Journal of Hazardous Materials, 34 (1993) 235–243
Elsevier Science Publishers B.V., Amsterdam

Environmental threats of discarded picture tubes and printed circuit boards

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(Received August 3, 1992; accepted August 12, 1992)

Abstract

Scrap picture tubes (television and monitor tubes) and printed circuit boards were investigated for their potential threat to the environment. First, a qualitative analysis of samples was carried out by atomic emission spectrophotometry. In addition, U.S. EPA Method 3050 (SW-846) and atomic absorption spectrophotometry (AAS) were employed to determine the total contents of heavy metals of interest. Finally, TCLP and AAS were used to evaluate the leaching toxicity of the samples. All color and amber picture tubes tested were found to be hazardous; whereas the green, white and paper-white picture tubes were not. For color picture tubes, lead and zinc concentrations of TCLP are greater than the current regulatory thresholds in Taiwan; while the amber one is hazardous because of its cadmium concentration. The environmental threats of those hazardous picture tubes are ascribed to leaching of heavy metals from the phosphors that are deposited on the inner side of the viewing screen of each picture tube. All tested printed circuit boards also were found to be hazardous as evidenced by their TCLP lead, zinc and cadmium concentrations. The findings in this work show that disposal of discarded TV sets, personal computers, video-game sets, etc. should be managed properly to avoid contamination of soil and groundwater. Several recommendations were made in this regard.

1. Introduction

Improper disposal of discarded television sets, personal computers, video-game sets, etc., is likely to cause soil and groundwater pollution due to the leaching of heavy metals within. Like many industrial countries, each year Taiwan discards several hundred thousand units of used TV sets, personal computers and so on. For color TV sets alone, it was estimated that at least 400,000 units were discarded annually for the past several years [1]. Part of these used home appliances may be reclaimed and recycled by domestic scrap processors. The remainder, that account for a good portion of the total, however, are still disposed of in an uncontrolled manner. In other words, a great quantity of picture tubes (television and monitor tubes) and printed circuit boards in those home appliances are not disposed of properly.

Improper disposal methods currently practiced include: (1) illegal dumping (not limited to "midnight dumping") in an open field, (2) illegal burning in an open field, and (3) disposal in a non-secure landfill. As a result, potential threats to human health and the environment are posed due to the pollution of air, soil and groundwater. An incident of illegal dumping and burning of defective printed circuit boards from a local manufacturer resulted in some 900 students in a nearby primary school being hospitalized or under medication on April 29, 1992 in Taiwan. The R.O.C. EPA immediately ordered the manufacturer to close the plant temporarily and to clean up the dump site of the incident.

The objective of this work was to study whether used/defective picture tubes and printed circuit boards generated by discarded home appliances and the manufacturers would be hazardous. Moreover, this investigation would ascertain whether soil and groundwater pollution problems can be caused by poor management of such wastes. This was determined by the TCLP leachate concentrations of heavy metals of interest.

2. Experimental

2.1 Materials

A total of 12 picture tube samples were studied in this work. Eight (defective 14" display/monitor tubes) were obtained from a local picture tube manufacturer; three were dismantled from used television sets (18" and 20" color ones and a 12" black/white one); and, one sample in powdered form was obtained from a domestic scrap picture-tube processor. The color shown on the viewing screen of a picture tube is of interest because it is used by this author to differentiate one picture tube from another. The displayed colors of the above picture tube samples are detailed in Table 1. To carry out various experiments, all picture tube samples except the Sample PT-1 were first crushed by a hammer, then ground with a mortar if needed.

Three printed circuit boards containing the resistors, capacitors, etc. were also studied in this work. These samples were obtained from the same TV sets mentioned above. The samples were first cut into three or four smaller pieces by a pair of big scissors. Further fragmentation was carried out by a German-made cutting mill (Retsch, Model SM-1).

2.2 Experiments

All samples of picture tube and the printed circuit board from a B/W TV set in triplicate were subjected to a qualitative analysis by atomic emission spectrophotometry (Baird Atomic, Model GX-1). In this test, generally, samples were ground very fine (−325 mesh) to have a better result.

To understand the heavy metal contents of each waste, specimens in triplicate were subjected to an acid digestion (Method 3050, SW-846, U.S. EPA), then analyzed by a Perkin-Elmer atomic absorption spectrophotometer. To evaluate

TABLE 1

List of displayed colors of picture tubes tested

Sample No.	Displayed color
PT1	*
PT2	Amber
PT3	Color
PT4	Color
PT5	White
PT6	Paper white
PT7	Color
PT8	Color
PT9	Green
PT10	Green
PT11	Paper white
PT12	White

* Sample PT1 was obtained, in powdered form, from a scrap picture-tube processor.

the leaching toxicity, the samples were first subjected to Toxicity Characteristic Leaching Procedure (known as the TCLP test) [2]. The leachates were acid-digested further (Method 3010, SW-846) before the determination of metals concentration by atomic absorption spectrophotometry (AAS).

3. Results and discussion

3.1 Picture tubes

Results of atomic emission spectrophotometry indicated that the major constituents of the samples were Si and Na; whereas minor constituents (less than 1%) were Al, Ba, Ca, K, Pb, and Sr. This finding is in accord with the typical glass compositions such as SiO_2, Na_2O, Al_2O_3, BaO, CaO, K_2O, PbO, and SrO.

In this work, results of atomic emission spectrophotometry also suggested this analysis was almost not able to detect the phosphor compositions except for Samples PT6 and PT11. Both PT6 and PT11 have a paper-white color emission. For these two specimens, a trace amount of In element was found. This is due to the fact that the paper-white color is emitted by the trichromatic phosphors blend. This phosphor blend is composed of $InBO_3$:Tb (green), $InBO_3$:Eu (red), and ZnS:Ag (blue). Normally, for a 14" picture tube/display tube, only about 2.26 g of relevant phosphors were deposited on the inner side of the viewing screen. It is possible that such a small amount of phosphors would be lost during sample preparation (crushing and grinding), which would result in the difficulty for detection.

Table 2 depicts the analytical results of pH, total heavy metals content, and TCLP leachate concentration. A review of these results shows high

TABLE 2

Total contents of heavy metals and their corresponding TCLP leachate concentrations for picture tubes tested

	Sample No.									
	PT1		PT2		PT3		PT4		PT5	
Item	A	B	A	B	A	B	A	B	A	B
Ni	20	<0.20	25	<0.20	10	<0.20	40	0.2	45	0.3
Cu	17.5	0.16	5	<0.10	7.5	<0.10	2.5	0.05	<0.05	<0.05
Cr	<0.2	<0.20	<0.20	<0.20	<0.2	<0.20	87.5	0.25	75	0.25
Cd	2.5	<0.20	278.2	0.86	1.4	<0.02	0.05	<0.02	71.65	0.02
Pb	345.6	6.60	96.4	1.50	4,126.5	113.5	10,000	21.3	86.4	1.7
Zn	79.5	1.40	15.9	0.23	506.8	216.3	775.5	32.62	506	0.36
Initial pH	—	10.03	—	9.28	—	7.70	—	9.65	—	9.19
Final pH	—	5.01	—	5.18	—	4.68	—	4.95	—	4.90

	Sample No.								
	PT6			PT7			PT8		
Item	A	B[a]	B[b]	A	B[a]	B[b]	A	B[a]	B[b]
Ni	4.3	<0.05	<0.05	76.9	1.31	<0.05	207.5	0.10	<0.05
Cu	1.1	<0.05	<0.05	3.2	<0.05	<0.05	3.3	<0.05	<0.05
Cr	4.7	<0.05	<0.05	1.0	<0.05	<0.05	2.8	<0.05	<0.05
Cd	4.2	<0.05	<0.05	25.2	<0.05	<0.05	0.5	<0.05	<0.05
Pb	104.3	2.43	0.80	5,930	394.5	303.90	11,790	380.2	128.3
Zn	73.6	0.49	0.15	1,398	50.7	37.40	2,380	45.9	14.4
Initial pH	—	9.80	9.80	—	9.60	9.6	—	9.70	9.70
Final pH	—	5.15	5.18	—	5.20	5.12	—	5.08	5.08

TABLE 2. Continued

Item	PT9 A	PT9 B^a	PT9 B^b	PT10 A	PT10 B^a	PT10 B^b	PT11 A	PT11 B^a	PT11 B^b	PT12 A	PT12 B^a	PT12 B^b
Ni	14.5	<0.05	<0.05	5.2	0.06	<0.05	3.9	<0.05	<0.05	<0.10	0.3	<0.1
Cu	3.4	<0.05	<0.05	10.9	<0.05	<0.05	5.3	0.06	<0.05	<0.05	<0.05	<0.05
Cr	0.3	<0.05	<0.05	1.0	<0.05	<0.05	2.7	<0.05	<0.05	<0.20	<0.1	<0.1
Cd	0.9	<0.05	<0.05	0.6	<0.05	<0.05	20.7	<0.05	<0.05	78	0.05	<0.05
Pb	100	1.65	0.60	81.8	2.19	0.71	100.5	2.30	1.03	106	1.5	0.7
Zn	1,480	2.82	2.07	1,169	2.63	2.26	317.2	0.41	0.17	1,688	0.58	0.33
Initial pH	—	9.80	9.80	—	9.85	9.85	—	9.65	9.65	—	8.90	8.96
Final pH	—	5.15	5.15	—	5.15	5.15	—	5.18	5.18	—	4.96	4.94

Notes: 1. Column A denotes the total content of each heavy metal.
2. Column B denotes the TCLP leachate concentration of each heavy metal.
3. All figures are in mg/L units except pH.

[a] Denotes particle sizes <0.6 mm; [b] Denotes particle sizes in the range of 0.6–2.36 mm.

levels of regulated heavy metals (such as cadmium, lead and zinc) in the original wastes. A similar trend for the TCLP test was observed for the same specimens.

For color picture tubes (PT3, PT4, PT7 and PT8), TCLP leachate concentrations of Pb and Zn indicated that all these specimens would be considered hazardous. A color picture results from a joint effect of red, blue and green phosphors. Compositions for the above phosphors are Y_2O_2S:Eu, ZnS:Ag and ZnS:Cu, Al [or (Zn, Cd)S:Cu, Al], respectively. Thus, phosphors are responsible for a high concentration of Zn in the TCLP leachate. Besides, the leaching of frit seal ($PbO–B_2O_3–ZnO$) would explain high levels of Pb and Zn in the TCLP leachate. Normally, 14" and 20" picture tubes contain 30 g and 55 g of frit seal, respectively.

For the amber (or orange) picture tube (PT2), its leachate concentration of Cd is greater than the regulatory threshold. This is due to a high content (63.2 wt%) of Cd in the phosphor $Cd_5Cl(PO_4)_3$:Mn.

The finely ground sample of mixed picture tubes (PT1) also is considered hazardous because of its Pb concentration. This might be due to the leaching of frit glass in the specimen.

Each display tube with the white picture (PT4 and PT12) showed a high content of Zn in the sample. Normally, blue and yellow phosphors are deposited on the white picture tube. The compositions for these phosphors are ZnS:Ag and (Zn, Cd)S:Ag, respectively. However, none of the heavy metals in the TCLP leachates exceeded the regulatory standards.

Monochrome green monitor tubes (PT9 and PT10) both showed a high content of Zn as well. Again, this is due to its green phosphor of ZnS:Cu, Al [or (Zn, Cd)S:Cu, Al]. None the less, these two specimens are considered non-hazardous as evidenced by their metal concentrations in the leachates.

Further study was conducted to determine the effect of particle size on the TCLP test for PT6 through PT12. The coarser fraction consisted of particles passing through a No. 8 sieve (2.36 mm) but retained on a No. 28 sieve (0.6 mm). The finer fraction represented all particles under 0.6 mm. Results of TCLP tests showed a higher level of metal concentration in the finer fraction for the same picture tube.

3.2 Printed circuit boards

To better understand the potential environmental impacts of discarded printed circuit boards it is worth giving them a general description. A printed circuit board, consists of epoxy resin filled with glass cloth (fiber glass) and a brominated flame retardant. About one-third of the surface for each side is covered with a copper layer (about 70 μm thick), which is partially covered with 8 μm thick of tin lead (60/40). If the finish is bare copper, a thin layer (about 0.5 μm) of alkylimidazole can cover the copper part. Each side is covered with 35 μm of a resin solder mask: acrylic resin (screening process), or epoxy resin (photo process). In a fire, the organic material may emit a number of hazardous substances into the air [3].

TABLE 3

Total contents of heavy metals and their corresponding TCLP leachate concentrations for printed circuit boards tested

Item	Sample No.						
	PCB-NL		PCB-SY		PCB-SP		
	A	B	A	B	A	B[a]	B[b]
Ni	85	0.60	95	0.60	70	1.4	1
Cu	142,695	<0.10	180,144	<0.10	112,500	1.2	<0.05
Cr	216.5	<0.20	6.6	<0.20	50	0.1	0.1
Cd	494.8	12.43	71.4	4.67	30	0.37	0.08
Pb	13,476.7	187.80	51,839.7	58.70	4,200	56	3.6
Zn	28,704.6	30.00	42,831.7	76.30	33,000	280	240
Initial pH	—	7.35	—	6.70	—	7.31	7.31
Final pH	—	4.88	—	4.80	—	5.30	5.30

Notes: 1. Column A denotes the total content of each heavy metal.
2. Column B denotes the TCLP leachate concentration of each heavy metal.
3. All figures are in mg/L units except pH.
[a] Denotes particle sizes in the range of 4–9.5 mm; [b] Denotes particle sizes <4 mm.

The result of atomic emission spectrophotometry showed that the specimen obtained from the 12" B/W TV set contained Fe, Cu, Sn, Si, Al, Ca, Mn, Ag, Ba, Cr, Ni, Zn and Pb. This is in good agreement with another study conducted by X-ray fluorescence [4]. It is believed that Fe and Ni are major compositions for IC components; Cu for conducting loop; Sn and Pb for solders; Ag for electronic contacts; Si for fiber glass; and Ca as an additive for epoxy resin.

The pH, heavy metal content, and TCLP leachate concentrations, for all specimens are shown in Table 3. From this table, it is evident that printed circuit boards in color TV sets contain high levels of Pb, Zn, Cu and Cd. A similar observation was found for the specimen from the B/W TV set except a lower content of cadmium. The results of the TCLP test also suggest that printed circuit boards are all hazardous. For specimens from color TV sets, the leachate concentration for Cd, Pb and Zn were much greater than the present R.O.C. regulatory thresholds. The leachate concentrations of Pb and Zn for specimen from the B/W TV set were also found to be not in compliance with the regulatory standards.

4. Conclusions

The TCLP test has showed that picture tubes for color and B/W TV sets and many display tubes for personal computers are hazardous. Color picture tubes are hazardous due to their Zn and Pb concentrations and the amber picture tube because of the Cd concentration. On the other hand, green, white and paper-white picture tubes would be considered nonhazardous according to present R.O.C. regulatory standards. The color ones are hazardous because of the compositions of their blue and green phosphors and frit seal. Cd in the phosphor is the reason for the amber picture tube being hazardous.

Printed circuit boards from color and B/W TV sets are considered hazardous as well. The reason is that the TCLP leachate concentrations of Cd, Pb and Zn are not in compliance with regulatory thresholds.

Due to the potential threats posed on the environment by the hazardous picture tubes and printed circuit boards, these wastes should be managed properly. Disposal of such wastes or anything containing these wastes in an uncontrolled manner is likely to cause soil and groundwater pollution due to the leaching of heavy metals associated with these wastes.

Recommendations

To control and mitigate the pollution from the discarded picture tubes and printed circuit boards, proper waste management is indeed necessary. To this end, several treatment methods and regulatory measures are suggested:

1. Use finely ground picture tube powders as a supplementary raw material for ceramic products such as floor tiles and the like. In so doing, heavy metals associated with the picture tubes would be very difficult to leach out under natural conditions.
2. Use phosphors containing no heavy metals as a replacement for heavy-metal-containing phosphors currently used for color emission of picture tubes. For instance, using $(Ba,Mg)AlO_3:Eu$ to substitute $ZnS:Ag$ (blue) and $(Ce,Mg)AlO_3:Tb$ to replace $ZnS:Cu,Al$ (green); or even $Y_2O_3:Eu$ (red) to substitute $Cd_5Cl(PO_4)_3:Mn$ (orange or amber).
3. Separate, recover and recycle various metals and the base materials of printed circuit boards. This is technically feasible in the laboratory as has been done by another researcher [4].
4. Employ technologies of solidification/stabilization, incineration, or pyrolysis as alternative disposal methods for the wastes studied, particularly printed circuit boards. Further studies should be conducted in this regard to evaluate the process.

Acknowledgements

This work was supported by R.O.C. EPA under project No. EPA-80-E3H1-09-23. The author would also like to express his gratitude to many of his former colleagues at the Energy & Resources Laboratories, ITRI for their experimental assistance.

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