Evaluation of Heavy Metal Release from the Disposal of Waste Computer Monitors at an Open Dump

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Abstract—Large quantities of waste computer monitors are presently being disposed in Nigeria. As much as 2.4 million units of ‘used’ computer monitors are imported annually into the country. Significant proportions of these imported devices are non-functioning and are never reused, but rather disposed of at open dumps. This study simulated the breaking of cathode ray tubes at open dumps and assessed the total available metals in the cathode ray tube glass; the printed wiring board and plastic components as well as the ability of rainwater to leach and mobilize the metals through batch extraction using weak electrolytes (CaCl₂, Ca(NO₃)₂, and H₂O). The total lead concentration (mg/kg) of the monitor components ranged from 645-2892 (mean 1271±918); 11.1-117 (45.6±44.2) and 3860-4581 (4129±290) in cathode ray tubes, plastic and printed wiring board samples respectively. The chromium concentrations in the components were generally <115mg/kg. The extractable Pb from the cathode ray tubes and printed wiring board failed to pass the established limit for leaching tests such as the toxicity characteristic leaching procedure limits used in toxicity characterization of solid waste (5mg/l). High Pb concentrations, 1.3-12% of the total lead, were leached by the weak electrolytes (53.7±7.74 - 248±33.3mg/l), and this is between 10-50 times the toxicity characteristic leaching procedure limit. The results of this study reveal the dangers of inappropriate management of computer monitors, especially the disposal at open dumps or with municipal solid waste.

Index Terms—Electronic waste, Cathode ray tube, Computer monitor, Nigeria, Weak electrolyte extraction, Waste characterization.

I. INTRODUCTION

Concern has been growing over the management practices for waste electrical and electronic equipment (WEEE) in the developing countries, where these potentially toxic materials are disposed of with municipal solid waste at open dumps and even into surface waters. A personal computer may contain up to 4g of gold and other valuable materials as well as toxic substances such as Pb, Cd, Hg, Cr etc. [1]. Cathode ray tubes (CRTs) are the technology used in most televisions and computer display screens. They are the viewing portion of these devices. The CRT unit is the largest component of a monitor and accounts for approximately 50-62% of the entire monitor [2] [3]. CRTs contain between 8-20% of lead by weight [4] [5] [6] [7] which could be as much as 0.68-2.72kg of lead (an average of 1.18kg of Pb) [8] [9]. Lead is purposely used in the CRT manufacture. For instance, lead in the form of lead oxide is used to provide the necessary shielding from x-rays generated within the operating CRT [10]. CRTs also contain certain small amounts of other toxic materials such as Cd, Ba, Cr etc. In fact, CRTs have been identified as the main source of Pb in electronics [9] [10] [11] [12] as well as one of the largest sources of Pb in the municipal solid waste (MSW) stream [5] [13] [14]. For instance, it was projected that by year 2000, CRTs would contribute 29.8% of all Pb in MSW or 98.7% of Pb from electronics [5] [10]. Management practices for WEEE even in the developed countries have been unsustainable, resulting in the loss of recoverable resources and environmental contamination. As a result, waste management experts are concerned over the release of toxic chemicals from CRTs when discarded to contaminate ground water [3] [15] [16].

Studies aimed at characterizing computer components using leaching techniques have in most cases reported that CRTs (especially color CRTs) consistently fail to pass the toxicity characterization procedure (TCLP) test [4] [5] [17] [18]. For example, the study by Li et al [4] reported a range of 150-500mg/l of Pb in the TCLP extract of computer printed wiring board (PWB) which is between 30-100 times the 5mg/l regulatory limit used in classifying wastes as hazardous. Townsend et al [5] reported a mean of 18.5mg/l in TCLP extracts of CRT of all kinds with a mean of 16.5 mg/l in TVs, 19.3 mg/L in computer monitors (color + monochrome) 22.2 mg/L in color CRTs and 0.03 mg/l for monochrome CRTs. As a result, CRTs have been declared ‘hazardous waste’ and strict regulations have been in place in the United States and other developed countries on the management of CRTs, especially banning the disposal of CRTs in landfills [4] [5] [17] [18] [19]. This combined with the unavailability of adequate and eco-efficient recycling infrastructure for CRTs even in the developed countries is driving the trans-boundary movement of WEEE, especially CRT-containing components into the developing countries. In fact, Zhang et al [20] observed that cost-effective recycling and processing of CRTs remain one of the most challenging
research areas in end-of-life WEEE management.

An estimated 400,000 units of secondhand desktop computers (PCs or monitors) are imported into Nigeria every month [21] [22]. If 50% of the imports are computer monitors, then an estimated 2.4 million units of computer monitor are imported annually (28.8 x 10^3 tonnes using an average weight of 12kg). A large proportion of the imported used electronics are non-functional and are never reused but rather disposed of with municipal solid waste into open dumps, which are most often set afire. CRTs are under high pressure, and the burning at open dumps could result in explosion of the CRTs, dispersing the toxic contents of the CRT.

This study aims at assessing the toxicity of computer monitor components by determining the total metal content of the various components and simulating the bioavailability of the metals at the disposal points by using weak electrolytes to assess the properties of the components and simulating the bioavailability of the metals. This study was carried out in Abia State, Southeastern Nigeria, between July and November 2007, with the aim of predicting and simulating metals release from electronic waste components discarded into the open dumps.

II. MATERIALS AND METHODS

A. Description of Samples

Five (5) waste computer monitors of different brands were obtained and used in this study in order to check variations in material composition that could result from differences in manufacturing processes, batch-to-batch inconsistencies and year of manufacture among others. The waste computer monitors were collected from a Non-Governmental Organization (NGO) that was discarding some of her ‘non-functioning computer donations’ that were donated by charity organizations overseas. Donations for ‘charity’ have been a means of disposing waste electronic devices in the developed countries. The computer monitors were dismantled/disassembled and separated into three parts/components: the CRT, the plastic housing unit and the PWB. The dismantling of the monitors revealed that in some samples, the brand name of the monitor differed from the brand name on the CRT. This supports the ‘outsourcing’ practiced in the electrical and electronic equipment (EEE) industry. Literature indicates a high level of outsourcing in the manufacturing of electrical and electronic equipment in which a brand manufacturer can acquire the various components for electronics manufacture from other manufacturers. These components are then assembled by the brand owner/manufacturer or shipped to another country where a third company undertakes the assembling.

B. Sample Preparation

1) Computer Monitor Plastic Housing

The sample preparation as described in our earlier study of mobile phone plastic housing was adapted and used in this study [24]. However, the plastic housing of computer monitor were thicker and stronger than the plastic housing of mobile phones. Hence, handsaw was used to cut out parts of the front and back housing components. Five replicate samples were collected for each computer monitor. The collected samples were size-reduced using a stainless steel scissors and thoroughly mixed before sample collection for analysis. The samples were analyzed ‘as is’ without washing, the aim being to assess the potential metal release when waste monitor plastic is burnt at an open dump.

2) Computer Monitor CRT

The cathode ray tubes were broken precisely at the neck (slightly below the electron gun) using a heavy hammer and the glass fragments/ phosphor dust collected for analysis. The aim of this method was to assess metal release from a broken CRT at disposal sites. Investigations at sites used for the disposal of electronic waste revealed that in most cases the CRTs break at or close to the neck section. The neck glass of colored CRT contains about 30% Pb by mass; while the panel, funnel and frit glass components contain 0-3%, 24% and 70% Pb by mass respectively [2] [5] [7] [21]. The entire CRT (or even the neck section) was not crushed or size-reduced as the aim was not to determine the total metal concentration of the entire device or a selected section, but rather to assess the pollution potentials of ‘freshly’ broken CRT. Samples were collected from the glass fragment-phosphor mixture released after breaking the CRT and used in this study. In Nigeria, waste monitors and CRTs in general are usually dumped at open dumps. The disposal practices and other waste management activities including those of the waste scavengers result in the breaking of discarded waste CRT. The collected samples were further size-reduced by crushing, but not to definite particle size. Similarly, this study was not aimed at digesting the entire glass components but rather to assess the extractable metals from the waste glass fragments released from the CRT. As a result, further size reduction to a particular mesh size was not carried out.

3) Computer Monitor PWB

The PWB samples were prepared using the method applied in the preparation of PWB of mobile phones as described in our earlier study [24]. The PWB samples were collected from five different portions of the PWB of each computer monitor. This was crushed and mixed thoroughly to make a composite before sample collection.

C. Sample Digestion Procedure

1) Digestion of PWB and CRT samples

The EPA SW 846 Method 3050B had been used in the few studies of waste electronic devices reported in literature [17] [26]. This method was used with slight modifications (especially with respect to refluxing and duration of heating). One-gram sample was digested using 10ml of 1:1 HNO₃ for about 15 minutes and allowed to cool. 5mL of concentrated HNO₃ was then added, and the solution heated for about 30 minutes and allowed to cool. More aliquots of the concentrated acid (5ml at a time) were added and the heating process repeated until no more brown fumes were evolved on heating. This indicates a completion of the digestion process.
Thereafter the sample solution was heated up to 90°C without boiling for close to one hour or until sample solution became about 5ml. The sample solution was allowed to cool and 2ml of deionized water and 3ml of 30% H₂O₂ added, and the heating process continued. However, care was taken at this stage to avoid excessive heating and/or vigorous effervescence in order to avoid losses of sample from boil-offs. The heating was continued until there was no change in the appearance of the sample solution. Where necessary, more of the H₂O₂ was added and the heating continued until no color change was observed. A maximum of 10ml of the H₂O₂ was used for each sample in order to reach complete digestion. On observation of no color change, the sample was heated without boiling until sample solution reduces to about 5ml. After this, the sample solution was allowed to cool, then 10ml of concentrated HCl was added to the digest, and the heating continued at about 95°C for about 15minutes. The sample digest was allowed to cool, filtered into a 50ml volumetric flask and made up to volume with deionized water.

2) Digestion of Plastic Samples

The plastic samples were prepared as described in our earlier report using a 1:1 mixture of H₂SO₄ (98%):HNO₃ (70%) [24].

D. Weak Electrolyte Batch Extraction (CRT and PWB)

Samples from the preparation of the computer monitor CRT and PWB for total metal determination were used in the batch extraction study. 5g sample was extracted using de-ionized water and two weak electrolyte solutions (0.1M calcium nitrate and 1M calcium chloride). This was aimed at assessing the mobility and bioavailability of the metal contents of these devices when discarded. 50ml of the solvent was measured with a calibrated measuring cylinder and transferred into an extraction bottle and 5g sample (1:10 ratio) extracted within a 1-hour period at room temperature (28±2°C). The extraction was carried out manually in order to mimic the effect of storm runoff at the disposal sites during rainfall. The extraction vessels were intermittently shaken to avoid excessive heating and/or vigorous boil-offs. The heating was continued until there was no change in the appearance of the sample solution. Where necessary, more of the H₂O₂ was added and the heating continued until no color change was observed. A maximum of 10ml of the H₂O₂ was used for each sample in order to reach complete digestion. On observation of no color change, the sample was heated without boiling until sample solution reduces to about 5ml. After this, the sample solution was allowed to cool, then 10ml of concentrated HCl was added to the digest, and the heating continued at about 95°C for about 15minutes. The sample digest was allowed to cool, filtered into a 50ml volumetric flask and made up to volume with deionized water.

E. Quality control and Quality assurance Protocol

Quality control/assurance measures were carried out to ensure reliability of results. All glass and plastic ware were appropriately cleaned and soaked in 5% HNO₃ overnight, rinsing severally with de-ionized water before storing clean. Sample preparation tools (hammer, pliers, etc) were appropriately cleaned after each sample to avoid cross contamination. Analytical grade reagents were used. Sample blanks and duplicates were also included. Other quality control/assurance measures applied in our study of the toxicity of waste electronic devices in Nigeria have been described elsewhere [24]. All samples were analyzed in triplicates.

III. RESULTS AND DISCUSSION

A very wide variation was observed in the results obtained in the components studied both for the individual results that were analyzed in triplicates and between the samples. This is indicated in the very high standard deviations of most of the results and the wide range of the data obtained. Results of studies of metal contents of EEE components and toxicity assessment of EEE components using batch extraction techniques have variously reported high variability in the results, even between samples of identical manufacturer and model. This variability has been attributed to differences in particle size composition of the sample, the possible heterogeneity of the electronic components, batch-to-batch inconsistencies in the manufacturing process among others [5] [17] [24].

A. Metal Concentrations in Monitor Component

1) Summary of metal concentrations in computer monitor components

The Pb concentration expressed in milligram per kilogram (mg/kg) ranged from 645±418 to 2892±1335 for CRTs, 11.1±9.2 to 117±48.4 for plastics and 3860±25.0 to 4581±197 for the PWB samples. The mean Cr concentration ranged from 18.4±1.70 to 91.2±79.0 for CRT, 44.6±16.9 to 113±72.0 for plastics and 36.7±2.3 to 47.9±12.2mg/kg respectively. The Pb concentrations of the plastic samples according to sample are 21.4 (monitor A), 11.1±9.20 (geometric mean 8.89) for B; 59.7±13.7 (58.5) for C; 117±48.0 (110) for D and 28.1±6.80 (27.7) for monitor E. A wider variation was obtained in the results of the Pb concentrations of the CRT glass for between and within sample analysis (Table 1).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Range</th>
<th>Median</th>
<th>Geometric Mean</th>
<th>RSE</th>
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<tr>
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<td>D</td>
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<td>E</td>
<td>591-1068</td>
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The Ni concentrations for the CRT and plastic samples analyzed were generally below the detection limit of the method except in the plastic sample of monitor B (66.85mg/kg). The Ni concentrations of the PWB samples showed a very wide variation and are; 14.7mg/kg for Monitor A; 7.0mg/kg for monitor B, 715mg/kg for monitor C and 589mg/kg for monitor D. The Cu concentrations of the CRTs were generally below the detection limit of the instrument (range ND-32.5mg/kg). The Cu concentration in the plastic housing ranged from 47.7±22.3 to 863±69.6mg/kg in the plastic housing and from 871±70.0 to 882±44.0 (range 792 –926) in the PWB samples. The few observed Cu concentrations in the plastic housing could be attributed to exogenous contamination as the samples were analyzed ‘as is’ without washing. The results indicated that the mean
metal concentrations of the PWB samples were generally close with a range of 3860-4581 mg/kg for Pb, 36.7-47.9 mg/kg for Cu in the TV plastic cabinet and a range of 630-4700 mg/kg in the CPU of PCs. The concentrations of metals in the computer monitor components according to sample are presented in Figures 1 and 2 for Pb in CRT and PWB; and Cr in CRT, plastic and PWB respectively.

The overall mean metal concentrations in the samples studied are presented in Table 2. Very high variation is observed in the Pb concentrations of EEE plastic reported in literature. The California Department of Toxic Substances Control (DTSC) reported Pb and Ni concentrations of 2176 mg Pb/kg and 1233 mg Ni/kg in plastic of telephone sets and 4667 mg Pb/kg and 1946 mg Ni/kg in plastics of cell phone [17], while Matsuto et al [25] reported a Pb concentration of 2250 mg/kg in TV plastic cabinet and a range of 249-254 mg/kg in mixed EEE plastic residue. Lincoln et al [26] reported a Ni concentration of 9247 mg/kg in the plastic housing of mobile phones. Similarly, our earlier study of the plastic housing of mobile phones indicated Pb and Cr concentration of 58.3±50.4 mg/kg (range 5.0-340 mg/kg) and 432±1905 mg/kg (5.0-11,000 mg/kg) respectively [24]. Li et al [4] reported a range of 12,000-26,000 mg Pb/kg in the motherboard of personal computers and a range of 630-4,700 mg Pb/kg in the CPU of PCs. The Cr concentration of 58.3±50.4 mg/kg is close to the results of the present study.

The other metals were all below their corresponding TTLC limits. Similarly, the metal levels in the plastic components were all below their corresponding TTLC limits. The European Union has several regulations that aim at controlling the levels of potentially toxic substances in electrical and electronic products and other consumer products. The European Community in the mid-1990s established a regulation to check the amounts of heavy metals in plastics (the European Community Packaging Directive, EC Directive 94/62/EEC). This Directive regulates the total amount of Cd, Cr, Hg, and Pb in plastic materials to <100 mg/kg. In the light of this regulation, all the CRT and PWB samples failed to pass this regulation with respect to Pb. Similarly, one monitor plastic sample exceeded the 100 mg Cr/kg. The recent EU Directive on the Restriction of Hazardous Substances in EEE (RoHS Directive) limits the content of Pb, Hg, and Cr in any homogenous material, parts or subassemblies used in EEE manufacture to 0.1%. All the PWB samples failed to pass this Directive.

### B. Summary of results of batch extraction studies

1) Summary of results of batch extraction studies

The results of the batch extraction study of computer monitor components for extractable Pb and Cu are presented in Figures 3 and 4 respectively. The summary of the extractable metals are shown in Tables 3 and 4 for Pb and Cu respectively. The extraction solvents used were unable to extract Ni and Cr from the samples. This could also be attributed to the very low concentrations of these metals in the samples (see Table 1). In most case, CaCl₂ extracted more metals compared to Ca(NO₃)₂ and H₂O. For example, CaCl₂ extracted Pb from all the CRT and PWB samples, whereas Ca(NO₃)₂ and H₂O could extract Pb from 1 and 4 CRT samples, and 3 and 1 PWB samples respectively (Table 3). Ca(NO₃)₂ and H₂O were unable to extract Cu from the CRT samples probably as a result of the very low concentration of Cu in the CRT samples (see Table 1).
The extraction of Pb from the CRT glass followed the order CaCl₂ > H₂O > Ca(NO₃)₂ while the extraction of Pb and Cu in the PWB samples followed the order CaCl₂ > Ca(NO₃)₂ > H₂O. In summary the mean extractable Pb from the samples ranged from 132±206mg/l (H₂O) to 146±140mg/l (CaCl₂) for CRT; and 53.7±7.74mg/l (Ca(NO₃)₂) to 248±33.3mg/l (CaCl₂) for PWB (Table 3).

The results of batch extraction of metals from the samples indicate that all the extractable Pb concentration exceeded the TCLP and SPLP limit for Pb (5mg/l), while the extractable Cu concentrations where all below the TCLP and SPLP limit for Cu (25mg/l). The amount of metal extracted from the samples was calculated as the extraction factor (EF) (Tables 3 and 4). The EF for Pb was above 10% in CRT samples (11.5% for CaCl₂ and 10.4% for H₂O) and 1.3-6% for PWB (1.3% for Ca(NO₃)₂ and 6.0% for CaCl₂). The EF for Cu were generally <2% in PWB samples. Ca(NO₃)₂ and H₂O could not extract Cu from CRT samples. CaCl₂ extracted a mean Cu concentration of 0.71±0.83mg/l with an extraction factor of 3.2%. Several batch extraction procedures are in use in the toxicity assessment of solid wastes. These include the toxicity characterization leaching procedure (TCLP), which simulates the conditions in an anaerobic landfill, and makes use of acetic acid, and the synthetic precipitation leaching procedure (SPLP), which is similar to the TTLC but uses a simulated acid rainfall (a mixture of H₂SO₄ and HNO₃).

2) Comparison of batch extraction studies with established limits

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Townsend et al [23] conducted a leaching study of computer and TV CRTs using the TTLC and SPLP methods and reported a Pb concentration in the extracts of 2.18mg/l and 413mg/l for the SPLP and TCLP procedures respectively. A lead concentration of 1.0-9.9mg/l (for SPLP) and 157-413mg/l (for TCLP) were also reported for shredded printed circuit boards [23]. These results compare well with the result of the present study (ND-296mg/l). However, the results of Townsend et al, [23] and the present study indicated that the batch extraction methods adopted could extract little or no Cu, Ni, and Cr from the PWB samples. Similar batch extraction studies have also indicated that in most cases, the EEE components investigated fail the TCLP test for Pb more often [16] [26] [27]. Townsend et al [3] reported Pb concentrations in leachates (TCLP) of 13-95mg/l (mean 47.7mg/l) for Pb and 0.02-0.9mg/l for Cu after the TCLP-study of nine computer monitors, and 12-43mg/l (mean 29mg/l) for Pb and 0.01-010mg/l for Cu in color TVs. All computers and TVs failed the TCLP test for Pb.

C. Environmental Consequences of Inappropriate Management

CRTs pose major challenges in electronic waste recycling
due to their volume, higher recycling costs, and disposal restrictions, especially in the developed countries [9]. In the developing countries, the main constraints are the absence of effective take back system (implementation of extended producer responsibility, EPR), and unavailability of formal recycling facilities or even sound solid waste management infrastructures [21] [28]. In Nigeria and other developing countries, these hazardous materials are disposed of with municipal solid waste into open dumps and surface water bodies, often used for domestic purposes. When disposed through these routes, toxic substances can leach and eventually contaminate surface and groundwater.

Options in the sound management of waste CRTs include reuse, remanufacturing, feedstock recycling and landfilling [29] [30]. Reuse options for CRT of waste computers are presently available. For instance, the CRTs of waste computer monitors can be regunned and then used in the manufacture of TVs of local brands and screens for video games [31]. Recycling CRTs from computer monitors is necessary in achieving sustainable development [20] [32] [33]. The two technologies currently available for CRT glass recycling are glass-to-glass and glass-to-lead recycling. To date, the preferred process for the disposal of CRT glass is to recycle it into new CRT glass [9]. Lee et al [29] noted that landfilling and incineration are not accepted as option in the management of waste computer monitors. This is because when landfilled, the lead they contain could pose a threat to the environment, due to the acidic leaching of high concentrations of heavy metals to the ground water [33]. Similarly, considering that the components contain brominated flame retardants in the plastic and PWB components, the incineration process of these materials could produce dioxins and furans in the gas mixture, which are indeed very toxic compounds. This cocktail of toxins could be transported long distances in the fly ash particulates (which could be inhaled) and significant quantities left in the ash and cinder. The results of this study indicate that storm runoff could easily wash these toxins to contaminate surface and ground water sources.

IV. CONCLUSION

The results of this study provide valuable information on the leachability/mobilization of heavy metals especially Pb from broken computer monitors at waste disposal points. Of much concern is the observation that deionized water extracted as much as 10% of the lead content of the CRT glass indicating the extent storm runoff could mobilize toxins from inappropriately disposed CRTs. The extractable Pb concentrations from the components exceeded the SPLP and TCLP limits and this is consistent with other studies, where Pb among other metals consistently fails these test in most electronic components. The results of this study confirm the toxicity of waste CRTs. We therefore recommend the adoption of sound management practices in the disposal of CRTs at the global level. Appropriate policy measures should be adopted to check the increasing trans-boundary movement of electronic wastes into the developing countries.

REFERENCES


