pb ions, but it can also be applied to absorb metal ions, especially Pb ions, as metal absorbent from aqueous system. The maximum Pb(II) adsorption capacity of 5.57 mg/g and is superior to some commercial sorbents, such as kaolinite and smectite. Further work will be focused on improving its adsorption capacity and possible commercialization (Pant and Singh, 2013).

4.3.4. Nano-Pb particle synthesis

Metal nanoparticles have been widely applied in various areas because their unique chemical, thermal, electromagnetic, and optical qualities. Pb nanoparticle is a remarkable nanomaterial with huge potential for application in lithium-ion batteries as negative electrode materials, high-energy radiation protection composites, catalysts, wavelength filters, and super-conducting materials (Martos et al., 2003; Michotte et al., 2003; An et al., 2004; Li et al., 2010).

Xing and Zhang developed a novel technology for producing Pb nanoparticle combined with vacuum carbon–thermal reduction and inert gas consolidation procedures. Their experimental setup is illustrated in Fig. 11. The argon gas supply system generally provided high-purity argon gas blown to the process chamber to remove air, and the function of the vacuum was maintained at subatmospheric pressure before heating. Then, Pb was evaporated as elemental Pb from funnel glass powder and mixed with 10% carbon powder in the reaction chamber and heated to a certain degree. Pb synthesis was followed by quenching in a water cooling system. Approximately 96.8% Pb was evaporated at optimal experimental conditions, and 4–34 nm nanometal particles were successfully formed by controlling temperature, holding time, process pressure, and argon gas flow rate at 1000 °C, 2–4 h, 500–2000 Pa, and 50–200 ml/min, respectively. This process is an effective and economic measure to detoxify and reutilize the waste funnel glass. Synthesis of nanometal particles may be commercialized in the near future after optimization (Xing and Zhang, 2011).

SHS is also a conventional method for manufacturing advanced materials, such as ceramics and ceramic-composites, because of its short reaction time, low-energy consumption and economic process. Patil et al. (1997) and Guojun et al. (2008) employed SHS with Mg(0) and Fe_2O_3 to produce nanoparticles, because the reaction of Mg and Fe_2O_3 provides enough energy to destroy the network intermediate. Over 90 wt% of Pb was extracted from the funnel glass when the funnel glass additions were less than 40 wt% in

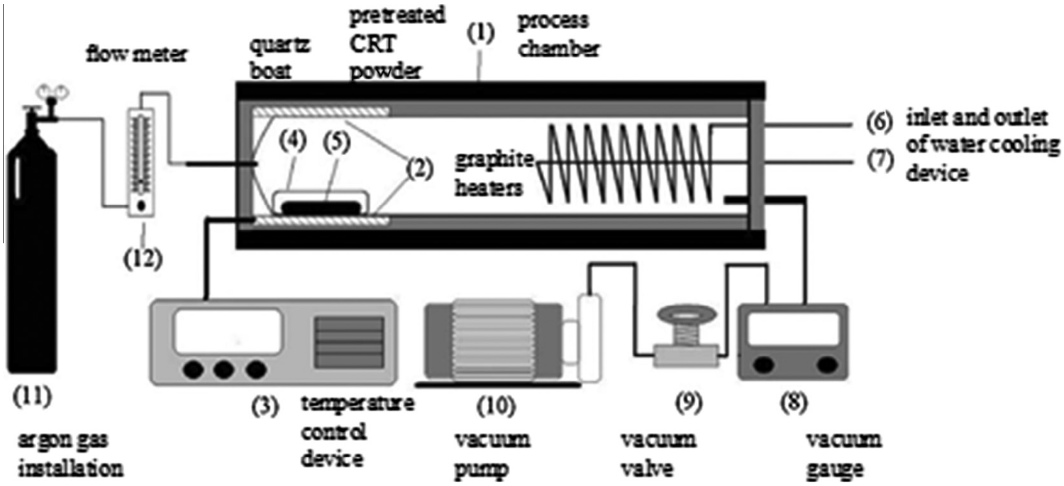

Fig. 11. Schematic diagram of lead nanoparticle fabrication installation (Xing and Zhang, 2011).

Table 4
Key parameters for some typical hydrometallurgical processes.

Agents	Temperature (°C)	Time	Extraction efficiency (%)	Advantages	Disadvantages	Assistant methods
3 M HNO_3 (Yuan et al., 2012)	95	2 h	92.5	High yield No structural defect Shorter time	High temperature	Mechanical activation
Na_2EDTA $Fe_2SO_4 \cdot 14H_2O$ (purity: 60–80%) (Sasai et al., 2008)	Room temperature	20 h	99.5	Higher yield Recoverable EDTA chelate reagent, lower energy-consumption, recovered silica can be reused for glass production	Generated drainage needed for treatment	Wet ball-milling
0.1 M HNO_3 (Saterlay et al., 2001)	Room temperature	1 h	>90	Shorter time Lower acid concentration	Wastewater needed to treat further Leachable Pb^{2+} also needing further process	Ultrasonic
0.02 M EDTA (Pant et al., 2014)	Room temperature	12 days	–	Low-cost Impurities such as Zn, Al, Si also be extracted	Time-consuming Waste water needed to be disinfection	Biological (*S. plymuthica*)

Table 5
Discharges and operation energy consumption data of different recycling methods of perton lead in obsolete CRT.

Recycling methods	Pollution classifications	Discharges (t)	Operation energy consumption (°C)	Product formats	Product safety	Maturity of technology
Pyrometallurgy (Tian et al., 2015)	Wastewater Exhaust gas Solid waste	2.500 0.010 22.673	600–1000	Elementary Pb	Known	Mature industrial applications
Hydrometallurgy (Tian et al., 2015)	Wastewater Exhaust gas Solid waste	27.610 4.780 8.000	<100	Pb^{2+} or other compounds	Known	Mature industrial applications
production regeneration	Wastewater Exhaust gas Solid waste	–	100–1000	Regeneration products	Study further	Lack industrial applications

– No specific data can be found is due to lack of relative research.

the original mixture. The mean grain size of 40–50 nm indicated good dispersion and morphology (Wang and Zhu, 2012).

5. Discussions

Traditional and rudimentary end-of-life treatment options for waste CRTs are landfilling and incineration. However, these processes are associated with serious air, water, and soil pollution, in addition to the threat they pose on human health. Landfilling may cause distribution of hazardous Pb into water bodies and soil, which causes damage to human health through the food chain. Therefore, pyrometallurgy, hydrometallurgy, and production regeneration have been explored in recent years. These techniques are focused on utilization-recycling to lessen the burden of Pb resources as well as protect the environment and human health. From Tables 4 and 5, it can be concluded that various reducing agents, such as carbon powder, Fe powder, and SiC, have been employed to decrease lead oxide in the pyrometallurgical process. This method is favorable for highly efficient recovery compared with hydrometallurgical process and product regeneration. In addition, the product from pyrometallurgy is elementary Pb, which can be reused in the production process with no additional treatment. However, the major disadvantage of this option is its high energy consumption because of the reaction temperature of more than 1000 °C and also emits fine dust particles and wastewater into environment. By contrast, hydrometallurgical techniques do not require high temperature during the reaction process, such that most of these processes require less than 100 °C for the reaction. However, hydrometallurgy product is in the form of Pb^{2+} or other compounds, which necessitates further treatment. This process also discharges harmful or hazardous wastewater into water bodies, thereby posing significant risks to the environment and human health because of the chemical reagents used in the reaction. Product regeneration technique immediately turns Pb into products without intermediate steps. However, a high energy consumption and safety of the product to human health are of great concern. Given discharges, operation energy consumption, Product formats and its safety and maturity of technology, pyrometallurgy is more adequate for recycling lead from waste CRT on the whole.

6. Conclusions

This review revealed that hazardous Pb in the form of PbO in the funnel glass of waste CRT glass is of particular concern. Improper handling or treatment may cause serious risks to the environment and human health. Efficient disposal of Pb from waste CRT is very challenging. Much improvement on waste CRT disposal is still necessary. Thus, pyrometallurgy, hydrometallurgy, and production regeneration are good choice to solve this problem. However, in the case of overall benefits, pyrometallurgy has an advantage over hydrometallurgy and production regeneration.

Therefore, the three summarized techniques can relieve environmental pollution to a certain extent compared with traditional landfilling and incineration. However, energy consumption should be reduced for pyrometallurgical technologies without compromising its high recovery rate. Hydrometallurgy should also be focused on the improvement of its recovery rate and reduction in wastewater. Product-regeneration is a favorable technology by transforming waste hazardous lead into valuable products in need of promising it's enough safety. Thus, establishing and perfecting relative testing technologies for recycling lead and products is essential. In recycling Pb, if Pb is equal to protogenetic Pb as shown by performance testing and prior to the introduction of relative products into markets, then human safety assessment should first be performed to avoid unnecessary harm.

Acknowledgments

This work was financially supported by Beijing Nova Program, National Natural Science Foundation of China (No. 21306004), and Academician Workstation in Yunnan Province.

References

An, J., Wu, H.X., Xin, Y.C., 2004. Preparation and research of resin/nano-lead composite for high-energy radiation protection. Eng. Plastics 32 (12), 14–17.

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., Falcone, R., Hreglich, S., 2005. Glass-ceramics obtained by the recycling of end of life cathode ray tubes glasses. Waste Manage. 25 (2), 183–189.

Andreola, F., Barbieri, L., Corradi, A., Lancellotti, I., 2007. CRT glass state of the art A case study: recycling in ceramic glazes. J. Eur. Ceram. Soc. 27 (2–3), 1623–1629.

Babbitt, C.W., Kahhat, R., Williams, E., Babbitt, G.A., 2009. Evolution of product lifespan and implications for environmental assessment and management: a case study of personal computers in higher education. Environ. Sci. Technol. 43 (13), 5106–5112.

Berkhout, F., Hertin, J., 2004. De-materialising and re-materialising: digital technologies and the environment. Futures 36 (8), 903–920.

Bernardo, E., Albertini, F., 2006. Glass foams from dismantled cathode ray tubes. Ceram. Int. 32 (6), 603–608.

Bernardo, E., Cedro, R., Florean, M., Hreglich, S., 2007. Reutilization and stabilization of wastes by the production of glass foams. Ceram. Int. 33 (6), 963–968.

Birdsall, R.E., Kiley, M.P., Segu, Z.M., Palmer, C.D., Madera, M., Gump, B.B., MacKenzie, J.A., Parsons, P.J., Mechref, Y., Novotny, M.V., Bendinskas, K.G., 2010. Effects of lead and mercury on the blood proteome of children. J. Proteome Res. 9 (9), 4443–4453.

Chan, Chris C.Y., Kirk, D.W., 1999. Behaviour of metals under the conditions of roasting MSW incinerator fly ash with chlorinating agents. J. Hazard. Mater. 64 (1), 75–89.

Chen, M., Zhang, F., Zhu, J., 2009a. Lead recovery and the feasibility of foam glass production from funnel glass of dismantled cathode ray tube through pyrovacuum process. J. Hazard. Mater. 161 (2–3), 1109–1113.

Chen, M., Zhang, F., Zhu, J., 2009b. Detoxification of cathode ray tube glass by self-propagating process. J. Hazard. Mater. 165 (1–3), 980–986.

Cossu, R., Lai, T., 2012. Washing of waste prior to landfilling. Waste Manage. 32 (5), 869–878.

Dexpert-Ghys, J., Regnier, S., Canac, S., Beaudette, T., Guillot, P., Caillier, B., Mauricot, R., Navarro, J., Sekhri, S., 2009. Re-processing CRT phosphors for mercury-free applications. J. Lumin. 129 (12), 1968–1972.

Dondi, M., Guarini, G., Raimondo, M., Zanelli, C., 2009. Recycling PC and TV waste glass in clay bricks and roof tiles. Waste Manage. 29 (6), 1945–1951.

Fernandes, R., Andreola, F., Barbieri, L., Lancellotti, I., Pascual, J., Ferreira, M., 2013. The use of egg shells to produce cathode ray tube (CRT) glass foams. Ceram. Int. 39 (8), 9071–9078.

Fernandes, H.R., Ferreira, D.D., Andreola, F., Lancellotti, I., Barbieri, L., Ferreira, J.M.F., 2014. Environmental friendly management of CRT glass by foaming with waste egg shells, calcite or dolomite. Ceram. Int. 40 (8), 13371–13379.

Gable, C., Shireman, B., 2001. Computer and electronics product stewardship: are we ready for the challenge? Environ. Qual. Manage. 11 (1), 35–45.

Grause, G., Yamamoto, N., Kameda, T., Yoshioka, T., 2014a. Removal of lead from cathode ray tube funnel glass by chloride volatilization. Int. J. Environ. Sci. Technol. 11 (4), 959–966.

Grause, G., Takahashi, K., Kameda, T., Yoshioka, T., 2014b. Lead removal from cathode ray tube glass by the action of calcium hydroxide and poly (vinyl chloride). Thermochim. Acta 596, 49–55.

Gregory, J.R., Nadeau, M., Kirchain, R.E., 2009. Evaluating the economic viability of a material recovery system: the case of cathode ray tube glass. Environ. Sci. Technol. 43 (24), 9245–9251.

Guo, H.W., Gong, Y.X., Gao, S.Y., 2010. Preparation of high strength foam glass–ceramics from waste cathode ray tube. Mater. Lett. 64 (8), 997–999.

Guojun, Y., Guangde, C., Huiming, L., 2008. Solid-state metasynthesis and characterization of AlN nanocrystals. Int. J. Refract Metal Hard Mater. 26 (1), 5–8.

Hui, Z., Sun, W., 2011. Study of properties of mortar containing cathode ray tubes (CRT) glass as replacement for river sand fine aggregate. Constr. Build Mater. 25 (10), 4059–4064.

Hui, Z., Poon, C.S., Ling, T.C., 2013. Properties of mortar prepared with recycled cathode ray tube funnel glass sand at different mineral admixture. Constr. Build. Mater. 40, 951–960.

Innocenzi, V., De Michelis, I., Ferella, F., Beolchini, F., Kopacek, B., Vegliò, F., 2013. Recovery of yttrium from fluorescent powder of cathode ray tube, CRT: Zn removal by sulphide precipitation. Waste Manage. 33 (11), 2364–2371.

Jang, Y., Townsend, T.G., 2003. Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates. Environ. Sci. Technol. 37 (20), 4778–4784.

Kageyama, H., Osada, S., Nakata, H., Kubota, M., Matsuda, H., 2013. Effect of coexisting inorganic chlorides on lead volatilization from $CaO–SiO_2–Al_2O_3$ molten slag under municipal solid waste gasification and melting conditions. Fuel 103, 94–100.

Kang, H., Schoenung, J.M., 2005. Electronic waste recycling: a review of U.S. infrastructure and technology options. Resour. Conserv. Recycl. 45 (4), 368–400.

Kiddee, P., Naidu, R., Wong, M.H., 2013. Electronic waste management approaches: an overview. Waste Manage. 33 (5), 1237–1250.

Kim, D., Quinlan, M., Yen, T.F., 2009. Encapsulation of lead from hazardous CRT glass wastes using biopolymer cross-linked concrete systems. Waste Manage. 29 (1), 321–328.

Konstantinos, K., John, N.H., Evangelos, G., 2014. Assessment of toxic metals in waste personal computers. Waste Manage. 34 (8), 1480–1487.

Kuchar, D., Fukuta, T., Onyango, M.S., Matsuda, H., 2007. Sulfidation treatment of molten incineration fly ashes with Na_2S for zinc, lead and copper resource recovery. Chemosphere 67 (8), 1518–1525.

Lairaksa, N., Moon, A.R., Makul, N., 2013. Utilization of cathode ray tube waste: encapsulation of PbO-containing funnel glass in Portland cement clinker. J. Environ. Manage. 117, 180–186.

Lee, C., His, C., 2002. Recycling of scrap cathode ray tubes. Environ. Sci. Technol. 36 (1), 69–75.

Lee, J., Pandey, B.D., 2012. Bio-processing of solid wastes and secondary resources for metal extractio: a review. Waste Manage. 32 (1), 3–18.

Lee, C.H., Chang, S.L., Wang, K.M., Wen, L.C., 2000. Management of scrap computer recycling in Taiwan. J. Hazard. Mater. 73 (3), 209–220.

Lee, C., Chang, C., Fan, K., Chang, T., 2004. An overview of recycling and treatment of scrap computers. J. Hazard. Mater. 114 (1–3), 93–100.

Li, R., Hao, H., Cai, W., Huang, T., Yu, A., 2010. Preparation of carbon supported Pd–Pb hollow nanospheres and their electrocatalytic activities for formic acid oxidation. Electrochem. Commun. 12 (7), 901–904.

Ling, T., Poon, C., 2011. Utilization of recycled glass derived from cathode ray tube glass as fine aggregate in cement mortar. J. Hazard. Mater. 192 (2), 451–456.

Ling, T., Poon, C., Lam, W., Chan, T., Fung, K.K., 2012. Utilization of recycled cathode ray tubes glass in cement mortar for X-ray radiation-shielding applications. J. Hazard. Mater. 199–200, 321–327.

Liu, J., Xu, X., Wu, K., Piao, Z., Huang, J., Guo, Y., Li, W., Zhang, Y., Chen, A., Huo, X., 2011. Association between lead exposure from electronic waste recycling and child temperament alterations. Neurotoxicology 32 (4), 458–464.

Liu, J., Huang, S., Sun, S., Ning, X., He, R., Li, X., Chen, T., Luo, G., Xie, W., Wang, Y., Zhuo, Z., Fu, J., 2014. Effects of sulfur on lead partitioning during sludge incineration based on experiments and thermodynamic calculations. Waste Manage.

Lu, X., Shih, K., Liu, C., Wang, F., 2013. Extraction of metallic lead from cathode ray tube (CRT) funnel glass by thermal reduction with metallic iron. Environ. Sci. Technol. 47 (17), 9972–9978.

Martos, M., Morales, J., Sánchez, L., 2003. Lead-based systems as suitable anode materials for Li-ion batteries. Electrochim. Acta 48 (6), 615–621.

Matsuno, Mototsugu, Tomoda, K., Nakamura, T., 2003. Volatilization mechanism of Pb from fly ash in municipal waste incinerator. J. Hazard. Mater. 44 (12), 2481–2488.

Méar, F., Yot, P., Cambon, M., Ribes, M., 2006a. The characterization of waste cathode-ray tube glass. Waste Manage. 26 (12), 1468–1476.

Méar, F., Yot, P., Ribes, M., 2006b. Effects of temperature, reaction time and reducing agent content on the synthesis of macroporous foam glasses from waste funnel glasses. Mater. Lett. 60 (7), 929–934.

Méar, F.O., Yot, P.G., Kolobov, A.V., Ribes, M., Guimon, M., Gonbeau, D., 2007. Local structure around lead, barium and strontium in waste cathode-ray tube glasses. J. Non-Cryst. Solids 353 (52–54), 4640–4646.

Menad, N., 1999. Cathode ray tube recycling. Resour. Conserv. Recycl. 26 (3–4), 143–154.

Michotte, S., Mátéfi-Tempfli, S., Piraux, L., 2003. 1D-transport properties of single superconducting lead nanowires. Physica C 391 (4), 369–375.

Milovantseva, N., Saphores, J., 2013. E-waste bans and US households' preferences for disposing of their e-waste. J. Environ. Manage. 124, 8–16.

Mineral Commodity Summaries, 2015. U.S. Geological Survey, Reston, Virginia.

Mueller, J.R., Boehm, M.W., Drummond, C., 2012. Direction of CRT waste glass processing: electronics recycling industry communication. Waste Manage. 32 (8), 1560–1565.

Murata, M., Sorrentino, F., 1996. Effect of large additions of Cd, Pb, Cr, Zn, to cement raw meal on the composition and the properties of the clinker and the cement. Cement Concr. Res. 26 (3), 377–385.

Nnorom, I.C., Osibanjo, O., Ogwuegbu, M.O.C., 2011. Global disposal strategies for waste cathode ray tubes. Resour. Conserv. Recycl. 55 (3), 275–290.

Nowak, B., Pessl, A., Aschenbrenner, P., Szentannai, P., Mattenberger, H., Rechberger, H., Hermann, L., Winter, F., 2010. Heavy metal removal from municipal solid waste fly ash by chlorination and thermal treatment. J. Hazard. Mater. 179 (1–3), 323–331.

Oguchi, M., Sakanakura, H., Terazono, A., 2013. Toxic metals in WEEE: Characterization and substance flow analysis in waste treatment processes. Sci. Total Environ. 463–464, 1124–1132.

Okada, T., Tomikawa, H., 2012. Leaching characteristics of lead from melting furnace fly ash generated by melting of incineration fly ash. J. Environ. Manage. 110, 207–214.

Okada, T., Yonezawa, S., 2013. Energy-efficient modification of reduction-melting for lead recovery from cathode ray tube funnel glass. Waste Manage. 33 (8), 1758–1763.

Okada, T., Yonezawa, S., 2014. Reduction-melting combined with a Na_2CO_3 flux recycling process for lead recovery from cathode ray tube funnel glass. Waste Manage. 34 (8), 1470–1479.

Okada, Takashi, Inano, H., Hiroyoshi, N., 2012. Recovery and immobilization of lead in cathode ray tube funnel glass by a combination of reductive and oxidative melting processes. J. Soc. Inform. Display 20 (9), 508–516.

Ongondo, F.O., Williams, I.D., Cherrett, T.J., 2011. How are WEEE doing? A global review of the management of electrical and electronic wastes. Waste Manage. 31 (4), 714–730.

Pant, D., Singh, P., 2013. Chemical modification of waste glass from cathode ray tubes (CRTs) as low cost adsorbent. In: pp. 226–232.

Pant, D., Joshi, D., Upreti, M.K., Kotnala, R.K., 2012. Chemical and biological extraction of metals present in E waste: a hybrid technology. Waste Manage. 32 (5), 979–990.

Pant, D., Singh, P., Upreti, M.K., 2014. Metal leaching from cathode ray tube waste using combination of Serratia plymuthica and EDTA. Hydrometallurgy 146, 89–95.

Pashkov, G.L., Mikhlina, E.V., Kholmogorov, A.G., Mikhlin, Y.L., 2002. Effect of potential and ferric ions on lead sulfide dissolution in nitric acid. Hydrometallurgy 63 (2), 171–179.

Patil, Kashinath C., Aruna, S.T., Ekambaram, S., 1997. Combustion synthesis. Curr. Opin. Solid State Mater. Sci. 2, 158–165.

Popovici, A., Popita, G.-E., Roba, C., Rusu, T., Tofana, V., Rosu, C., 2013. A proposal for cathode ray tubes waste recycling. J. Environ. Prot. Eco. 14 (4), 1703–1710.

Rath, S.S., Nayak, P., Mukherjee, P.S., Roy Chaudhury, G., Mishra, B.K., 2012. Treatment of electronic waste to recover metal values using thermal plasma coupled with acid leaching – a response surface modeling approach. Waste Manage. 32 (3), 575–583.

Resende, L.V., Morais, C.A., 2015. Process development for the recovery of europium and yttrium from computer monitor screens. Miner. Eng. 70, 217–221.

Ris, M.D., Dietrich, K.N., Succop, P.A., Berger, O.G., Bornschein, R.L., 2004. Early exposure to lead and neuropsychological outcome in adolescence. J. Int. Neuropsych. Soc. 10 (2), 261–270.

Romero, D., James, J., Mora, R., Hays, C.D., 2013. Study on the mechanical and environmental properties of concrete containing cathode ray tube glass aggregate. Waste Manage. 33 (7), 1659–1666.

Sasai, R., Kubo, H., Kamiya, M., Itoh, H., 2008. Development of an eco-friendly material recycling process for spent lead glass using a mechanochemical process and Na_2EDTA reagent. Environ. Sci. Technol. 42 (11), 4159–4164.

Saterlay, A.J., Wilkins, S.J., Compton, R.G., 2001. Towards greener disposal of waste cathode ray tubes via ultrasonically enhanced lead leaching. Green Chem. 3 (4), 149–155.

Shi, X., Li, G., Xu, Q., He, W., Liang, H., 2011. Research progress on recycling technology of end-of-life CRT glass. Mater. Rev. 11, 129–132.

Song, Q., Li, J., 2014. Environmental effects of heavy metals derived from the e-waste recycling activities in China: a systematic review. Waste Manage. 34 (12), 2587–2594.

Spalvins, E., Dubey, B., Townsend, T., 2008. Impact of electronic waste disposal on lead concentrations in landfill leachate. Environ. Sci. Technol. 42 (19), 7452–7458.

Sua-iam, G., Makul, N., 2013. Use of limestone powder during incorporation of Pb-containing cathode ray tube waste in self-compacting concrete. J. Environ. Manage. 128, 931–940.

Tan, Q.Y., Li, J.H., 2015. Recycling metals from wastes: a novel application of mechanochemistry. Environ. Sci. Technol. 49, 5849–5861.

Tian, X., Wu, Y., Gu, Y., Yin, X., Li, M., 2015. Quantitative research of environmental benefits of recycling lead from obsolete CRT. Res. Environ. Sci. 28 (2), 283–290.

Tsydenova, O., Bengtsson, M., 2011. Chemical hazards associated with treatment of waste electrical and electronic equipment. Waste Manage. 31 (1), 45–58.

Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y., Deveci, H., 2012. Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner. Eng. 25 (1), 28–37.

Wadanambi, L., Dubey, B., Townsend, T., 2008. The leaching of lead from lead-based paint in landfill environments. J. Hazard. Mater. 157 (1), 194–200.

Wang, Y., Zhu, J., 2012. Preparation of lead oxide nanoparticles from cathode-ray tube funnel glass by self-propagating method. J. Hazard. Mater. 215–216, 90–97.

White paper on WEEE recycling industry in China, 2013. CHEARI.

Wu, Y., Wang, B., Zhang, Q., Li, R., Sun, C., Wang, W., 2014. Recovery of rare earth elements from waste fluorescent phosphors: Na_2O_2 molten salt decomposition. J. Mater. Cycles Waste Manage. 16 (4), 635–641.

Xie, F., Liu, L., Li, J., 2012. Recycling of leaded glass: scrap cathode ray glass and fluorescent lamp glass. Proc. Environ. Sci. 16, 585–589.

Xing, M., Zhang, F., 2011. Nano-lead particle synthesis from waste cathode ray-tube funnel glass. J. Hazard. Mater. 194, 407–413.

Xu, Q., Li, G., He, W., Huang, J., Shi, X., 2012. Cathode ray tube (CRT) recycling: current capabilities in China and research progress. Waste Manage. 32 (8), 1566–1574.

Xu, Q., Yu, M., Kendall, A., He, W., Li, G., Schoenung, J.M., 2013. Environmental and economic evaluation of cathode ray tube (CRT) funnel glass waste management options in the United States. Resour. Conserv. Recycl. 78, 92–104.

Yamashita, M., Wannagon, A., Matsumoto, S., Akai, T., Sugita, H., Imoto, Y., Komai, T., Sakanakura, H., 2008. Leaching behavior of CRT funnel glass. J. Hazard. Mater. 184 (1–3), 58–64.

Yan, L., Shi, K.H., Liu, Y.Z., 2008. Synthetic assessment and selection of panel–funnel separating techniques of end-of-life CRT glass. J. Anyang Inst. Technol. 6, 19–21.

Yot, P.G., Méar, F.O., 2009. Lead extraction from waste funnel cathode-ray tubes glasses by reaction with silicon carbide and titanium nitride. J. Hazard. Mater. 172 (1), 117–123.

Yuan, W., Li, J., Zhang, Q., Saito, F., 2012. Innovated application of mechanical activation to separate lead from scrap cathode ray tube funnel glass. Environ. Sci. Technol. 46 (7), 4109–4114.

Yuan, W., Li, J., Zhang, Q., Saito, F., Yang, B., 2013. A novel process utilizing mechanochemical sulfidization to remove lead from cathode ray tube funnel glass. J. Air Waste Manage. Assoc. 63 (4), 418–423.

Zekkos, D., Kabalan, M., Syal, S.M., Hambright, M., Sahadewa, A., 2013. Geotechnical characterization of a municipal solid waste incineration ash from a Michigan monofill. Waste Manage. 33 (6), 1442–1450.

Zhang, S., Yang, M., Liu, H., Pan, D., Tian, J., 2013. Recovery of waste rare earth fluorescent powders by two steps acid leaching. Rare Met. 32 (6), 609–615.

Waste Management 57 (2016) 220–225

Contents lists available at ScienceDirect

Waste Management

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

Recycling WEEE: Extraction and concentration of silver from waste crystalline silicon photovoltaic modules

Pablo Dias *, Selene Javimczik, Mariana Benevit, Hugo Veit, Andréa Moura Bernardes

Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGE3M), Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves, 9500, 91509-900 Porto Alegre, RS, Brazil

ARTICLE INFO

Article history:
Received 12 January 2016
Revised 8 March 2016
Accepted 9 March 2016
Available online 12 March 2016

Keywords:
Crystalline silicon
E-waste
Recycling
Silver recovery
Solar panel

ABSTRACT

Photovoltaic modules (or panels) are important power generators with limited lifespans. The modules contain known pollutants and valuable materials such as silicon, silver, copper, aluminum and glass. Thus, recycling such waste is of great importance. To date, there have been few published studies on recycling silver from silicon photovoltaic panels, even though silicon technology represents the majority of the photovoltaic market. In this study, the extraction of silver from waste modules is justified and evaluated. It is shown that the silver content in crystalline silicon photovoltaic modules reaches 600 g/t. Moreover, two methods to concentrate silver from waste modules were studied, and the use of pyrolysis was evaluated. In the first method, the modules were milled, sieved and leached in 64% nitric acid solution with 99% sodium chloride; the silver concentration yield was 94%. In the second method, photovoltaic modules were milled, sieved, subjected to pyrolysis at 500 °C and leached in 64% nitric acid solution with 99% sodium chloride; the silver concentration yield was 92%. The first method is preferred as it consumes less energy and presents a higher yield of silver. This study shows that the use of pyrolysis does not assist in the extraction of silver, as the yield was similar for both methods with and without pyrolysis.

1. Introduction

1.1. WEEE

Waste Electrical and Electronic Equipment (WEEE) or e-waste, according to EMPA (Swiss Federal Laboratories for Materials Science and Technology), is the term used to describe old, end-of-life or discarded electrical appliances, including discarded computers, consumer electronics, and refrigerators (EMPA, 2009). The amount of WEEE generated worldwide seems to be underestimated, and there are no precise methods to determine the total amount. Globally, the upward trend in WEEE generation and production should continue to grow due to new technologies and affordable electronics (Ongondo et al., 2011). E-waste contains both valuable and hazardous materials, which require special handling and recycling methods. WEEE contains a significant number of precious metals, such as indium, silver and palladium. As these elements are often present in low concentrations and in complex components, their recovery is not easy (Nelen et al., 2014), and a large proportion of these precious metals is lost in the recycling process (Chancerel et al., 2009). Moreover, WEEE may contain heavy metals, brominated flame retardant (Wang and Xu, 2014) and a variety of toxic substances that can contaminate the environment and threaten human health, if the end-of-life phase is not meticulously managed (Kiddee et al., 2013).

The extraction of precious metals by mining is associated with negative environmental impacts due to significant greenhouse gas emissions and energy, water, and land usage (Ayres, 1997). The use of secondary raw material is becoming more important because the ore grade in primary production is decreasing (Simon et al., 2013). The environmental impacts of secondary production in state-of-the-art operations are much lower than in primary production (Hagelüken and Meskers, 2009). In addition to environmental protection and legislation, recycling is also driven by economic interests. The limited quantity of precious metals in reserve and their high economic value provide additional incentives to improve the recovery and research of precious metals from WEEE (Chancerel et al., 2009).

1.2. Photovoltaic modules

Solar modules convert energy from sunlight into electricity without using a rotor, heat engine or gears. Recently, they have

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* Corresponding author.
E-mail addresses: pablo.dias@ufrgs.br (P. Dias), hugo.veit@ufrgs.br (H. Veit).

http://dx.doi.org/10.1016/j.wasman.2016.03.016
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attracted a great deal of attention due to their potential application for alternative energy generation. Many countries have already benefitted from the photovoltaic industry (Wang et al., 2008). The range of current technologies for manufacturing photovoltaic modules (or PV modules) is divided into three generations. First generation PV modules contain crystalline silicon (c-Si), which may be monocrystalline, polycrystalline or ribbon sheets. Second generation PV modules include thin film amorphous silicon (a-Si), cadmium telluride (CdTe), multi-junction cells (a-Si-μc-Si), copper indium gallium diselenide (CIGS), and copper indium diselenide (CIS). Third generation PV modules include concentrator photovoltaic (CPV) and emerging technologies such as dye-sensitized solar cells, organic solar cells, hybrid cells, passivated emitter rear contact cell (PERC) and passivated emitter rear-locally-diffused (PERL). Currently, the majority (approximately 80%) of worldwide production consists of crystalline silicon cells (first generation) (Paiano, 2015).

According to Radziemska (2014), crystalline silicon PV modules are made from the following materials, which are listed in order by decreasing mass: glass, aluminum frames, EVA (ethylene-vinyl acetate) copolymer transparent encapsulating layers, photovoltaic cells, installation boxes, Tedlar protective foil and assembly bolts. A typical cross-section of these modules, with several layers of distinct materials, is shown in Fig. 1. The metallic electrodes are placed in the front and the rear of the silicon cell. The front electrodes are typically made of silver and the rear electrodes of silver and aluminum (Pinho and Galdino, 2014).

1.3. Recycling photovoltaic modules

At the end of their lifespan, PV modules become solid waste (e-waste). The lifespan of first generation PV modules is approximately twenty years and approximately one million tons of PV modules are forecast to be disposed of in 2035, based on the growth in the solar industry (International Energy Agency, 2013). As the PV market continues to grow, so will waste, even if such waste appears with a long time delay (Kazmerski, 2006).

Improper disposal of solar modules can generate significant environmental impacts. These devices contain cadmium and lead, which can leach into the soil and consequently pollute the environment. PV modules and other WEEE are composed of glass, aluminum, rare earths, brominated flame retardants (BFRs) and other hazardous substances (Widmer et al., 2005).

In general, the process of recycling PV modules starts with the removal of EVA resin. Several methods can be employed to remove the EVA, such as dissolution by nitric acid and thermal decomposition (usually pyrolysis) (Bruton, 1994). Most recycling research regarding PV modules aims to recover high-purity silicon and glass, leaving behind other materials such as silver, copper and aluminum. Table 1 presents a summary of experimental work conducted on the recycling of PV modules.

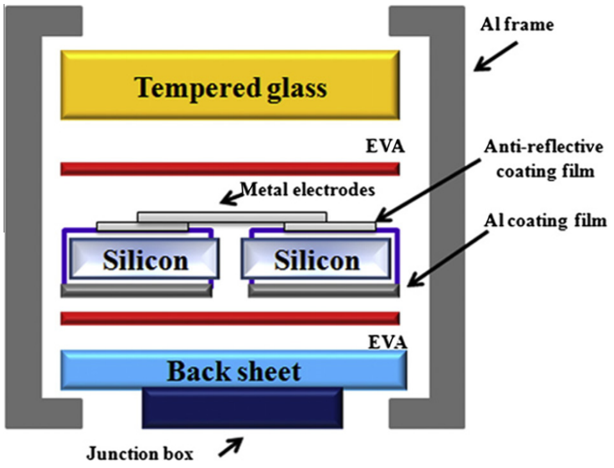

Fig. 1. Typical structure of c-Si PV modules: cross-sectional view (Kang et al., 2012).

1.4. Silver in photovoltaic modules

From an economic point of view, pure silicon, recoverable from spent cells, is the most important material due to its cost and scarcity (Radziemska and Ostrowski, 2010). However, given the high complexity of c-Si cell recycling, other useful materials such as glass, aluminum and silver are becoming increasingly useful for improving the economic viability of recycling processes (Tao and Yu, 2015). Table 1 shows that older studies focused on recovering silicon whereas the latest works tend to recover more materials.

Silver is a precious metal in high demand, and it is used in PV modules (Pinho and Galdino, 2014). Swerdrup et al. (2014) suggest that silver production will reach its peak in 2030, and because of its rapid usage and limited availability, the future silver supply will be soon at risk (2075). When mined, silver's concentration in the U.S.'s deposits must reach 700 g/t in order to be economically minable as a primary product (USGS, 2015). Despite the importance of this metal, the current high demand and its increasing market price, there are few published studies regarding the recovery of silver from PV modules. Authors such as Radziemska (2014) and Tao and Yu (2015) suggest that silver from PV modules can be extracted by nitric acid leaching followed by electrolysis. Palitzsch and Loser (2011) claim to recover aluminum in the form of poly-aluminum-chlorides through a demetallization process with an aluminum chloride and water solution while silver is extracted using nitric acid. Nieland et al. (2012) also aimed to extract silver from PV modules using hydrogen peroxide in combination with organic and non-organic catalyzers. All of these results, however, lack quantification and yield extraction analysis.

The objective of this study is to analyze the silver present in PV modules. This study aims to characterize the silver's distribution

Table 1
Summary of experimental work conducted on PV recycling.

Authors	Process	Materials Recovered
Frisson et al. (2000)	• Pyrolysis in a conveyer belt furnace and pyrolysis in a fluidized bed reactor • Etching using a sequence of 15% HF, 4–1 $H_2SO_4 \cdot H_2O$ solution, 40% HNO_3 • Emitter etch in 20% NaOH	• Silicon
Radziemska and Ostrowski (2010)	• Removal of the aluminum coating by etching, using 30% KOH to remove Al metal coatings • Etching using a mixture of 250 ml HNO_3 (65%), 150 ml HF (40%), and 150 ml CH_3COOH (99.5%) 3 ml Br_2 for removing Ag coatings, AR coatings and n-p junctions	• Silicon
Kang et al. (2012)	• Recovery of glass using organic solvents • Thermal decomposition to remove the adhesive layer and recover the semiconductor • Obtainment of 99.99% pure silicon by immersion of the recovered cell in an etching solution combined with surfactant	• Glass • Silicon
Wang et al. (2012)	• Two-step heating process for PV module thermal delamination • Acid etching to remove tin-lead coating from copper and metal impurities from the silicon wafer	• Glass • Silicon • Copper

within the module and to determine its quantity in the modules. Moreover, this study evaluates two different silver extraction procedures, compares them and gives quantified data to assist future studies on PV module recycling.

2. Materials and methods

Experiments were performed with crystalline silicon modules (c-Si modules) such as the one in Fig. 2. The aluminum frames were removed from all modules.

2.1. Characterization

The experiments were conducted in two steps. The first step, characterization, was intended to identify the location and arrangement of the silver. The characterization step also evaluated if the silver could be leached through hydrometallurgical procedures and quantified the amount of silver present in the modules. The procedures used in the characterization step are displayed in Fig. 3.

To obtain the semiconductor material from the modules, $1 \times 1\ cm^2$ pieces of the PV module were immersed in a 95% H_2SO_4 solution for two days with constant agitation at room temperature. The solutions were filtered using 45 μm filter paper, the semiconductor particles were separated and collected. The collected material was then rinsed, dried and milled with an alumina mortar.

To leach the silver present in the semiconductor powder, 100 ml of a 64% nitric acid (HNO_3) solution was placed in a beaker with 5 g of the semiconductor. Leaching was carried out for 2 h at room temperature. To evaluate if all silver present in the semiconductor had been leached, the silver present in the PV modules was analyzed using a Thermo Niton XL3t (Thermo Scientific, Massachusetts, USA) X-ray fluorescence before and after leaching. These results encouraged a study regarding the concentration of the silver present in the PV modules.

In the interest of better analyzing the composition of the photovoltaic cell, $2 \times 2\ cm^2$ pieces were cut off of the modules. The front glass layer of the samples and their adhesive layer were manually removed. Samples were then observed under an optical microscope.

PV modules were milled four times in a knife mill and the resulting powder was immersed in 3:1 aqua regia (3 parts hydrochloric acid 38% to 1 nitric acid 60%) with a solid-liquid ratio of $0.1\ g\ L^{-1}$, under magnetic agitation. The immersion lasted 2 h at 60 °C. To quantify the silver present in the module, the resulting solution was analyzed by atomic absorption spectroscopy (AAS) using a 3300 Spectrometer (PerkinElmer, Massachusetts, USA). Although there is a risk of precipitating silver chloride when using aqua regia, this solution was chosen because it is a common procedure for metals characterization from WEEE (Kasper et al., 2011).

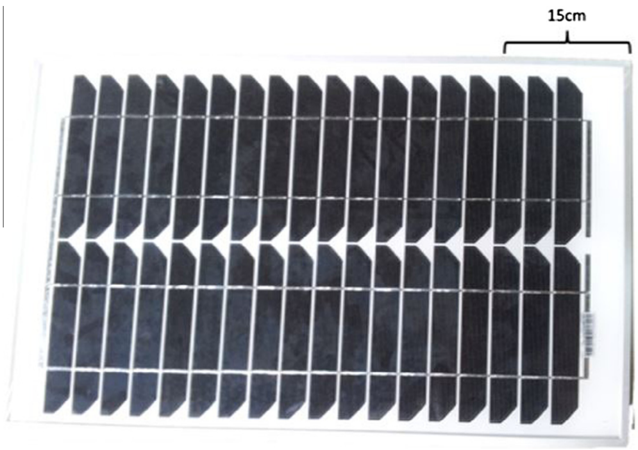

Fig. 2. Silicon PV module.

2.2. Extraction and concentration

The second step was the evaluation of two similar silver extraction and concentration procedures. The first procedure involved only the use of mechanical (milling, sieving) and hydrometallurgical (leaching in HNO_3) approaches. The second procedure included the same steps as the first one, while adding a pyrolysis process to remove the organics from the waste PV module, thus concentrating the silver and releasing it from any adhesive material. These two procedures were evaluated and compared, as shown in Fig. 4.

According to Dias et al. (2016), 81% of the module's silver tends to concentrate at a particle size fraction smaller than 0.5 mm. Thus, to concentrate the silver, the milled modules were separated into two groups, based on the particle size. To separate the powder, a mesh 35 (0.5 mm aperture) was used. The sieving occurred in a vibrating sieving device; for every 300 g of material, the equipment vibrated for 15 min with an amplitude of 1 mm. The two obtained fractions (smaller than 0.5 mm and larger than 0.5 mm) were stored separately (d80 = 1.24 mm). The smaller fraction was used for the silver extraction procedure. In total, 15 g of milled module were quartered and leached in 300 ml of HNO_3 64% at room temperature for 2 h, under magnetic agitation. The solution was filtered (using 45 μm filter paper), and the solid was reserved. The filtered solution was analyzed using AAS to quantify the silver concentration; this sample was called X1. Afterward, 1.5 g of 99% sodium chloride (NaCl) was added to the leached solution in a two-step process. First, 1.05 g was added and the solution was stirred. A precipitation was observed; the precipitate was filtered and reserved. The second step was the addition of the remaining 0.15 g to ensure complete precipitation. No precipitation was observed. The solution was once again stirred and filtered. This new solution was called X2, and it was also analyzed using AAS. This same procedure was repeated with samples that had undergone a pyrolysis process. These samples were called Y1 (before NaCl was added) and Y2 (after NaCl was added). These procedures were repeated three times (triplicate) for each group, X1-X2 and Y1-Y2. These silver concentration procedures were adapted from Rojas (2009).

In the pyrolysis process for the Y1-Y2 group, a furnace structure was assembled to control the process, as shown in Fig. 5. The pyrolysis was carried out using $150 \times 30\ cm^2$ alumina boat-shaped crucibles, which were filled, weighed, and placed inside the furnace. Each crucible was then removed, weighed and replaced in the furnace every hour. The approximate weight for each sample was 9.0 g. The dwell temperature chosen was 500 °C, and 1 L/min nitrogen airflow was maintained throughout the whole process (adapted from Zeng et al., 2004). If there was no mass loss between two weighings, the pyrolysis was assumed to be complete.

3. Results

The extracted semiconductor underwent X-ray fluorescence to confirm the presence of silver. The averages from 5 XRF measurements are displayed in Table 2.

The results shown in Table 2 confirm the presence of silver in the module's semiconductor. Table 3 shows the information obtained from the X-ray fluorescence performed after the chemical leaching with HNO_3.

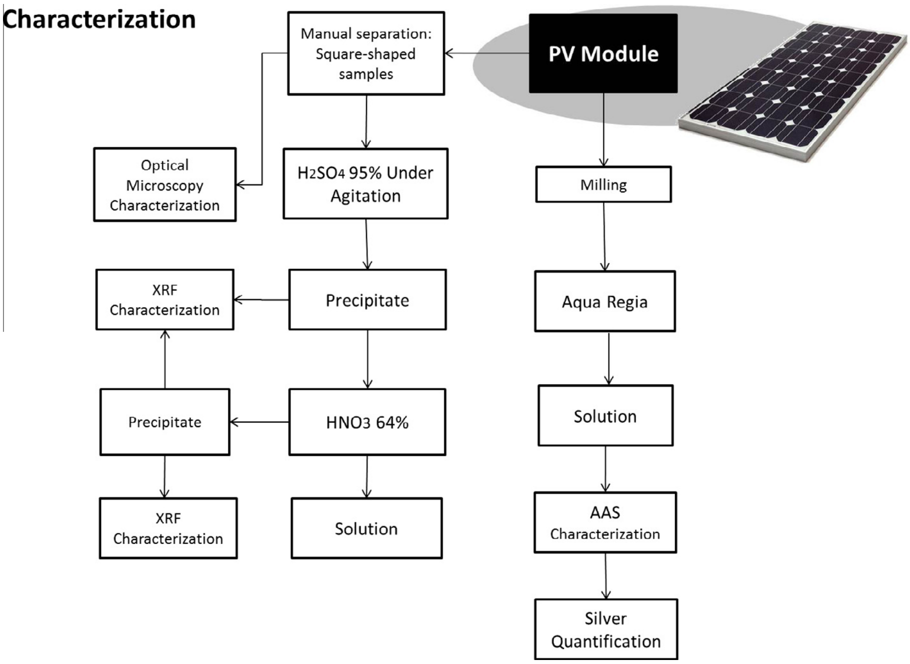

Fig. 3. Flowchart illustrating the procedures used in the characterization step.

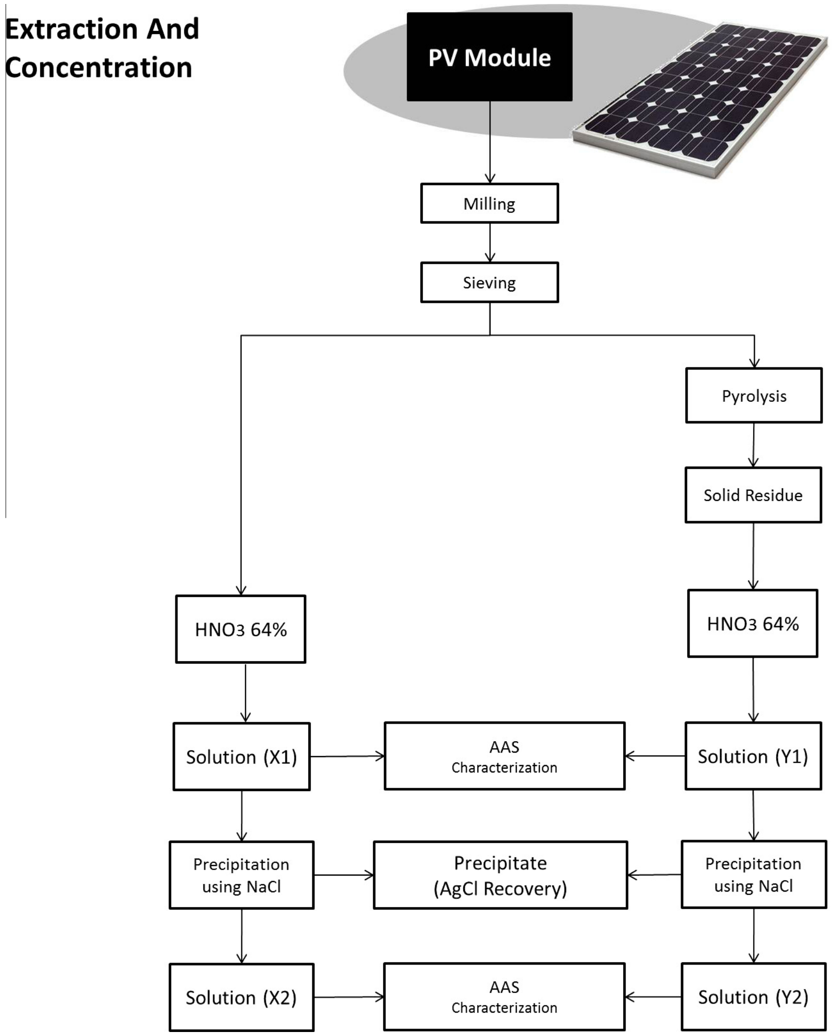

Fig. 4. Flowchart illustrating the procedures used in the extraction and concentration step.

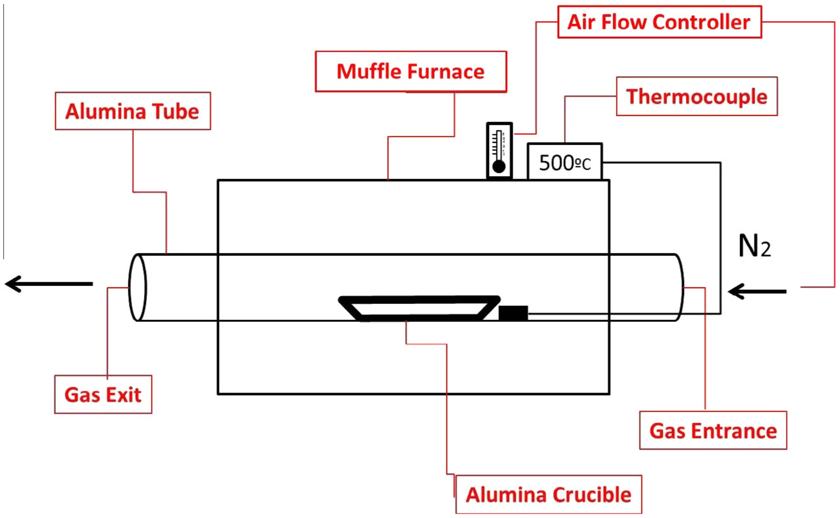

Fig. 5. Schematic illustration of the furnace setup.

Table 2
Average XRF results obtained from the semiconductor extracted from the modules.

Parameter	(wt%)	Deviation (±2σ)
Silicon	98.20	±0.33
Silver	1.40	±0.02
Chromium	0.14	±0.01
Copper	0.04	±0.01
Lead	0.08	±0.007

Table 3
Average XRF results obtained from the leached semiconductor extracted from modules.

Parameter	(wt%)	Deviation (2σ)
Silicon	99.94	±0.41
Silver	ND	–
Chromium	ND	–
Copper	ND	–
Lead	0.04	±0.001

Based on Table 3, it is possible to infer that the leaching method was able to transfer all silver present in the semiconductor into the acid solution.

To visualize the arrangement of the silver in the photovoltaic cell, optical microscopy was performed. Figs. 6 and 7 show the microscopy with magnifications of 100 times and 200 times, respectively.

Fig. 6 indicates that silver is deposited on the semiconductor as a single straight thread. These threads are distributed throughout the photovoltaic module and have a thickness of approximately 100 μm (Fig. 7).

The result obtained from the AAS (aqua regia leaching) for the silver concentration was 0.0635% or approximately 600 silver grams per module ton. This concentration is comparable to a United States high grade silver reserve (1100–800 g/t) (Swerdrup et al., 2014).

The results obtained from the AAS performed in samples X1, X2, Y1 and Y2 are presented in Table 4.

Table 4 reveals that it is possible to precipitate most of the silver present in the milled module using both suggested procedures. In the samples not subjected to pyrolysis, approximately 94% of the silver present in the sample was concentrated as silver chloride while the silver concentration reached 92% in samples subjected to pyrolysis. The concentrated silver chloride was a white powder

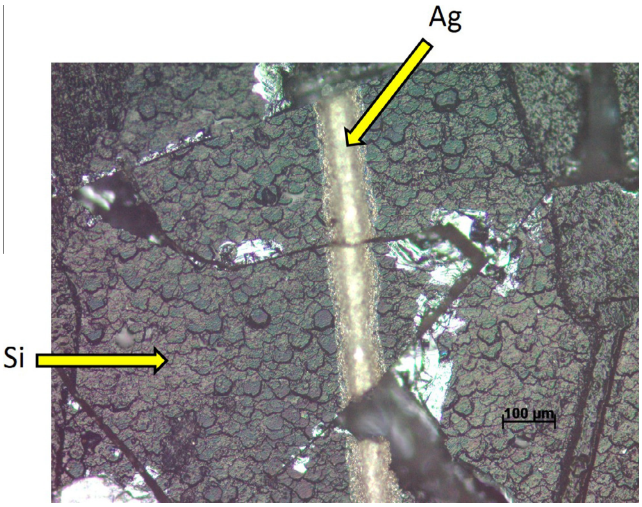

Fig. 6. Optical microscopy image of the PV module sample, 100× magnification.

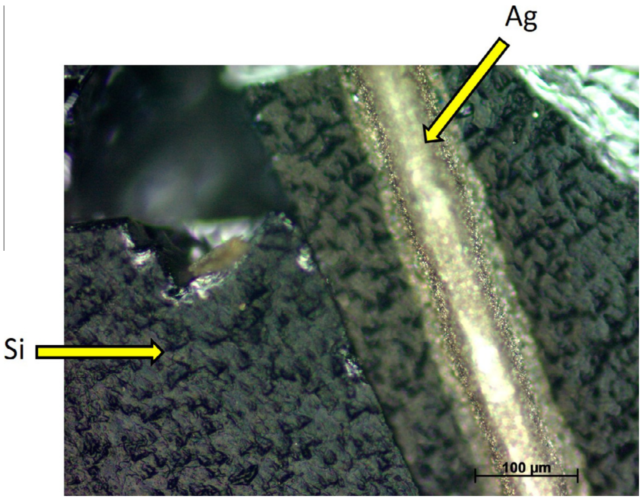

Fig. 7. Optical microscopy image of the PV module sample, 200× magnification.

Table 4
Results from the AAS from samples X1, X2, Y1 and Y2.

Group	X (without pyrolysis) (%)	Y (with pyrolysis) (%)
Silver (Ag) - Prior to precipitation (X1, Y1)	0.17	0.16
Silver (Ag) - Post precipitation (X2, Y2)	0.011	0.013
Yield	93.91	91.87

collected in the filter paper. As the yield results for leaching with and without pyrolysis were very similar, the pyrolysis of the milled modules was not demonstrated to be advantageous. Pyrolysis is intended to concentrate silver from the waste module by eliminating the organic matter. Moreover, if any of this organic matter (such as the adhesive layer) were to block the silver leaching, pyrolysis would resolve this issue. However, pyrolysis consumed energy to heat the furnace, inert gas (nitrogen) and time but did not increase silver extraction. Thus, for extracting silver from PV modules, the leaching procedure without pyrolysis is better than the procedure with pyrolysis.

4. Conclusions

The key conclusions from this study are as follows:

- Silver present in first generation PV modules is found on the semiconductor layer in the shape of small silver threads (100 μm width).
- The average amount of silver found in the modules is 630 g/t.
- The procedure to concentrate silver from the PV module consisted of: manual removal of the aluminum frame, milling of the modules, sieving and selecting the fraction with particle sizes smaller than 0.5 mm, leaching the obtained powder in nitric acid and precipitating the leached solution using 99% sodium chloride. This process was able to concentrate 94% of the silver present in the PV module.
- Pyrolysis did not assist in silver extraction from PV modules. Thus, in module recycling procedures, silver recovery should be performed before the use of pyrolysis.

Future studies should evaluate the application of this study's procedure along with the recovery of other valuable materials from PV modules.

Acknowledgments

The authors are grateful to CAPES, CNPq, FINEP and FAPERGS (Brazil) for their financial support. Project number 472727/2012-5.

References

Ayres, R.U., 1997. Metals recycling: economic and environmental implications. Resour. Conserv. Recycl., 145–173

Bruton, T.M., 1994. Re-cycling of high value, high energy content components of silicon PV modules. In: Proceedings of the 12th EC-PVSEC, Amsterdam, Netherlands, pp. 459–463.

Chancerel, P., Meskers, C.E., Hagelüken, C., Vera, S., 2009. Assessment of precious metal flows during preprocessing of waste electrical and electronic equipment. J. Ind. Ecol., 791–810

Dias, P.R., Benevit, M.G., Veit, H.M., 2016. Photovoltaic solar panels of crystalline silicon: characterization and separation. Waste Manage. Res. 34 (3), 235–245.

EMPA, Swiss Federal Laboratories for Materials Science Technology, 2009. e-Waste Definition <http://ewasteguide.info/node/201> (Retrieved 04 25, 2015).

Frisson, L., Lieten, K., Bruton, T., Declercq, K., Szlufcik, J., De Moor, H., Goris, M., Benali, A., Aceves, O., 2000. Recent improvements in industrial PV module recycling. In: 16th European Photovoltaic Solar Energy Conference, 1–5 May 2000, Glasgow, UK.

Hagelüken, C., Meskers, C., 2009. Technology challenges to recover precious and special metals from complex products. In: R'09 Twin World Congress, Davos, Switzerland.

International Energy Agency, 2013. Photovoltaic Power Systems Programme – Trends 2013 in Photovoltaic Applications.

Kang, S., Yoo, S., Lee, J., Boo, B., Ryu, H., 2012. Experimental investigations for recycling of silicon and glass from waste photovoltaic modules. Renew. Energy 47, 152–159.

Kasper, A.C., Berselli, G.B., Freitas, B.D., Tenório, J., Bernardes, A.M., Veit, H., 2011. Printed wiring boards for mobile phones: characterization and recycling of copper. Waste Manage. 31 (12), 2536–2545 (December).

Kazmerski, L.L., 2006. Solar photovoltaics R&D at the tipping point: a 2005 technology overview. J. Electron Spectrosc. Relat. Phenom. 150, 105–135.

Kiddee, P., Naidu, R., Wong, M.H., 2013. Electronic waste management approaches: an overview. Waste Manage. 33, 1237–1250.

Nelen, D., Manshoven, S., Peeters, J.R., Vanegas, P., D'Haese, N., Vrancken, K., 2014. A multidimensional indicator set to assess the benefits of WEEE material recycling. J. Clean. Prod. 83, 305–316.

Nieland, S., Neuhaus, U., Pfaff, T., Radlein, E., 2012. New approaches for component recycling of crystalline solar modules. Electronics goes Green 2012+ (EGG 2012).

Ongondo, F., Williams, I., Cherrett, T., 2011. How are WEEE doing? A global review of the management of electrical and electronic wastes. Waste Manage. 31, 714–730.

Paiano, A., 2015. Photovoltaic waste assessment in Italy. Renew. Sustain. Energy Rev. 41, 99–112.

Palitzsch, W., Loser, U., 2011. A new and intelligent de-metallization step of broken silicon cells and silicon cell production waste in the recycling procedure of crystalline Si modules. In: Proceedings of the 37th IEEE Photovoltaic Specialists Conference (PVSC 2011), pp. 003269–003270.

Pinho, J.T., Galdino, M.A., 2014. Engineering Manual for Photovoltaic Systems Retrieved from Rio de Janeiro: CEPEL – CRESESB <http://www.cresesb.cepel.br/publicacoes/download/Manual_de_Engenharia_FV_2014.pdf> (Last Accessed: 01/07/2016).

Radziemska, E.K., 2014. Recycling of Photovoltaic Solar Cells and Modules – The State-Of-Art. LAP LAMBERT Academic Publishing, Saarbrucken, Germany.

Radziemska, E.K., Ostrowski, P., 2010. Chemical treatment of crystalline silicon solar cells as a method of recovering pure silicon from photovoltaic modules. Renew. Energy 35, 1751–1759.

Rojas, C.E., 2009. Reciclagem de Sucata de Jóias para a Recuperação Hidrometalúrgica de Ouro e Prata. MSc Dissertation. UFMG.

Simon, F.-G., Holm, O., Berger, W., 2013. Resource recovery from urban stock, the example of cadmium and tellurium from thin film module recycling. Waste Manage. 33, 942–947.

Swerdrup, H., Koca, D., Ragnarsdottir, K.V., 2014. Investigating the sustainability of the global silver supply, reserves, stocks in society and market price using different approaches. Resour. Conserv. Recycl. 83, 121–140.

Tao, J., Yu, S., 2015. Review on feasible recycling pathways and technologies of solar photovoltaic modules. Sol. Energy Mater. Sol. Cells 141, 108–124.

USGS, U.G., 2015. Mineral Commodity Summaries – January.

Wang, R., Xu, Z., 2014. Recycling of non-metallic fractions from waste electrical and electronic equipment (WEEE): a review. Waste Manage. 34, 1455–1469.

Wang, T.Y., Lin, Y.C., Tai, C.Y., Sivakumar, R., Rai, D.K., Lan, C.W., 2008. A novel approach for recycling of kerf loss silicon from cutting slurry waste for solar cell applications. J. Cryst. Growth 310, 3403–3406.

Wang, T.-Y., Hsiao, J.-C., Du, C.-H., 2012. Recycling of materials from silicon base solar cell module. In: Proceedings of the 38th IEEE Photovoltaic Specialists Conference, pp. 2355–2358.

Widmer, R., Oswald-Krapf, H., Sinha-Khetriwal, D., Schnellmann, M., Böni, H., 2005. Global perspectives on e-waste. Environ. Impact Assess. Rev. 25, 436–458.

Zeng, D., Born, M., Wambach, K., 2004. Pyrolysis of EVA and its application in recycling of photovoltaics. J. Environ. Sci. 16 (6), 889–893.