Environmental Technology
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tent20

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Accepted author version posted online: 28 Feb 2012.Published online: 05 Apr 2012.

Environmental Technology
Vol. 33, No. 22, November 2012, 2547–2551

'ADVANCED TREATMENT TECHNOLOGIES FOR WASTE RECYCLING': SELECTED PAPERS FROM THE 'INTERNATIONAL CONFERENCE ON SOLID WASTE–MOVING TOWARDS SUSTAINABLE RESOURCE MANAGEMENT', 2–6 MAY 2011, HONG KONG SAR

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(*Received 30 September 2011; final version received 19 February 2012*)

The purpose of this work was to achieve a better understanding of the generation of toxic chemicals related to specific processes in scrap computer recycling and disposal, such as thermal recycling of printed circuit boards (PCBs) and the landfilling or dumping of cathode ray tubes (CRTs). Tube furnace pyrolysis was carried out to simulate different thermal treatment conditions for the identification of the by-products and potential environmental risk from thermal recycling of PCBs. The Toxicity Characteristic Leaching Procedure (TCLP) and a column test were used to study the leaching characteristics of lead from waste CRT glass, which is one of the most important environmental concerns arising from the disposal of e-waste. The results indicate that more attention should be paid to the benzene series when recycling PCBs under thermal conditions, especially for workers without any personal protection equipment. The impact of immersion on the leaching of lead from CRT leaded glass was more effective than the impact of washing only by acid rain. Thus when waste leaded glass has to be stored for some reason, the storage facility should be dry.

Keywords: e-waste; cathode ray tube; printed circuit board; environmental risk, recycling

1. Introduction

E-waste is becoming a major environmental concern globally because of the high rate of generation rate and the potential detrimental impacts on the environment caused by the toxic chemicals associated with it. It is reported that e-waste is growing at about 4% per year and has become the fastest growing waste stream in the industrialized world [1]. About 50–80% of the e-waste collected for recycling in industrialized countries ends up in recycling centres in China, India, Pakistan, Vietnam and the Philippines [1], taking advantage of the lower labour costs and less stringent environmental regulations in these countries.

In China, most e-waste has been processed by small companies that lack of pollution control facilities, resulting in serious local environment pollution [2]. A good understanding of the generation, transport and fate of the toxic chemicals related to e-waste is necessary before environmentally sound management of e-waste can be implemented. Although some studies have reported the contamination situation in e-waste recycling areas/clusters in China, these have focused on the surrounding environment such as water, soil and sediment [3–6]. More work is needed to characterize the generation and transport of hazardous materials when recycling and disposing of e-waste.

Scrap computers are one of the most significant kinds of e-waste in terms of volume and complex composition. The emphasis of this work is to achieve a better understanding of the environmental risk associated with specific processes during scrap computer recycling and disposal. The thermal treatment of printed circuit boards (PCBs), which contain brominated flame retardants (BFRs), and the final disposal of cathode ray tube (CRT) leaded glass, including by landfilling and dumping, are the two significant processes resulting in environmental risk. These were selected as the focal points of this work [1,2].

Pyrolysis is a useful chemical recycling technique that has been widely researched as a method of recycling synthetic polymers. Several studies have been dedicated to investigating the products formed during the thermal degradation of PCBs. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethyl) phenol and *p*-hydroxyphenol, as well as bisphenol A, tetrabromobisphenol A, methyl phenols and bromophenols [7–12]. In addition, a study using the US Environmental Protection Agency (USEPA) Toxicity Characteristic Leaching Procedure (TCLP) has shown that lead leached from CRTs produces an average concentration of 18.5 mg/L in TCLP extracts [13]. This exceeds the TCLP regulatory limit of 5.0 mg/L in China, resulting in the waste being classified as hazardous due to its toxicity characteristic.

Existing research on the thermal treatment of PCBs has focused primarily on use of an inert atmosphere such as

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ISSN 0959-3330 print/ISSN 1479-487X online

http://dx.doi.org/10.1080/09593330.2012.668943
http://www.tandfonline.com

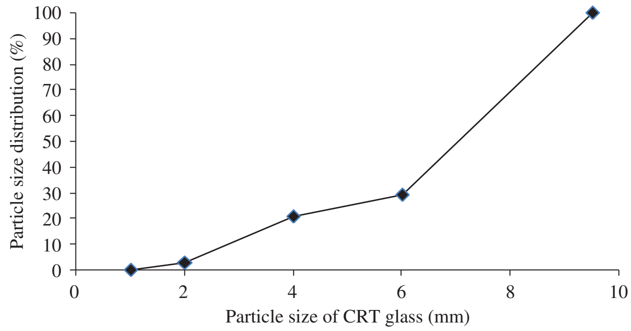

Figure 1. Particle size distribution of CRT leaded glass.

Table 1. Elemental analysis of the used printed circuit board.

Element	wt.%	Element	wt.%
C	50.8436	Pb	1.9781
Fe	10.5379	Br	1.9532
Si	9.9594	Sn	1.6882
Al	5.3611	Mn	1.6093
O	4.1954	Ba	0.3976
Cu	3.4668	Cr	0.1694
Ca	2.8777	Sb	0.1463
Zn	2.3947		

Table 2. Proximate analysis of printed circuit board investigated in study.

Fraction	Ash	Volatiles	Fixed carbon	Moisture
wt.%	70.04	21.08	8.54	0.44

nitrogen and helium. In reality, however, this process is more often carried out in an oxidizing atmosphere. In addition, the long-term risk from the treatment of CRT leaded glass with municipal solid waste (MSW) has not been clarified clearly. The purpose of this study was to achieve a better understanding of the pyrolysis characteristics of PCBs in an oxidizing atmosphere and the long-term risk of CRT leaded glass from scrap computers when landfilled or dumped.

2. Materials and methods

2.1. *Materials*

The PCBs and CRT leaded glass used in this study were obtained from scrap computers collected from residents by the electronic waste recycler TES-AMM in Suzhou, China. The CRT leaded glass was crushed into small pieces with a particle size of diameter 1–9.5 mm; the particle size distribution is shown in Figure 1. The content of PbO in the CRT leaded glass was 22%.

The waste PCBs were cut into pieces about 5 cm × 5 cm in size and then crushed into small pieces of less than 1 cm × 1 cm using a shear crusher. The waste PCBs were analysed by X-ray fluorescence spectrometry (XRF). The elemental composition of the waste PCBs is shown in Table 1 and the proximate analysis results are shown in Table 2.

2.2. *Experiment procedures*

A laboratory-scale fixed bed tubular batch reactor (BR) was used to investigate the pyrolysis characteristics of PCBs in different atmospheres (Figure 2). The experiments were mainly aimed at the recovery and characterization of the different fractions of decomposition products. A typical sample weight in the experimental runs was 80 g. Experimental runs were performed using a purge gas flow of pure nitrogen and oxygen to control the reaction environment and to limit the extension of secondary gas phase reactions. Volatile products emitted during thermal degradation were transferred by the gas flow to a series of cold traps maintained at −20°C through use of a sodium chloride brine/ice bath. Condensable products were recovered at the end of the run from the cold traps for chromatographic analysis. The traps were followed by a gas sampling bag for gas analysis to explore the emission of some gaseous pollutants of concern.

For the leaded CRT glass, a previously described ten-step sequential leaching procedure was used to determine the long-term leachability of CRT leaded glass [14]. The leaching reagents used in every step were unaltered, that is, the TCLP was repeated. This test was to simulate the long-term environmental risk aroused by treatment of CRT leaded glass with MSW. Leaching solution used in this procedure was acetic acid buffer solution with a pH of 4.93.

Another type of leaching test was used to study the leaching characteristic of CRT leaded glass when dumped in the open. The test involved a continuous flow of leaching solution through waste material placed in a column. The leaching columns were made of organic glass composed of polymethyl methacrylate (PMMA).

Two kinds of leaching columns were used in the experiments. One was used to simulate the dynamic leaching scenarios in unsaturated conditions, as shown in Figure 3 (left). The other was used to simulate the dynamic leaching in saturated conditions, with some leaded glass immersed in the leaching solution used, as shown in Figure 3 (right). The leaching solution used was composed of sulfuric acid, nitric acid and other inorganic minerals that was to simulate acid rain with a pH of 4.43.

Qualitative and quantitative analysis of the decomposition products was carried out by gas chromatography/mass spectrometry (GC/MS) methods. Further details are reported elsewhere [8]. Lead concentrations in the leachate were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES, Thermo IRIS, US).

3. Results and discussion

3.1. *Pyrolysis yields of PCBs*

The solid, liquid and gas yields (wt.%) was obtained in PCBs pyrolysis experiments carried out at 275, 325, 400, 500 and 625°C (Table 3). At 275 and 32°C, pyrolysis was incomplete since solid yield was much higher than at the other temperatures, while at 400, 500 and 625°C,

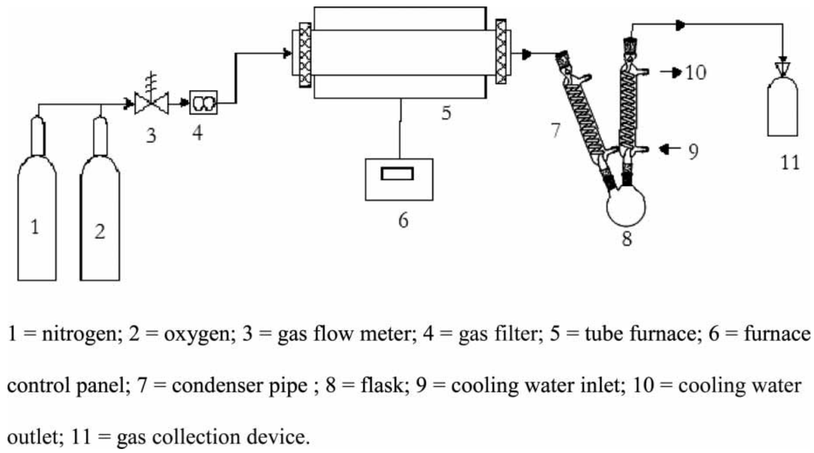

Figure 2. Schematic experimental set-up for tube furnace experiments.

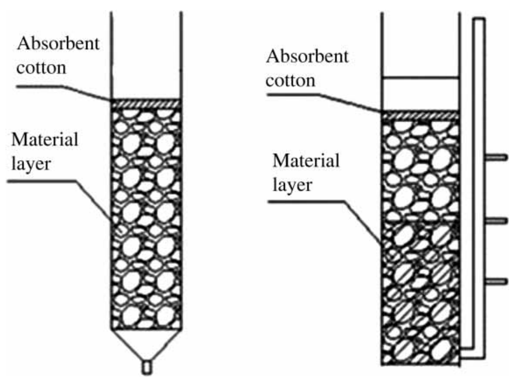

Figure 3. Leaching columns used in dynamic leaching procedure.

Table 3. PCB pyrolysis yields under different atmosphere (wt.%).

Atmosphere	Pyrolysis fraction	Yield (wt.%)				
		275°C	325°C	400°C	500°C	625°C
Nitrogen	Solid	95.0	83.6	79.4	78.4	
	Liquid	2.6	7.4	11.0	12.6	
	Gas	2.4	9.0	9.5	9.0	
Simulated air	Solid	97.6	90.0	75.9	75.1	73.5
	Liquid	1.4	5.9	7.8	8.2	7.3
	Gas	1.0	4.1	16.3	16.7	19.2

the solid yields were approximately equal. Comparing the PCB pyrolysis yields in nitrogen and simulated air ($79N_2 + 21\%O_2$ by volume), pyrolysis above 400°C was more complete in simulated air than in nitrogen; this may result from the oxidation of the PCBs.

3.2. *Degradation products formed in PCB pyrolysis*

The products were identified in the fractions recovered from PCB pyrolysis. HBr, bromphenol and brominated bisphenol-A derivatives were the dominant compounds, a finding comparable with existing research [15–17].

Table 4. Benzene series yields at different temperatures under different atmospheres.

Atmosphere	Substance	Yield (mg/kg)			
		275°C	325°C	400°C	500°C
Nitrogen	Benzene	8.76	28.26	55.72	75.35
	Methylbenzene	0.216	6.04	9.72	21.96
	Dimethylbenzene	0	2.03	8.05	73.63
	Ethylbenzene	0.15	2.63	9.67	8.8
	Styrene	0	0.911	0	0.65
	Total	9.12	39.87	83.16	180.39
Simulated air	Benzene	14.91	2.61	251.4	1402.73
	Methylbenzene	0.99	0.74	258.76	992
	Dimethylbenzene	0.32	0.22	280.53	628.73
	Ethylbenzene	11.51	28.42	752.95	543.86
	Styrene	2.32	2.43	489.69	759.2
	Total	30.06	34.42	2033.31	4326.52

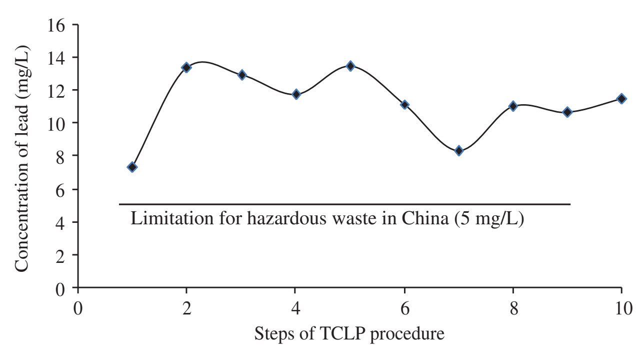

Figure 4. Concentrations of lead leaching from multistep TCLP procedure (solid : liquid = 1 : 10).

However, the benzene series of compounds (including benzene, methylbenzene, dimethylbenzene, ethyl benzene and styrene) were detected in this study but are not mentioned in the previous studies. The yields of the benzene series in the liquid and gas fractions are presented in Table 4. Concentrations of the benzene series in the pyrolysis fractions are much higher at temperatures above 400°C and

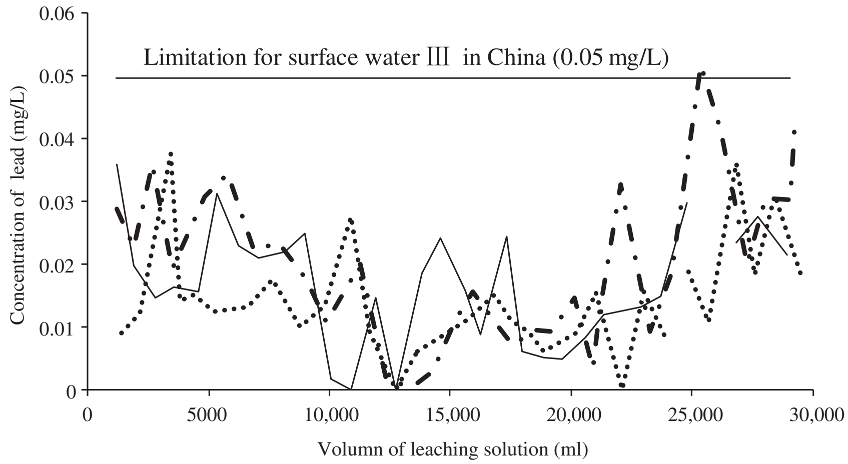

Figure 5. Concentrations of lead leaching from dynamic column test procedure (3 parallel tests).

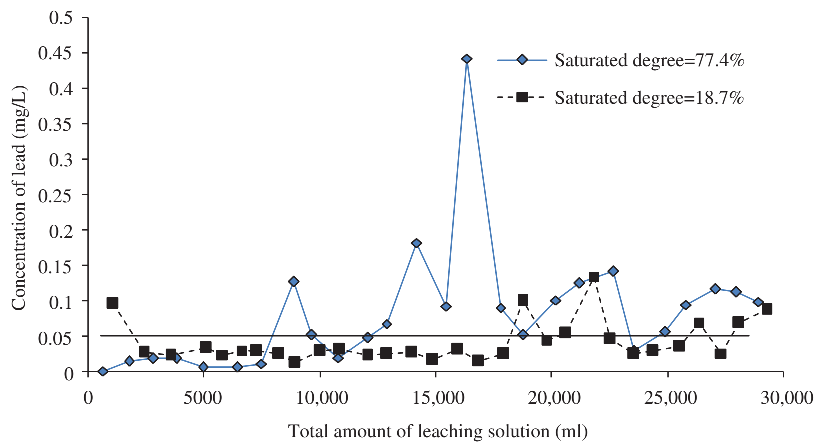

Figure 6. Influence of saturated degree on the leaching of lead from CRT leaded glass.

much higher in simulated air than in nitrogen; this may also be the result of the oxidation of PCBs.

The benzene series are known to be carcinogenic and volatile. This makes it necessary to pay special attention to these substances when recycling PCBs under thermal conditions, especially the baking of PCBs without any personal protective equipment in developing countries.

3.3. Leaching of lead from CRT glass

A multistep sequential leaching procedure was used to determine the maximum leaching ability of lead when landfilled with municipal solid waste. The column test was designed to simulate the leaching characteristics of leaded glass when dumped in the open without any pretreatment. The results are presented in Figures 4–6.

Figure 4 shows that, after a ten-step sequential leaching procedure, the concentration of lead still exceeds the TCLP regulatory limit of 5.0 mg/L in China, which would result in the waste being classified as hazardous due to its toxicity characteristic. However, the total amount of lead leaching from the CRTs only contributes less than 1% of the total in the leaded glass. This suggests the lead would continue to be released for quite a long time at a high concentration, posing a significant environmental risk.

Figure 5 shows that the leachability of lead is really weak when the leaching solution just washes through the void space among CRT glass particles without retention. The concentration of lead is lower than the limit of 0.05 mg/L, which is the standard for surface water III in China, which can be used as the source of drinking water or for fish farming posing little environmental risk.

When the waste leaded glass is dumped outside in the open, water can sometimes be retained for a long time after rain. We therefore explored the influence of the degree of saturation with water in the leaching of lead from waste leaded glass. The degree of saturation was calculated using the ratio of the depth of water and the height of waste materials. The degree of saturation had a significant impact on the leaching of lead (Figure 6). Most of the concentrations were above the limit for surface water III when the saturated degree was 77.4%, while only some were above the limit when the saturated degree was 18.7% and hardly any was above the limit when the saturated degree was 0 as shown in

Figure 5. From these results, we concluded that the impact of immersion on the leaching of lead from CRT leaded glass was more effective than the impact of washing only by simulated acid rain. Thus when waste leaded glass has to be stored for some reason, no water should be allowed to be retained in the warehouse or other storage facility.

4. Conclusions

The environmental risk associated with the recycling and disposal of scrap computers varies with the characteristics of the waste and the disposal scenario. Concentrations of the benzene series of compounds in pyrolysis fractions of PCBs are much higher at temperatures above 400°C and in simulated air than in nitrogen (possibly due to the oxidation of the PCBs). The benzene series of compounds are known both carcinogenic and volatile, making it necessary to pay special attention to these substances when recycling PCBs under thermal conditions, especially their baking by workers without any protection in developing countries.

The risks arising from the landfilling of cathode ray tubes with municipal solid waste (MSW) should not be ignored. Lead would continue to be released for quite a long time at a concentration above 5 mg/L when disposed of with MSW, posing a significant environmental risk to the environment and especially to groundwater. The impact of immersion on the leaching of lead from CRT leaded glass was more effective than the impact of washing only by acid rain. Thus CRT leaded glass should be banned from being landfilled with MSW and managed as hazardous solid waste. When the waste leaded glass had to be stored temporary for some reason, no water should be retained in the warehouse or other storage facility.

Acknowledgement

The work was supported financially by the Environmental Protection Public Welfare Project (201109035) and the National Natural Science Foundation of China (20977056).

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