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Gianini Kroes

[MANAGEMENT OF WASTE CRTS IN BRAZIL]

The replacement of CRT devices with newer technologies such as LCDs and Plasma Screens has resulted in a large amount of waste CRTs. The sound disposal of these waste CRTs is discussed for Brazil.

SUMMARY

CRT televisions and computer monitors have been rapidly replaced by devices with newer technologies such as LCDs and plasma screens. This replacement has resulted in a vast amount of waste CRTs. CRT disposal is of environmental concern because of their toxic components. Brazil has the reverse logistic recycling procedure for e-waste in place, however waste CRTs are not processed in an environmentally and economically sound manner. The objective of this study was a literature survey on the global processing of waste CRT in order to improve the processing of waste CRTs in Brazil. The first chapter discusses the elemental composition of CRTs and the adverse environmental effects resulting from incorrect disposal. The most abundant toxic compound in CRTs is lead. Global CRT disposal strategies are presented in the sequential chapter. The last chapter discusses the current disposal strategies of CRTs in Brazil and proposes a different route, based on global strategies. The production of lead from CRT funnel glass using hydrometallurgy is recommended. This process is environmentally and economically sound.

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TECHNOLOGICAL CHARACTERIZATION OF CRT MONITORS

Cathode ray tubes (CRTs) were an integral part of computer screens and television monitors. The advancements in technology, however, have resulted in CRT devices being replaced by newer technologies such as liquid crystal displays (LCDs) and plasma screens. Presently, CRTs are obsolete and are considered waste. Figure 1 depicts a CRT, removed from its casing.

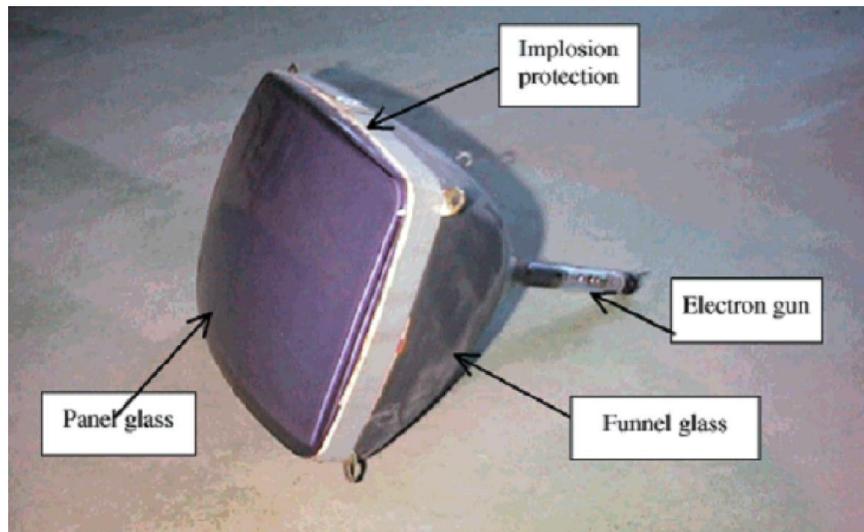


FIGURE 1 THE APPEARANCE OF A COLOR CRT[3]

Figure 2 depicts a television set with the cover removed and shows the CRT attached to a circuit board.



FIGURE 2 A TELEVISION SET WITH COVER REMOVED[4]

Television screens and computer monitors containing CRTs are considered hazardous waste because of the various toxic components. CRT panel glass is coated with heavy metals and funnel glass contains a high amount of lead (Pb). In addition, the batteries and printed circuit boards (PCBs) also contain Pb. The plastics contain flame-retardant bromine and the television/computer monitors can even contain mercury [5]. These devices also contain valuable metals such as copper, iron, silver and gold within the wires and PCBs [5]. Proper disposal and recycling of these CRT containing devices is necessary to preserve the environment and doing so can even be profitable.

On average, two thirds of the weight of a television set and/or computer screen is composed of the CRT (Figure 3). The CRT is 85 % glass; this glass is further divided into panel glass (65%), funnel glass (30%) and neck glass (5%) [6]. Neck glass is the glass that encapsulates the electron gun(s). The first types of CRTs were monochrome; as technology advanced these were replaced by color CRTs. The main differences between color CRTs and monochrome CRTs are:

- A monochrome CRT contains a single electron gun while a color CRT contains three.
- A monochrome CRT has a single (white) phosphor while a color CRT has three; red, green and blue.
- A monochrome CRT does not contain frit (Figure 5).

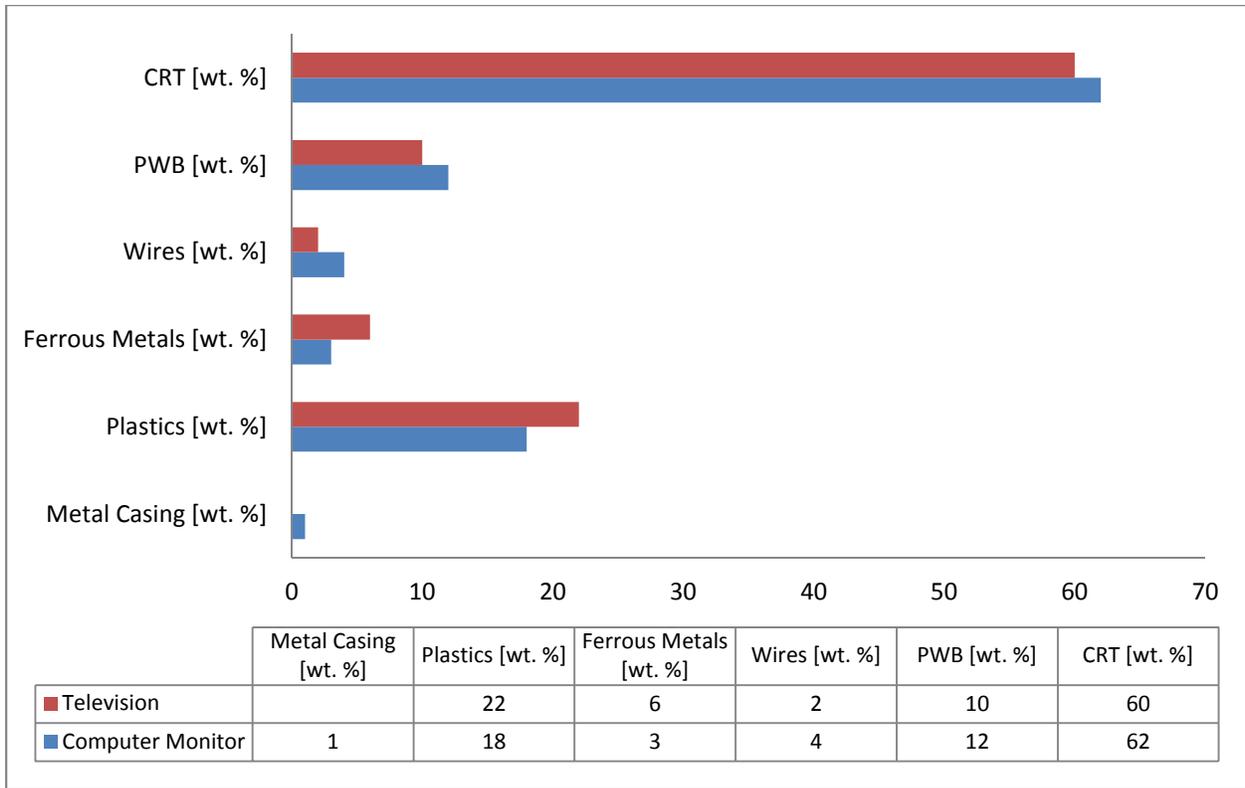


FIGURE 3 AVERAGE PARTS COMPOSITION OF COMPUTER MONITORS AND TELEVISIONS BY WEIGHT [7]

Most monochrome CRTs have already been replaced by color CRTs, therefore this report will focus more on color CRTs. Color CRTs are more advanced and contain more harmful compounds than monochrome CRTs, such as additional phosphors and frit seals [6]. This implies that stricter environmental regulations should be enforced when disposing of color CRTs, in comparison to monochrome CRTs. This also implies that the sensible disposal strategies used for color CRTs are applicable to monochrome CRTs but not vice versa. Figure 4 shows the schematic representation of a color CRT.

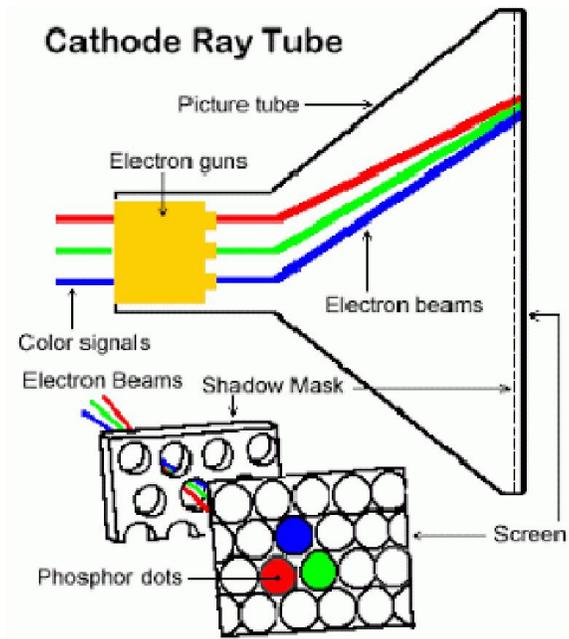


FIGURE 4 SCHEMATIC REPRESENTATION OF A COLOR CRT [8]

CHARACTERIZATION OF CRT GLASS [6]

The glass used in CRTs needs to possess certain qualities; these are X-ray absorption, electric resistivity, a high light transmittance and a suitable thermal expansion. The thermal expansion is required for the glass to be compatible with the sealing metal and the other glass present in the screen. Color CRTs use four different types of glass, each produced according to their specific technical requirements. These are:

1. Panel glass - homogeneous barium-strontium glass of a greenish-blue color.
2. Funnel glass - lead glass.
3. Neck glass - very high lead content glass.
4. Frit glass - a low melting lead glass, only present in color CRTs

Lead is required for its X-ray shielding properties. However, a high lead content causes browning of glass. This is inconsequential for neck and funnel glass but browning of panel glass will adversely affect the visibility of the screen. Due to this, panel glass is mostly leadless and the X-ray absorption properties are a result of the amount of barium (Ba), strontium (Sr) and zirconium (Zr) present. Alkali oxides can also cause browning. To mitigate this effect more than one alkali oxide is integrated in panel glass; typically sodium (Na) and potassium (K) are used. Antimony (Sb) is added during glass production to prevent bubble formation and titanium (Ti) is added to panel glass to prevent solarization. Nickel (Ni) and cobalt (Co) are added to tint the panel; this tint is required to give panel glass the correct light transmission. Table 1 presents the oxide content of the different types of glass found in television screens and computer monitors.

Panel and funnel glass are coated with various chemicals. The inner surface of (color) CRT panel glass contains four coatings, these are:

1. A mixture of carbon and surfactants, producing a carbon black and clear stripes layer.
2. Three fluorescent color powders, called phosphors, a layer rich in heavy metals.
3. A wax-like layer (lacquer) to smooth out and seal the fluorescent powders in place.
4. An aluminum film, to enhance the brightness.

The funnel glass contains two coatings, these are:

1. A non-reflective black graphite coating on the inner surface of the glass; this coating is a good electrical conductor [3].
2. An external layer of carbon black paint.

TABLE 1 THE OXIDE COMPOSITION (WT. %) OF COLOR CRT GLASS [6]

Oxide	TV + PC Panel	TV + PC Funnel	Neck
SiO₂	61.23	56.72	50.00
Al₂O₃	2.56	3.42	1.00
Na₂O	8.27	6.99	2.00
K₂O	5.56	5.37	10.00
CaO	1.13	3.12	2.00
MgO	0.76	2.02	0.00
BaO	10.03	4.03	0.00
SrO	8.84	1.99	0.00
Fe₂O₃	0.10	0.11	0.00
Sb₂O₃	0.30	0.30	0.30
CoO	0.02	0.00	0.00
TiO₂	0.35	0.19	0.00
ZrO₂	0.91	0.24	0.00
ZnO	0.18	0.22	0.00
PbO	0.02	15.58	34.00
NiO	0.03	0.02	0.00
Total	100	100	100

The elemental composition of the coatings has been determined with XRF and is presented in .

Table 2.

TABLE 2 THE ELEMENTAL COMPOSITION OF THE FLUORESCENT COATINGS FOUND IN COLOR CRTS[3]

Element	Content (wt. %)	Element	Content (wt. %)
F	1.6	NiO	0.65
Na₂O	2.6	CuO	0.1
Al₂O₃	11.3	ZnO	28.2
SiO₂	2.8	Ga₂O₃	0.016
P₂O₅	0.082	Y₂O₃	9.5
SO₃	37.4	CdO	3.9
Cl	0.019	I	0.019
K₂O	0.47	BaO	0.51
CaO	0.17	La₂O₃	0.013
V₂O₅	0.04	Ta₂O₅	0.35
Cr₂O₃	0.034	WO₃	0.59
MnO	0.027	PbO	0.13
Fe₂O₃	0.069		

THE HEALTH RISK INVOLVED WITH IMPROPER CRT DISPOSAL[9]

This sub-chapter will mention the various elements found in CRTs and the health risks involved with exposure.

Antimony (Sb): Used as a melting agent during CRT glass production and is also found in plastic computer housing and solder alloy. Sb is classified as a carcinogen and prolonged inhalation of high concentrations can cause stomach pain, vomiting, diarrhea and stomach-ulcers.

Barium (Ba): Present in CRT glass and CRT gutters in vacuum tubes. Short-term exposure causes brain swelling, muscle weakness, heart damage, liver damage and spleen damage.

Brominated flame retardants (BFRs) such as: *polybrominated biphenyls (PBBs)*, *polybrominated diphenyl ethers (PBDEs)* and *tetrabromobisphenol (TBBPA)*: These are used as flame retardants in plastics and printed circuit boards. Combustion of BFRs emits toxic vapors that can induce hormonal disorders.

Cadmium (Cd): Used in the phosphors. Cadmium irreversibly affects human health, particularly the kidneys.

Chlorofluorocarbons (CFC): Used in cooling units and insulation foam. These substances adversely affect the ozone layer, resulting in greater incidence of skin cancer.

Lead (Pb): Found in CRTs, solder, PCBs and cables. Lead can cause blood disorders and damage to the brain, nervous system, kidneys and the reproductive system. Low concentration exposure can induce brain and nervous system damage in fetuses and young children. Accumulation of lead in the environment has both immediate and delayed adverse effects on human health.

Mercury (Hg): Found in the PCB. Exposure can cause damage to the brain, kidneys and fetuses.

Nickel (Ni): Present in CRTs, computer housing and PCBs. Exposure can cause allergic reactions, bronchitis, reduced lung function and lung cancer.

Polyvinyl chloride (PVC): Present in cables and plastic housing. Incomplete combustion of PVC produces hydrochloric acid, which can cause respiratory problems.

The elements present in the coatings (.

Table 2) are predominantly heavy metals and can cause pollution problems when disposed of incorrectly [3]. At the time of writing, no literature was found regarding the environmental effects of the coating as a result of improper CRT disposal.

In general, the most polluting component in CRTs is lead. On average, color CRTs contain 1.6 to 3.2 kg of lead [10]. In addition, the solder found in PCBs contains approximately 50 g of tin-lead per m², with a tin to lead ratio of 60:40 [10]. The next sub-chapter discusses lead leachability.

LEAD LEACHABILITY (TCLP)[11]

Lead is present in funnel and neck glass as lead oxide (PbO). The lead leachability of different types of CRT-containing devices has been determined by Musson and coworkers. The tests were done in accordance with the Environmental Protection Agency's (EPA) toxicity characteristic leaching procedure (TCLP). The permitted upper limit of lead leachability is 5.0 mg/L. However, the results indicated an average leachability of 18.5 mg/L. This classifies CRTs as hazardous waste. The TCLP testing procedure was designed to predict worst case scenarios, resulting in potentially inaccurate results for actual landfills. The lead content of the glass used is presented in Table 3.

TABLE 3 LEAD CONTENT BY WT. % OF VARIOUS TYPES OF CRT GLASS USED BY MUSSON FOR THE TCLP LEAD LEACHABILITY TESTS [11]

Glass	Color CRT [%]	monochrome CRT [%]
Panel	0-3	0-3
Funnel	24	4
Neck	30	30
Frit	70	n.a.

Frit has the highest amount of lead and is presented in Figure 5; monochrome CRTs do not contain frit.

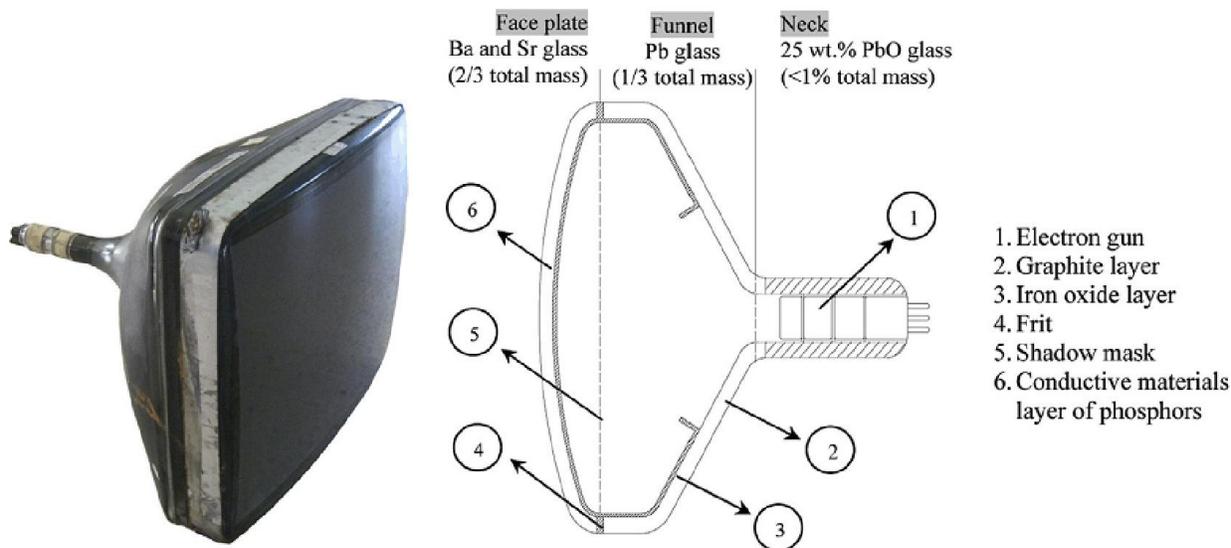


FIGURE 5 ANATOMY OF A COLOR CRT [12]

The average glass distribution of the CRTs tested by Musson was as follows:

- 4.9 % neck
- 25.2 % funnel
- 69.9 % face

The extraction fluid used during the leachability test consisted of glacial acetic acid, water and sodium hydroxide (pH 4.93 ± 0.5). Table 4 presents the leachability results.

TABLE 4 LEACH LEACHABILITY RESULTS OF VARIOUS CRTS BY MUSSON, WITH 5 MG/L AS THE MAXIMUM ALLOWED LIMIT [11]

Category	No. of samples	No. of exceeding regulatory limits	Av. Leachable lead conc. [mg/L]
All CRTs tested	36	21	18.5
Television	10	4	16.5
Computer monitors	26	17	19.3
CRTs - 1988 and before (color CRTs)	13 (10)	7 (7)	13.5 (17.5)
CRTs - 1989 to 1993 (color CRTs)	11 (8)	6 (6)	29.5 (40.6)
CRTs - 1994 to 1998 (color CRTs)	12 (12)	8 (8)	13.9 (13.9)
Color CRTs	30	21	22.2
Monochrome CRTs	6	0	< 1.0

The results indicate that all the monochrome CRTs have a negligible (<1.0 mg/L) lead leachate concentration. Due to this, monochrome CRTs can be considered solid waste only and not hazardous solid waste. On the other hand, color CRTs should be considered hazardous and as a result, require specific disposal protocols.

In addition to the average lead leachate concentration of CRTs, Musson also looked at the effect of sample heterogeneity and particle size on the leachate concentrations.

SAMPLE HETEROGENEITY

The sample heterogeneity tests resulted in peculiar results for the frit glass. Frit glass contains both leaded glass (frit seal) and leadless glass. The leachability was determined for two samples of the frit seal, which resulted in lead concentrations of 492 and 575 mg/L. When the leachability test was performed on the glass just adjacent to the seal, the concentrations were 10.8 and 13.3 mg/L.

PARTICLE SIZE EFFECT

The smaller particle size glass showed a more significant leachability; the authors accredit this to the greater surface area of the smaller particles. Musson also states that this measurement may reveal the inability of the leaching solution to penetrate an intact CRT. This indicates that lead leaching can possibly be prevented when entire color CRTs are disposed in landfills.

CRT DISPOSITION

The TCLP procedure was designed to predict worst case scenarios. The leachability of lead is correlated with the pH of the leaching solution. Realizing the same TCLP acidity in an actual landfill remains questionable. To conclude: monochrome CRTs can be considered solid waste only, while color CRTs should be classified as hazardous solid waste in accordance with the TCLP results. As a result, special (costlier) disposal protocols should be implemented when discarding color CRTs. The higher cost associated with color CRT disposal may provide more incentive to recycle and/or re-use color CRTs.

LEAD LEACHABILITY USING MSW [10]

Follow up research was performed on the same (funnel) glass of the 30 color CRTs mentioned in the previous study, with municipal solid waste (MSW) leachate as leaching fluid. This research was carried out in order to obtain more realistic results. In addition to the glass, lead solder-containing printed wire boards (PWBs) were also subjected to the leaching tests. The PWBs, also called printed circuit boards, originated from the motherboards of the computers. The TLCP uses an acidic

extraction fluid (acetic acid) and is performed at a pH value of around 4.9. The acidity of a landfill, in general, is more neutral. The California’s waste extraction test (WET) and the synthetic precipitation leaching procedure (SPLP) were also performed. The summary of the leaching test results is presented in Table 6.

Table 5 summarizes the protocols of these tests. The summary of the leaching test results is presented in Table 6.

TABLE 5 LEACHING TEST PROTOCOLS USED BY JANG [10]

Standardized leaching tests				
	TCLP	WET	SPLP	MSW leachate
pH of leaching solution	4.93 ± 0.05 (acetic acid and sodium hydroxide)	5.00 ± 0.05 (citric acid and sodium hydroxide)	4.20 ± 0.05 (sulfuric and nitric acids)	7.6
No. of CRTs and PWBs used	30/10	30/10	30/10	30/(20 or 10) ^a
Solid to liquid ratio (g of waste to L of solution)	100 g/2 L	100 g/1 L	100 g/2 L	100 g/2 L
Extraction period	18 ± 2h	48 h	18 ± 2h	18 ± 2h

^a Set A used 10 PWBs from 2001 and Set B used 20 PWBs from 2002.

TABLE 6 LEACHING TEST RESULTS BY JANG [10]

Standardized leaching test					
		MSW leachate	TCLP	WET	SPLP
Initial pH		7.60	4.93	5.00	4.20
CRT	avg. Pb conc. (mg/L)	4.06	413	350	2.27
	avg. final pH	7.67	5.08	5.07	9.73
PWB	avg. Pb conc. (mg/L)	2.23	162	3.15	0.95
	avg. final pH	7.69	4.97	5.14	7.70

The final lead concentration in the leachate using MSW as the extraction fluid is 4.06 mg/ L for CRT funnel glass and 2.23 mg/L for PWBs. For CRTs and PWBs to be classified as hazardous solid waste, these values have to exceed 5.0 mg/L. The TCLP and WET tests indicated that CRTs and PWBs are

hazardous. However, these results are unlikely to represent an actual landfill. Part of this is due to the more neutral pH of the MSW liquid. These tests, however, don't take into account how lead will react with other compounds already present in the landfill or the effect of the frit seal on the concentration. Although the TCLP can overestimate the toxicity of color CRTs, the MSW leachate can underestimate it. The safest option is to utilize waste CRTs by recycling or re-use instead of landfilling.

RESEARCH OF THE STATE OF KNOWLEDGE ABOUT RECYCLING OF MONITORS

This chapter summarizes the global management strategies involved with CRTs; conventional end-of-life (EoL) applications of out-of-use CRTs and the research on alternate uses of waste CRTs.

GLOBAL APPLICATIONS OF WASTE CRTS [7]

The incorrect disposal of waste electrical and electronic equipment (WEEE) is detrimental to the environment. The European Union has implemented certain directives to prevent this. The WEEE Directive is designed to increase the recycling and re-use of e-waste, minimizing the amount of e-waste that goes into landfills and/or incinerators. The restriction of hazardous substances (RoHS) Directive is more precautionary; it limits the use of toxic substances such as Pb, Hg, Cd and brominated flame retardants in the production of equipment. The European Union has also adopted extended producer responsibility (EPR). EPR holds the producers responsible for the recovery, recycling, reprocessing and disposal of electronics. This means that consumers can always return their e-waste to the producer. The funds required for the EoL of these devices is included in the sales price.

Product stewardship (PS) is the alternative to EPR, practiced in the USA. PS holds the person (designer, producer, vendor, retailer or consumer) in possession of the device, responsible for minimizing the environmental impacts of the product. EPR has proven to be the superior alternative because:

- EPR obliges producers to design for the environment (DfE), because the correct disposal of the product is their responsibility. PS on the other hand does not prevent the usage of toxic materials.
- Producers are always responsible for the EoL of EEE under EPR. Under PS, the EoL responsibility is always transferred to the new proprietor of the device. Due to this, export of the product is “encouraged”.

As a result, products produced under PS are more likely to be toxic and exported. It was observed for the USA in 2002 that 80% of the collected e-waste was exported.

Other factors that encourage e-waste export from developed countries are:

- The landfilling/ incineration of CRTs is often restricted or banned domestically, due to their toxic contents. This means that the disposal cost of CRTs are high and export is inexpensive in comparison.
- Recycling facilities are unwanted in most neighborhoods due to risks involved with the toxic material being processed. With the bans on landfilling and incineration, storage and export become the only viable options.
- Recycling of CRTs is, in general, not a profitable process. However, over-seas recycling costs less than domestic recycling. Glass-to-glass CRT recycling in the USA is about \$0.50 per pound while it's \$0.05 in China. This difference is a result of lower labor costs and different work practices.
- The ignorance of the toxicity of CRTs in developing countries and the lax enforcement of existing laws against hazardous waste disposal/import make export to these countries reasonably easy. Furthermore, the outdated models from developed countries are often the latest models for the developing countries and are therefore coveted.

The Basel Convention was formed in order to prevent the export of hazardous waste. However, e-waste is still being exported through unsanctioned routes. To conclude: Europe has developed recycling technologies due to its legislations while the U.S.A. exports most of its e-waste instead of utilizing sound disposal procedures.

CONVENTIONAL END OF LIFE OPTIONS FOR CRTS [7]

The EoL options for CRTs can be categorized as:

- Re-use – re-use as is, repair and re-use, and remanufactured and re-use
- Recycle
- Landfill
- Incinerate (with and without energy recovery)

These options are presented in Figure 6.

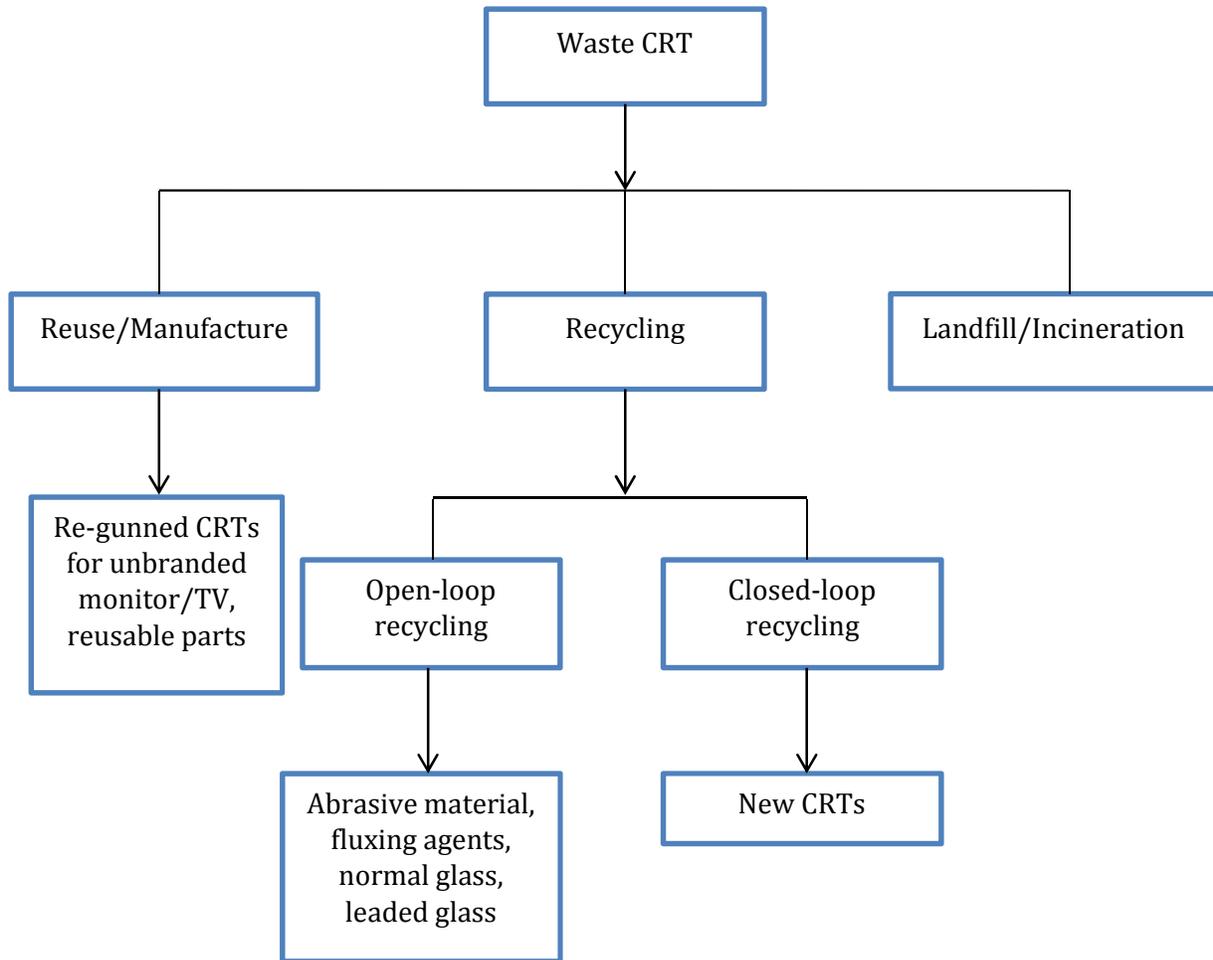


FIGURE 6 END OF LIFE OPTIONS OF WASTE CRTS [7]

RE-USE

Working CRTs can still be used and do not need to be discarded. Faulty CRTs can be repaired to working order and retained. A common repair practice is the replacement of the electron gun. These repaired CRTs can be rebranded and/or used in video game consoles. However, these methods only delay the problem associated with CRT recycling/disposal and do not offer a permanent solution. Non-functional CRTs can be harvested for parts, in order to repair other CRTs. Disassembly of CRTs is often performed manually, but the process is gradually becoming automated. Automated disassembly is hindered by:

- Correct product identification
- A wide variety of parts within a single product type; different parts used by different manufacturers

- Altered configurations as a result of consumer repairs
- Jammed, missing and damaged components

Repair is uncommon in the developed world, because the repair costs are often comparable to the cost of new and/or improved equipment.

RECYCLING

The recyclable parts from television sets and computer monitors are:

- Plastics - high impact polystyrene (HIPS), acrylonitrile-butadiene styrene (ABS), and polycarbonates (PC).
- Metals - precious metals like copper, silver and gold usually present in PWB.
- Glass - both leaded and leadless.

Other materials that can be harvested are: conductive coatings, low carbon steel shadow masks and luminescent materials. The electron guns and metal frames are recycled in metal smelting plants. There are two recycling options for CRT glass. These are glass-to-glass (closed loop) recycling and glass-to-lead (open loop) recycling.

GLASS-TO-GLASS

Glass-to-glass recycling is/was preferred because this method uses waste CRT glass in the production of new CRT glass (closed loop recycling). The glass (both funnel and panel) is separated from the non-glass components and ground into cullet. This cullet is then adjusted to the right composition and used for the production of new CRT glass. Glass-to-glass recycling is labor intensive because of the manual separation of the various parts. The following steps are required:

- Separate the CRT from the television or monitor
- Remove the non-glass from the exterior of the CRT
- Release the vacuum from the CRT
- Crush the CRT and remove the non-glass components
- Remove the phosphor
- Prepare a uniform cullet and separate lead glass from leadless glass (optional)

The lead and leadless glass can be separated post-crushing by sensor guided automated sorting. Alternatively, prior to crushing, the funnel and panel glass can be separated by sawing or heated/laser cutting. The phosphor is removed and discarded as hazardous waste. Glass-to-glass

recycling limits the amount of toxic waste that goes into the environment and it also reduces the costs involved with obtaining new raw materials. However, commercial CRTs have been out of production since 2003 and as a result, glass-to-glass recycling is difficult to realize today[13].

GLASS-TO-LEAD

Glass-to-lead recycling produces lead from CRT leaded glass (open-loop recycling). The glass is used as a fluxing agent during lead smelting and the products are metallic lead and copper. The process starts by separating the CRT from the casing. Afterwards, the CRT is processed in the furnace. Glass-to-lead recycling is less intricate than glass-to-glass recycling and is therefore often automated. The automated environment is safer for the workers, because they are less likely to be exposed to toxic substances. Glass-to-lead recycling is cheaper than glass-to-glass recycling and presently more viable. In addition to lead production, other open-loop options for CRT glass are:

- Use in decorations - decorative tiles, glass and lighting products, or reflectors used in roads.
- Lead utilization - use leaded glass for its lead content. Nuclear waste encapsulation, X-ray shielding and industrial glass panels are some of the applications.
- Glass aggregate - replacing other aggregates such as silica or (river) sand in concrete production.
- Use as a precursor for fiberglass and glass wool production.
- Use in sand blasting procedures.

Recycling CRT glass has the following advantages:

- Prevents the pollution associated with CRT disposal.
- Lessens the environmental impact associated with the fresh production of (leaded) glass when reutilizing (leaded) CRT glass
- Lessen the environmental impact associated with the harvesting (mining and processing) of virgin materials when CRT glass is used in glass production or as a fluxing agent/aggregate etc.

The applications of recycled CRT glass are largely limited because of the lead content. The unknown composition of recycled CTR glass is also problematic when used in fresh glass production. Small impurities in the recycled glass can severely affect the quality of the new glass.

INCINERATION AND LANDFILLING

Landfilling and incineration are renounced because of their potentially adverse environmental effects. Incineration produces toxic vapors and landfilling produces toxic leachate. The higher heating values (HHV) of CRT-device plastic and crude oil are 40 MJ/kg and 44 MJ/kg respectively [14]. Utilizing these plastics in energy recovery, with incineration, is therefore viable. The benefits of energy recovery are: reduced consumption of fossil fuels, reduced emission of greenhouse gasses and a reduction in required landfill space. CRT devices contain up to 20 wt. % plastics. However, these plastic contain flame retardants and/or halogens. During incineration, special precautions should be taken to prevent the emission of toxic vapors.

COMMON RECYCLING/SCRAPPING TECHNIQUES APPLIED TO CRTS[5]

A brief summary of an article by Lee and coworkers [5] is presented here.

SEPARATION OF FUNNEL AND PANEL GLASS

The difference in composition between funnel and panel glass often requires separation; this is achieved by:

- Electric-wire heating method
- Gravitational-fall method

FLUORESCENT COATING REMOVAL

The fluorescent coatings contain different heavy metals. These metals can cause contamination problems during the processing steps of recycled panel glass and therefore need to be removed.

Removal is performed by:

- Vacuum-suction method.
- Ultrasonic-cleaning method
- Wet-scrubbing method
- Sandblasting method

PCB RECYCLING

PCBs are part of television sets and computer monitors and are recycled as followed:

- Copper-smelting method
- Physical separation method
- Scrapping method

A detailed comparison/evaluation of these various methods is found in the source article.

THE HANDLING OF WASTE CRTS IN SELECTED COUNTRIES [7]

The source of this chapter dates back to 2011, due to this some of the information presented might be outdated.

AUSTRALIA

Australia has the infrastructure to recycle CRT panel glass into: normal glass, fiberglass batts and flux for lead smelting. Funnel glass is recycled as: fiberglass batts, flux for lead smelting and lead glass for new CRT production if desired. However, some CRTs still end up in landfills.

ASIAN COUNTRIES

CHINA

China, as most developing countries, does not have/use formal CRT recycling procedures. The CRTs are often manually disassembled and the valuable and easily accessible materials are harvested. Fortunately, designated CRT glass recycling companies are in development/use.

INDIA

India uses informal CRT recycling. Informal remanufacturing is common practice in India, where CRTs are being re-gunned (replacement of the electron gun). CRTs are also dismantled for parts for use in the production of unbranded (or locally branded) devices. The glass of redundant CRTs is shipped to the glass market. The informal recycling has contaminated the environment noticeably.

JAPAN

Japan has formal recycling of WEEE, with EPR in place for refrigerators, washing machines, air conditioners and CRTs. CRTs have to be recycled by at least 55 % by law. Television sets and computers are recycled by manually removing the deflections yokes and power cords. The rest of the material is shredded; ferrous metals are recovered with magnetic separation and non-ferrous materials are separated with eddy current separation. The CRT is divided into panel and funnel

glass and sequentially turned into cullet. The costs for the EPR are provided by the consumers post purchase. Consumers pay a collection and a recycling fee when returning EoL products.

KOREA

Korea also has the EPR in effect, where at least 53% of collected e-waste should be recycled. The rest of the e-waste is either landfilled or exported. CRTs are recycled through the glass-to-glass and the glass-to-lead route. However, the offshore production and obsolescence of CRTs, make glass-to-glass recycling increasingly difficult. As a result CRT cullet is used for bricks, aggregate, glass tiles, rubbing compounds for jeans and as smelting flux. The EPR in Korea is an extension of the “waste deposit-refund system”. With this system, recyclable products have an additional cost (deposit) and the cost is refunded based on the amount of WEEE recycled.

TAIWAN

As of 2001, Taiwan has a formal recycling infrastructure for CRTs. The following procedure is recommended:

- The phosphor coating is treated with stabilization and solidification techniques.
- CRT funnel glass is/was recycled into new CRT funnel glass
- The plastic is recycled, landfilled or incinerated (with energy recovery).

The collection centers in Taiwan handling scrap computers pay reward money for EoL products. This gives people incentive for returning their e-waste.

EUROPEAN COUNTRIES

In the European Union most of the states have formal recycling facilities; however in some cases these facilities are not adequate. There is a research for eco-efficient routes for managing electronic waste, such as the Cost Management System for greening electrical and electronic equipment (green) and the Recytube Project. The Recytube Project aims to produce high quality secondary raw materials (SRM) from EoL CRTs.

BELGIUM

UMICORE Precious Metal Refining is located in Belgium; this is an advanced recycling facility that can handle most metal containing wastes (including electronic). This facility handles global waste.

GERMANY

The WEEE Directive has changed the processing of EoL e-waste in Germany. The waste glass from CRTs is used as: filling material in mines and striking surfaces on sandpaper and matches.

SPAIN

Spain has inadequate waste collection points for waste and there is no separation between WEEE and municipal waste. As a result some WEEE ends up in landfills and dumpsites

SWEDEN

Sweden has Boliden, a designated WEEE recycling facility. In addition, IBM Sweden has incorporated a take-back program for old computers to ensure they are processed in an environmentally correct way. The leaded glass (neck and funnel) from the CRTs is shipped to IBM Holland to be recycled.

THE NETHERLANDS

The Netherlands houses a large IBM recycling facility to handle leaded glass. In addition, the country also has SIMS Recycling solutions and a designated CRT processing facility in Echt.

THE UNITED STATES

The USA has formal recycling for CRTs, however the facilities are inadequate. As a result, most of the WEEE is stored, landfilled, incinerated or exported. The PS Directive and increasing bans on landfilling resulted in export becoming their most viable option.

AFRICAN NATIONS

South Africa is the only country with formal recycling of e-waste. However most of the recycling is based on PWBs and not CRTs. In other African countries, the disposal of waste CRTs takes place in open dumps and in open surface water bodies.

CURRENT RESEARCH OF WASTE CRTS APPLICATIONS

BIOPOLYMER FORMATION

Kim and coworkers [15] have used CRT glass with biopolymers in the production of concrete. The CRT-biopolymer-concrete (CBC) composite is produced with ground CRT glass (neck, funnel and panel), xanthan gum and guar gum. Ground CRT glass and sand were used as aggregate. EPA TCLP showed a non-hazardous lead leachability for the CBC. The compressive strength test indicated comparable results for CBC and regular concrete. Applications of CBC are:

- Use as regular construction material (bricks, blocks, decorative tiles)
- Use as marine concrete, due to its resistant to sulfur and chloride ions
- Use for environmental barriers, provides a layer that prevents metal and low level nuclear waste leaching
- Use for X-ray shielding protection layers, e.g. nuclear reactor isolation

GLASS FOAM PRODUCTION WITH EGGSHELLS

Cleaned CRT glass (funnel and panel) has been used by Fernandes and coworkers [16] for the production of glass foam with (waste) eggshells. The process takes place with glass powder in the temperature range of 600 to 800 °C. Eggshells are used in this process as the calcium carbonate source. The environmental advantages of this process are: the relatively low process temperature range and usage of waste raw materials. The authors did not mention the lead leachability of the foam.

SELF-PROPAGATING DETOXIFICATION

Chen and coworkers [17] have published a self-propagating process that detoxifies waste CRT glass by encapsulating the heavy metals. The process uses CRT glass powder with ferric oxide and magnesium. Once ignited the reaction could sustain itself (self-propagating), when the glass content was 60 wt. % or less. The metals in the product were converted to a more stable form and therefore safe to use in construction material. The EPA TCLP measurement showed acceptable values for the lead leachability. Some applications of the product are: X-ray shielding products, use in nuclear power plant reactors, use for environmental barriers and as encapsulation matrix to prevent leaching.

FLUORESCENT POWDER

YTTRIUM RECOVERY

Innocenzi and coworkers [18] investigated the recovery of yttrium (Yt) and zinc (Zn) from the fluorescent powder of color CRTs with hydrometallurgy and sulfuric acid. Yttrium can be recovered as yttrium oxide (YtO) with a yield between 75 and 80 %. This process can be profitable due to the high economic value of yttrium.

PLASTICS

PYROLYSIS OF PLASTICS

Hall and coworkers [19] have performed pyrolysis with WEEE, including the plastic parts of CRT devices. CRTs produced mono-substituted aromatic and aliphatic hydrocarbons. These hydrocarbons can be used for chemical and/or fuel production.

PANEL GLASS

CST PRODUCTION

Chen and coworkers [20] produced crystalline silicotitanate (CST) using waste CRT panel glass as silicon source. CST is an inorganic ion exchanger capable of removing e.g. ^{137}Cs and ^{90}Sr radionuclides, from defense waste. The captured Cs can afterwards be immobilized into a ceramic or a glass. The residue contains Ba and Sr and is suitable as a raw material for Ba and Sr metallurgy.

GLAZE PRODUCTION

The panel glass from television and computer monitor CRTs has been used by Andreola and coworkers [21] to produce ceramic glazes. The commercial frit used in glaze production was replaced (for 30%) with cleaned EoL panel glass. The research also compared the environmental impacts associated with the production of fresh commercial frit from raw materials and those associated with recycling CRT glass. The results indicate that using CRT glass is the better option. Commercial frit glaze and CRT glaze have comparable aesthetics and chemical resistances.

PORCELAIN STONE WARE BASED ON CRT PANEL GLASS

Andreola and coworkers [22] have also evaluated the usage of CRT panel glass as fluxing agent for the production of porcelain stoneware. CRT glass was used to replace Na-feldspar (up to 35 wt. %), feldspar is the most expensive compound used in porcelain production. The properties of the porcelain depend on the amount of CRT glass added. Small amounts (5 wt. %) of CRT glass improve the densification process and enhance the mechanical properties. When 35 wt. % or more was substituted, the effects were detrimental because the glass reacts with porcelain raw materials, altering the properties significantly.

FUNNEL GLASS

LEAD RECOVERY AND FOAM GLASS PRODUCTION WITH A PYROVACUUM PROCESS

Chen and coworkers [23] have developed a pyrovacuum process that detoxifies CRT funnel glass and uses the glass residue to produce foam glass. The pyrovacuum process is a reduction process where lead oxide reacts with carbon to form lead and carbon monoxide. Up to 98.6 % Pb can be recovered from funnel glass with this process. The produced lead has a purity of 99.3 %. The foam glass produced from the residue showed a lead leachate concentration below the TCLP limit.

LEAD OXIDE NANOPARTICLE PRODUCTION BY A SELF-PROPAGATING REACTION

Wang and coworkers[24] have used CRT funnel glass for the production of PbO particles with self-propagating high-temperature synthesis (SHS). The reaction takes place in the presence of MgO and Fe₂O₃ and produces PbO nanoparticles with a size of 40-50 nm. The amount of lead recovered depends on the amount of funnel glass added. More than 90 wt. % lead could be recovered when no more than 40 wt. % funnel glass was used in the feed. The TCLP results of the residue were 0.02 – 0.18 mg/L lead, well below the limit. However, the authors note that Mg is expensive and as a result, this process might not be viable on a larger scale.

CRT FUNNEL GLASS AS FINE AGGREGATE IN CEMENT MORTAR

The use of funnel glass as an aggregate in cement mortar has been investigated by Ling[25]. The research was based on treated and untreated crushed funnel glass, denoted as TFG and n-TFG respectively. TFG was washed with nitric acid to remove the lead from the surface. The glass replaced sand for 50 or 100% as aggregate. The following was observed:

- The addition/substitution of glass cullet increased the fluidity of the fresh mortar, reduced the water absorption and reduced the drying shrinkage of the cement mortar
- There is weak(er) bonding between glass and cement, compared to sand and cement. The flexural and compressive strengths decreased with increasing glass content. The lowest strength was observed for n-TFG, the author states that this is due to the retardation effects lead has on cement hydration.
- The addition of funnel glass (n-TFG and TFG) increased the hardened density of the mortar and the X-ray shielding properties
- The lead leaching of TFG cement was below the TCLP limit; n-TFG surpassed it.

FUNNEL GLASS AS AGGREGATE IN SCC WITH LIMESTONE

River sand was mixed with CRT glass cullet, in the proportions of 20 and 40 wt. % , and was used as aggregate in self-compacting concrete (SCC) by Sua-iam and coworkers [12]. Limestone powder (LS) was added to the SCC mixture in 5, 10 or 15 wt. % to suppress potential viscosity effects of the concrete and to enhance the workability. Using self-compacting concrete instead of regular concrete provides a safer work environment for the workers. In addition, limestone powder is a difficult to dispose of waste product from the stone-crushing industry, with adverse environmental impacts if not handled properly. Using LS and CRT waste glass increased the fluidity and viscosity and reduced the setting time of the concrete proportionally to the amount of aggregate added. Usage of CRT waste glass and LS has environmental benefits because it mitigates the landfilling and potential toxic exposure associated with these compounds. Leaching tests (TCLP) of the SCC indicated that limestone powder immobilized Pb sufficiently for SCC not to be considered hazardous.

FLUORESCENT LAMP GLASS AND LEAD PRODUCTION

Xie and coworkers [1] have proposed the usage of leaded waste CRT glass as raw material for leaded fluorescent lamp glass (glass-to-glass recycling). Fluorescent lamps in China are still produced with leaded glass; reusing CRT leaded glass for their production can be viable. The production of fluorescent glass with recycled glass has environmental/economic advantages compared to the production of fresh glass. However, producing fluorescent lamps is not a permanent solution to the lead problem. In Europe, fluorescent lamps are already Pb free (RoHS Directive) and soon, this can also be the case for China.

The authors propose metallic lead production from the leaded glass as the alternative option with pyrometallurgy (glass-to-lead recycling). Funnel glass with over 20% lead content provides both lead and silicon flux for the process. The article mentioned lead production by SKS technology (Figure 7). The resulting lead slag contains less than 5% Pb and is therefore suitable for the cement industry.

Hydrometallurgy is also a more viable option for recovering lead from glass. Compared to pyrometallurgy, it is more easily controlled, exact and predictable [26]. The process is based on the dissolution of lead in acid (e.g. nitric or acetic acid) followed by lead collection through electronic deposition. With this method, up to 90 % lead can be recovered and up to 95 % lead can be removed from funnel glass.

ALKALINE HYDROMETALLURGY

Zhang and coworkers [2] have published a hydrometallurgical process to recover lead from funnel glass using an alkaline solution. Conventional processes use acidic solutions. Zhang used NaOH as a solvent, because other heavy metals typically do not dissolve in alkaline solutions. Lead was dissolved using a planetary ball mill (mechano-chemical extraction) at 70 °C and the amount of lead extracted was 97.4 %. The lead was collected out of the solution using electrical deposition with a purity of 97.2 %. Disregarding the investments cost, a profit of € 750 per ton metallic lead was calculated using Pb powder costs of 2012. The glass residue was environmentally safe to use in foam glass production.

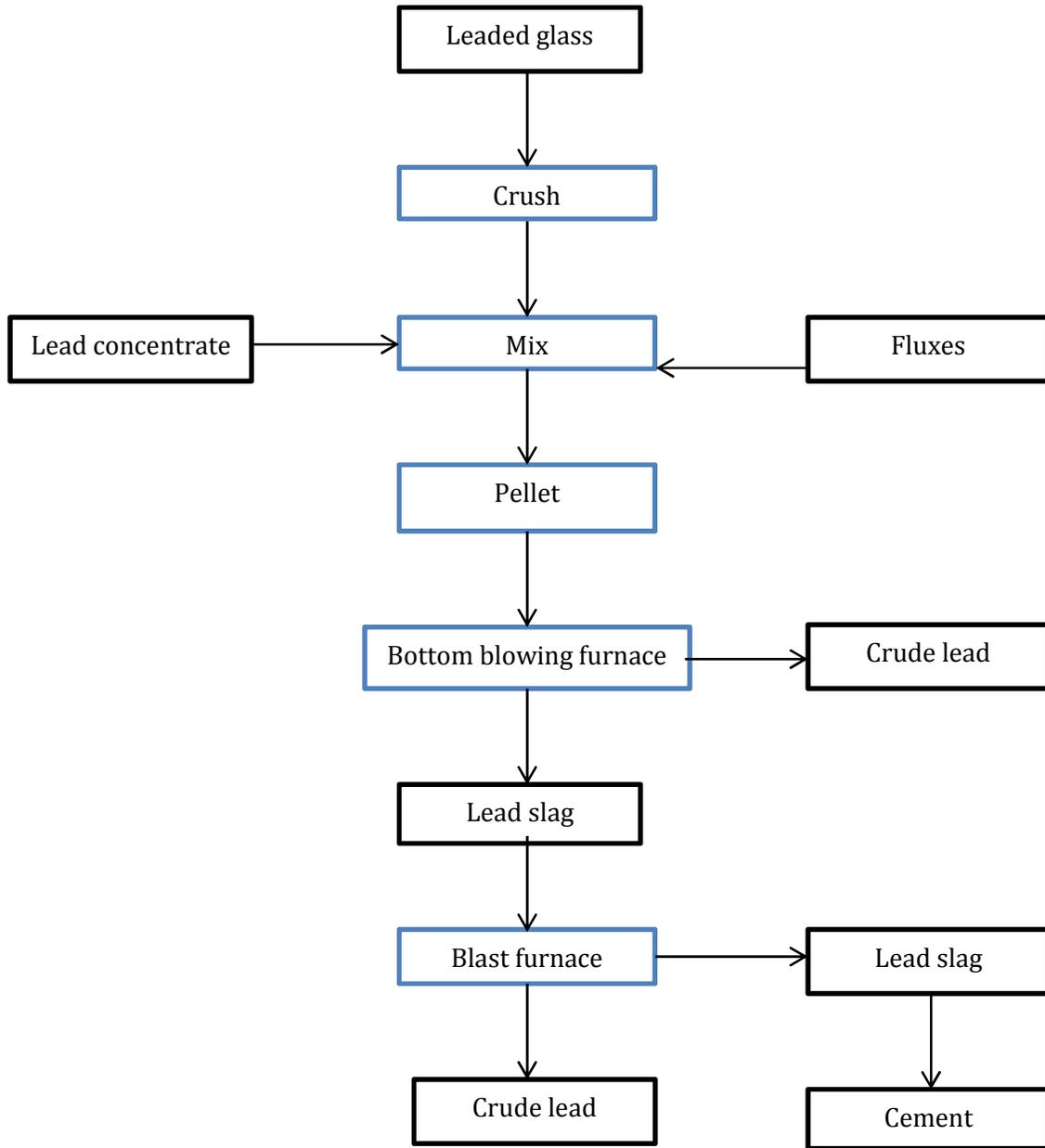


FIGURE 7 LEAD PRODUCTION FROM FUNNEL GLASS (SKS TECHNOLOGY) [1]

DEFINITION OF TECHNICAL ROUTES FOR RECYCLING MONITORS

This chapter summarizes the current practices of waste CRTs in Brazil and evaluates the applicability of foreign disposal strategies.

CURRENT WASTE CRT DISPOSAL PROCEDURES IN BRAZIL [27]

As of 2014, a law is in place that forbids open landfilling of e-waste. Brazil has the reverse logistics protocol in place for processing e-waste by federal law. However, these laws are not severely enforced and the punishments for breaking the law are not clearly defined. Reverse logistics holds the whole producer chain (manufacturers, distributors, importers and retailers) and consumers responsible for collecting and treating waste materials. The consumer's responsibility is to bring e-waste to the distributors and retailers. Afterwards, the distributors are responsible for delivering the e-waste to the manufacturers and importers. The manufacturers and importers are responsible for the sound disposal of the e-waste. There are however some problems with this system:

- The consumers have no incentive to bring their e-waste to the retailers, other than a lax enforced law.
- The retailers don't have storage to receive e-waste from the consumers and refuse to spend funds on acquiring storage.
- When the retailers do receive e-waste, they refuse to spend funds on the transport costs associated with delivering the e-waste to the manufacturers/importers.
- Too many mediators are involved in the reverse logistics chain.

The different states in Brazil also have their own laws with regulation about the disposal of e-waste. São Paulo for example has a big electrical/electronic market and therefore also well-developed laws for proper e-waste handling. However other states, for example Rio de Janeiro, have out-dated laws without implementation of the reverse logistic model. São Paulo has the highest GNP of all the Brazilian states and also the most significant electronic/electrical manufacturing capacity.

The largest amount of waste CRTs in São Paulo are stored by consumers, due to a lack of incentive for recycling. There are some private companies that handle the recycling of CRTs. Ambiente standard© is a company that collects CRT devices from consumers for dismantling. The metal, glass and plastic are recovered and sold.

Other companies, e.g. Descarto Certo©, act as a collection/processing facility to whom the consumer has to pay a fee when bringing the CRT in. The CRT is dismantled and the parts are processed. Descarto Certo© also works with companies and recycles their e-waste.

SUPPLEMENTING CURRENT RECYCLING LEGISLATIONS IN BRAZIL

The current practice for environmentally friendly disposal of CRTs and waste electronics is an agreement with various parties in the chain, (producers, importers, traders and consumers) who share responsibility in the recycling of the product. However, the collection of waste electronics is not managed optimally. Implementing a deposit-refund system can give consumers incentive to return their e-waste. The suggested procedure is that the cost of electronics have an extra cost added, this will consist of the deposit and possibly the recycling costs. After usage, the consumer brings this product to a collection facility/ returns the product to the retailer for further processing and the deposit is refunded. This procedure won't solve the current waste CRT problem but will mitigate some e-waste problems in the future.

Retailers also require incentive to deliver their collected e-waste to the importers or manufactures for further processing. This can, for example, be achieved by force of law or by imposing a tax, with a refund of the tax money if the targeted amount of e-waste is recycled.

Implementing a Brazilian equivalent of EPR, WEEE and RoHS Directive will improve the current EoL of e-waste in Brazil. With EPR, the manufacturers and importers will be forced to collect e-waste. Currently, e-waste collection is a problem in Brazil, preventing recycling. The equivalent of the WEEE Directive will ensure that sound recycling of e-waste takes place. The RoHS Directive equivalent will prevent the usage of environmentally hazardous substances in new products.

RECOMMENDED APPROACH FOR WASTE CRTS IN BRAZIL

Lead is the most abundant pollutant in (color) CRTs. To prevent lead pollution, correct disposal is required. During the time CRTs were still in production, leaded glass was best utilized in glass-to-glass recycling. However, CRTs have become obsolete and as a result, alternative recycling routes (glass-to-lead) need to be explored.

The previous chapter mentioned various recycling technologies for leaded glass (funnel). Lead recovery has the most potential to be economically viable. Lead can be sold or used for other applications, and the glass residue can be used in concrete production, metal smelting, glass

production or glass foam production. Lead can be recovered by hydrometallurgy and pyrometallurgy. Hydrometallurgy is a more controlled process and does not require as much energy as pyrometallurgy. To separate lead from CRT funnel glass using pyrometallurgy, temperatures of up to 1000 °C are required to melt SiO₂. Hydrometallurgy for lead recovery can be performed in acidic or alkaline solutions. The benefit of using an alkaline solution is that Pb is selectively dissolved. The research by Zhang [2], mentioned in the previous chapter will be explained in further detail and calculations for Brazil will be presented in order to evaluate the feasibility. The alkaline lead recovery process is schematically presented in Figure 8.

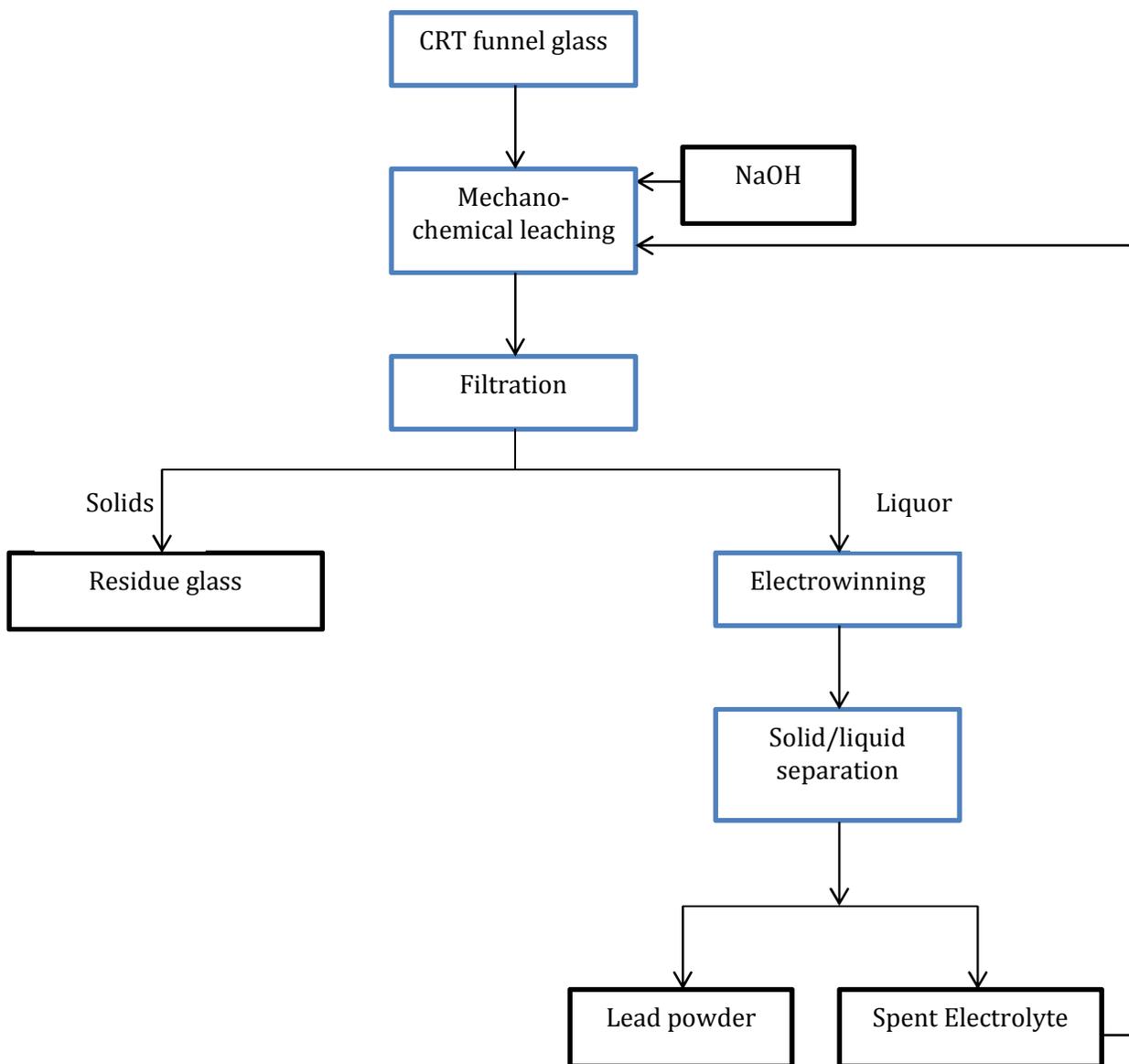


FIGURE 8 AKALINE EXTRACTIVE LEAD PRODUCTION FROM CRT FUNNEL GLASS[2]

The process starts with the combining of ground CRT funnel glass (< 10 mm) with 5 M NaOH. The highest amount of lead extracted (97.4 %) was obtained using a stirring ball mill at 70 °C with a minimum rotational speed of 500 r/min. The process is referred to as the mechano-chemical extraction of lead. During the process the mechanical activation and chemical leaching take place in parallel. NaOH was used because of its selective solubility towards lead. The average metal content of the funnel glass is presented in Table 7 and the metal concentration in the leaching liquid is presented in Table 8.

TABLE 7 ELEMENTAL COMPOSITION CRT FUNNEL GLASS USED FOR THE MECHANO-CHEMICAL EXTRACTION BY ZHANG [2]

Elements	Aluminum	Barium	Calcium	Bismuth	Iron	Sodium	Lead	Zinc	Magnesium
Wt. %	1.44	0.68	3.1	0.05	0.59	5.9	25.1	0.16	1.09

TABLE 8 AVERAGE ELEMENTAL CONCENTRATION IN THE MECHANO-CHEMICAL EXTRACTION SOLUTION [2]

Elements	Lead	Aluminum	Barium	Calcium	Bismuth	Iron	Zinc	Magnesium
[g/ L]	17.2	0.37	0.048	0.017	0.012	0.007	0.025	0.011

The ball mill is used to activate the funnel glass in order to enhance leachability of lead. During the activation, the following takes place:

- Increase of the glass surface area.
- Increase of the surface reactivity.
- Changing of the crystalline structure; generation of non-bridging oxygen-hole-centers and peroxy radical formation

The defects generated by mechanical activation are, however, temporary. When lead extraction was performed in series, i.e. activation followed by leaching, the results were inferior compared to parallel mechano-extraction. The lead product is collected as a powder with electro deposition, with a yield and purity of 97.5% and >97.2 % respectively. After lead recovery, the NaOH solution can be reused for additional lead extraction. On average, 50 to 60 g of NaOH is lost per kg of lead produced. The glass residue in the article is used for foam production, but other applications such as concrete or ceramic production are also viable. The glass residue is almost leadless and therefore not hazardous.

The calculated profit for the process was €750, - per ton of lead produced. In the following section, calculations of this process will be applied to the estimated available amount of CRTs in Brazil to evaluate the viability of this process.

FEASIBILITY OF ALKALINE LEAD PRODUCTION IN BRAZIL

The calculations are based on an estimated amount of CRTs per house in Brazil, in 2001. This year was chosen because after 2001, CRTs were most likely replaced with newer technology televisions and computer monitors. The data was obtained from Teleco©[28] and it was assumed that houses contained no more than one CRT television and/or no more than one CRT monitor. The amount of lead per television was estimated to be 2 kg and per computer monitor 1 kg, these values are based on data from Nnorom [7]. The same profit mentioned by Zhang was used during these calculations. Table 9 presents the results. The net profit of this process, excluding initial investments, is close to € 60.000.000,-

TABLE 9 FEASIBILITY OF ALKALINE LEAD PRODUCTION IN BRAZIL

Houses in Brazil (2001)	41000000
% of houses with TV (2001)	89%
% of houses with PC (2001)	13%
Amount of houses with TV (2001)	36490000
Amount of houses with PC and also Monitor (2001)	5166000
Total of monitor and TV	41656000
Total amount of Pb [ton]	78146
Net profit (R\$)	R\$ 164,106,600.00

The profit is expected to be even greater, because only data from 2001 was used and it was assumed that only one CRT TV and/or CRT monitor was available per house. Houses most likely contain(ed) more than one CRT television.

The production of lead, from CRT funnel glass, produces leadless glass as a byproduct. This glass can be used for an additional profit. The panel glass is also neglected during the evaluation of the process. Panel glass contains the phosphor materials, rich in yttrium oxide. Yttrium oxide can be extracted with (acidic) hydrometallurgy [18]. On average, about 50 g of yttrium oxide can be collected from a CRT [7], which has a value of ~ €100,- (Sigma-Aldrich, 17/6/2014). The remaining panel glass, free of phosphors, can be used for glass foam production or construction materials. Lastly, the plastics can be used for energy recovery.

The proposed recycling process for CRTs for Brazil is presented in **Error! Reference source not found.** The usage of the glass and the metals recovered is situational (Sit), depending on what is required. The precious metals can be sold for additional profit.

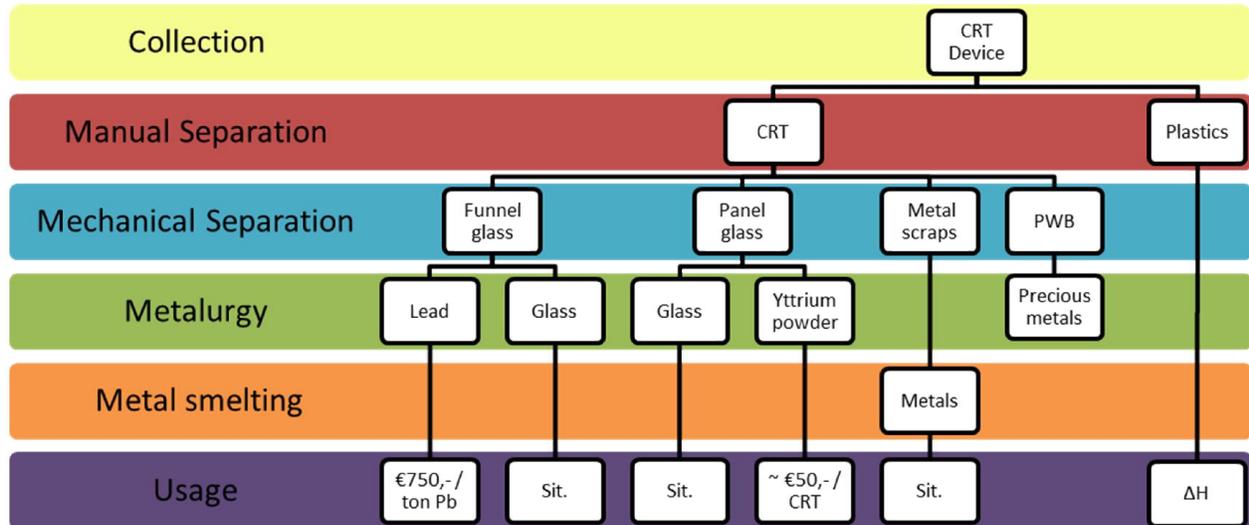


FIGURE 9 RECOMMENDED WASTE CRT RECYCLING PROCEDURE FOR BRASIL

CONCLUSION

CRTs were common in every household; present in television sets and computer monitors. The estimated amount of CRTs in Brazil is close to 42.000.000. Recently, these devices have been replaced with newer, flat screen models. This replacement resulted in a large quantity of obsolete CRTs. CRTs are considered hazardous waste due to their high lead content and require special disposal strategies. The estimated amount of lead in Brazil present in CRTs is close to 80.000 ton. Previously, leaded CRT glass could be re-used for the production of new CRT glass. However, this option is no longer available due to the cease in CRT production. Alternative use of CRT glass is very limited due to its toxicity. In the European Union and developed Asian countries such as Japan and South Korea the sound recycling of waste CRTs is common practice. In developing countries such as China and India “backyard recycling” of CRTs takes place, causing severe pollution. Other developing countries do not recycle and just dispose the waste CRTs in landfills or open surface water bodies. Developing countries, e.g. USA, also export waste CRTs to the developing world as means of dealing with e-waste. A viable way to circumvent the lead problem associated with CRTs is to separate the lead from the glass. Lead removal can be achieved with hydro- and pyrometallurgy. Hydrometallurgy is less expensive due to the lower energy required and is performed in a more controlled environment. The production of lead from waste CRTs has been calculated to be profitable in Brazil. Considering the estimated amount of CRTs in Brazil, the preliminary profit using alkaline hydrometallurgy was calculated to be € 60.000.000,-. Additional studies are required, considering logistics etc., if this process is to be implemented in Brazil.

LIST OF ABBREVIATIONS

CRT: cathode ray tube

LCD: liquid crystal display

PCB: Printed circuit board

EPA: Environmental Protection Agency

TCLP: Toxic characteristic leaching procedure

MSW: Municipal solid waste

PWB: Printed wire board (synonymous with PCB)

WET: Waste extraction test

SPLP: Synthetic precipitation leaching procedure

EEE: Electric and electronic equipment

WEEE: Waste electric and electronic equipment

RoHS: Restriction on hazardous substances

EPR: Extended producer responsibility

PS: Product stewardship

DfE: Design for environment

EoL: End of Life

CBC: CRT-biopolymer-concrete

CST: Crystalline silicotitanate

TFG: Treated funnel glass

nTFG: Non treated funnel glass

SCC: Self compacting concrete

LS: Limestone powder

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