ARTICLE IN PRESS

Waste Management xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Exposure to hazardous substances in Cathode Ray Tube (CRT) recycling sites in France

Marie-Thérèse Lecler *, François Zimmermann, Eric Silvente, Frédéric Clerc, Alain Chollot, Jérôme Grosjean

Department of Process Engineering, Institut National de Recherche et de Sécurité, rue du Morvan 54519, Vandoeuvre, France

ARTICLE INFO

Article history:
Received 20 October 2014
Accepted 22 February 2015
Available online xxxx

Keywords:
WEEE
Chemical risk
Exposure assessment
Cathode ray tubes
Recycling
Ambient concentration

ABSTRACT

The Waste Electrical and Electronic Equipment (WEEE) or e-waste recycling sector has grown considerably in the last fifteen years due to the ever shorter life cycles of consumables and an increasingly restrictive policy context. Cathode Ray Tubes (CRTs) from used television and computer screens represent one of the main sources of e-waste. CRTs contain toxic materials such as lead, cadmium, barium, and fluorescent powders which can be released if recycling of CRTs is not appropriate. Exposure to these harmful substances was assessed in nine workshops where CRT screens are treated. Particulate exposure levels were measured using a gravimetric method and metals were analysed by plasma emission spectrometry. The maximum levels of worker exposure were 8.8 mg/m^3, 1504.3 μg/m^3, 434.9 μg/m^3, 576.3 μg/m^3 and 2894.3 μg/m^3 respectively for inhalable dust, barium, cadmium, lead and yttrium. The maximum levels of airborne pollutants in static samples were 39.0 mg/m^3, 848.2 μg/m^3, 698.4 μg/m^3, 549.3 μg/m^3 and 3437.9 μg/m^3 for inhalable dust, barium, cadmium, lead and yttrium. The most harmful operations were identified, and preventive measures for reducing the chemical risk associated with screen recycling were proposed. Workplace measurements were used to define recommendations for reducing the chemical risks in CRT screens recycling facilities and for promoting the design and development of "clean and safe" processes in emerging recycling channels.

1. Introduction

Linked to rapid advances in electrical and electronic device technology and ever-shorter innovation cycles, Waste Electrical and Electronic Equipment (WEEE) is one of the fastest growing waste streams, especially in Europe. The management of such waste is regulated by the European Directive 2002/96/EC (2003) which has been recast in Directive 2012/19/EU (2012). The purpose of the directive is to promote the reuse and recycling of WEEE in a sustainable way from the environmental and human health perspectives. In addition to these regulatory requirements, the high growth in treatment facilities can also be explained by an increasing demand for the raw materials contained in these appliances (ferrous metals, plastics, non-ferrous metals, glass).

As WEEE recycling activities increase worldwide, many studies have been published on the assessment of their environmental and health impact (OECD 2003; Sépulveda et al., 2010; Tsydenova and Bengtsson, 2011; Oguchi et al., 2013; Rosenberg et al., 2011). They reveal that improper handling and recycling of WEEE can lead to significant health issues for workers with the emission of these harmful substances such as heavy metals and halogenated substances (flame retardants), with hazards mainly associated with size reduction and separation operations.

One of the main streams of WEEE is constituted by Cathode Ray Tubes (CRTs) which have been replaced by flat screens over the last ten years. In Western Europe, CRT waste has been estimated at 300,000 metric tons. In France, the amount of collected screens was about 100,000 metric tons in 2011 (Ademe, 2011), those screens being handled in about one hundred industrial sites (Ademe, 2012). Compliance with the 2003 European WEEE directive (Directive 2002/96/EC) and the accreditation in 2006 of three French producers compliance schemes (Eco-systemes, Ecologic and European Recycling Platform (ERP)), have led to increase collection of screens and to improve the organisation of the CRT screen recycling sector. The minimum targets of recycling efficiency of CRT screen fall within the scope of the WEEE directive (Directive 2012/19/EU), i.e. 75% shall be recovered and 65% shall be recycled.

* Corresponding author. Tel.: +33 383509853.
E-mail address: marie-therese.lecler@inrs.fr (M.-T. Lecler).

http://dx.doi.org/10.1016/j.wasman.2015.02.027
0956-053X/

Please cite this article in press as: Lecler, M.-T., et al. Exposure to hazardous substances in Cathode Ray Tube (CRT) recycling sites in France. Waste Management (2015), http://dx.doi.org/10.1016/j.wasman.2015.02.027

CRTs are mainly composed of 85% glass and 15% plastics and metal (Menad, 1999; Andreola et al., 2007; Méar et al., 2006). The glass components are classified in four parts:

– The front part or panel made of barium and strontium glass, with an inside layer coated with fluorescent powder containing mainly yttrium but also heavy metals, and rare earths; this part represents two-thirds of the total mass of the CRT.
– The funnel or cone made of leaded glass (22–25% lead in the form of lead oxide).
– The frit made of a heavily leaded glass (up to 85% lead). This part connects together the funnel and the panel.
– The neck made of a very lead-rich glass.

Depending on its age and its manufacturer, a CRT can contain from less than 1 kg to about 3 kg of lead, mainly located in glass (Tsydenova and Bengtsson, 2011). A smaller quantity is mixed with tin in the form of solder. Nnorom et al. (2011), Kiddee et al. (2013) and Okada and Yonezawa (2014) have reviewed different strategies used for recycling CRT waste across the world. The decrease in demand for CRTs has had a major impact on recycling modes, and CRT recycling has moved from closed-loop recycling to open-loop recycling (Herat, 2008). With the presence of lead and barium in CRT glass, foam glass, the ceramic industry and concrete alveolus seem to be the most promising outlets for CRT glass recycling. But the presence of toxic lead can be a brake on using the new product. That is why, a variety of methods for recovery of lead from funnel glass have been proposed in previous studies (Chen et al., 2009a,b; Matsumoto et al., 2012; Okada et al., 2012; Wang and Zhu, 2012; Okada and Yonezawa, 2014). The other fractions are re-used as secondary raw materials (Andreola et al., 2005; Bernardo and Albertini, 2006), except the fluorescent powders collected which are landfilled. However, new processes are being developed for recovering yttrium from fluorescent powder of cathode ray tubes (Innocenzi et al., 2013).

Very few studies have been focused on assessment of occupational exposure in CRT reuse and recycling activities (Savary et al., 2008; Peters-Michaud et al., 2003; Hebisch and Linsel, 2012). Surprisingly, the atmospheric values measured by Peters-Michaud et al were very low for lead and cadmium (4.3 $\mu g/m^3$ and <0.1 $\mu g/m^3$) and well below the OSHA Permissible Exposure Limits (respectively 50 $\mu g/m^3$ and 5 $\mu g/m^3$) but they pointed out that surface contamination on the CRT preparation table and on the floor behind the CRT cutter was ten times higher than the recommended value of 50 $\mu g/ft^2$. The US Department of Housing and Urban Development has set the hazard level for lead in dwellings that are in good condition at 50 $\mu g/ft^2$ on hardwood floors and 250 $\mu g/ft^2$ on interior window sills. The general literature clearly shows that workers in CRT glass recycling operations may be exposed to high levels of heavy metals.

The current descriptive article was aimed at identifying the various processes used in France in screen recycling activities, at assessing levels of exposure and pollution with the pollutants emitted for each type of process during the different screen recycling operations (dismantling, preparation of the CRT, decontamination), at identifying the pollutant sources using real-time measurements and at recommending prevention solutions for the most emissive operations.

2. Material and methods

2.1. CRT processing at recycling sites

The treatment procedures used and the organisation of the CRT screens treatment lines available in France are both mature and stable.

CRT screens treatment can be split into three steps:

a. Screen dismantling, which consists in all of the operations necessary to obtain a bare tube. Using hand tools (screwdrivers, hammer and tweezers), the operator manually removes the plastic components, the cables, the printed wiring boards, the copper deviator, the electron gun and the cathode ray tube. To avoid any implosive hazards, the operator releases the vacuum, generally with a screwdriver used as a drill.
b. Tube preparation includes removing the anti-implosive metal frame and sometimes cleaning the tube (for removing labels and glue). The electron gun may be broken at this stage too with a hammer. The operator cuts the anti-implosive frame with a fixed or a handheld grinder.

The screen dismantling and tube preparation are generally carried out on workstations without ventilated confined enclosure.

c. Cathode ray tubes are depolluted using two approaches:

The first approach is to separate the panel glass from the funnel glass using techniques such as hot-wire cutting with separation by thermal shock, diamond sawing, and removing the fluorescent coating by aspiration or wet-brushing.

The second is to shred the whole CRT mechanically or manually, to collect the luminescent powders either by aspiration or after washing the broken glass, and to recover the glass.

For the three steps of CRT screen treatment, the employees have access to masks FFP2, FFP3 and/or power air purifying respirator.

Measurement campaigns were performed in nine workshops that treat CRTs in order to assess the levels of occupational exposure and pollution. The nine sites are representative of the overall CRT treatment processes in French. Three of the recycling sites (F, G and I) were dedicated to screen dismantling only, one site handled tube preparation and decontamination only (C), and five recycling sites performed all three treatment operations (Table 1). The various treatment processes and their different steps were studied to evaluate their potential for releasing hazardous substances into the work atmosphere, and to highlight safer practices and riskier practices.

2.2. Sampling, analysis and measurement methods

2.2.1. Characterization of the different CRT components

2.2.1.1. Luminescent powders analysis. Luminescent powders recovered on the front part of used CRTs with a spatula were analysed by induced plasma spectrometry (ICP Varian 720-ES, Australia) after chemical attack of the solid samples in order to evaluate concentrations of various elements in the powder. In the acid attack 1 g

Table 1
Measurement campaign details.

Treatment facilities	Dismantling	Tube preparation	Decontamination processes	
			Splitting of glass	Shredding
A	X	X	X	
B	X	X	X	
C		X		X
D	X	X	X	
E	X	X	X	
F	X			
G	X			
H	X	X		X
I	X			