Thermal processes for lead removal from the funnel glass of CRT monitors

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Abstract

The disposal of CRT monitors increases each year, generating millions of tons of waste containing various types of materials. The glass present in CRT tubes displayed about 20%–25% of lead oxide. If improperly disposed of, this glass can be leached directly in nature or may cause environmental contamination, especially with lead. Because of this leaching possibility, this waste is classified as Class I solid waste, according to the NBR 10004. Thermal processing of these glass tubes was seen as an alternative to remove lead from the glass matrix. Parameters such as reaction time, percentage of reducing agent, the reaction temperature, and atmospheric environment of the system were analyzed in this work. It was concluded that it is possible to remove the lead from the glass matrix by thermal processing. The removal of 92% of the lead from the glass was obtained at 800°C, a vacuum of 1.3 kPa, with 5% carbon as a reducing agent, and 18 hours of thermal processing.

Keywords: lead removal, CRT monitors, electrical waste and electronic equipment.

1. Introduction

The constant development in technology promotes, among other consequences, the abandonment of old equipment that has been replaced by new ones. The so-called planned obsolescence generates tons of electronic equipment that are discarded annually. Among these devices are the cathode ray tube (CRT) monitors.

The CRTs are present in computer monitors, television sets, old medical equipment, and several other utensils. With the emergence of new technologies such as liquid crystal display (LCD), light emitting display (LED), and recently the organic light emitting display (OLED), the old cathode ray technology fell into disuse. The industry of CRT has almost stopped production and the sales of CRT monitors have decreased significantly (KIM, 2009).

There is no exact number of the amount of CRT monitors that are discarded annually worldwide. However, some countries, like the United States, China, and Taiwan, discarded annually a total estimated in 3.2 million, 5 million, and 1 million televisions and monitors, respectively (NNOROM, 2011).

In Brazil, there are only studies of estimated electronic waste generation. According to Rocha (2009), the annual

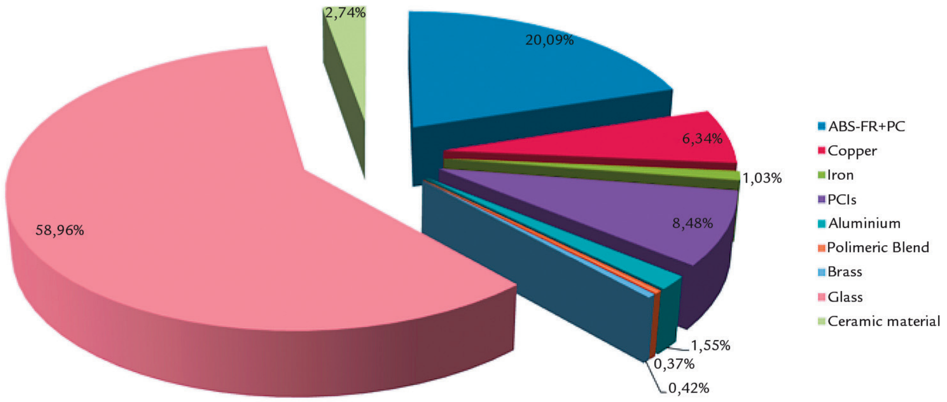

Figure 1
Mass distribution of the major materials in the CRT monitor.

generation of televisions is estimated to be 135,000 tons. According to the study by UNEP (2009), this number would be 137,000 tons/year.

The CRT monitors and the CRT televisions are made of three main components, namely the printed circuit board, the polymeric frame and the CRT tube. These components are of primary interest for recycling, since they are the major components of the monitors. Figure 1 shows the mass distribution of the major materials found in CRT monitors (De OLIVEIRA, 2012).

The recycling of the components of CRTs has difficulties in logistical and environmental friendly disposal. CRT monitors and televisions are heavy equipment thanks to the CRT tube that is made of glass; beyond that, a small percentage of metal materials such as copper, aluminum, steel, and precious metals hinders the profit of segregation. These factors make the logistics of CRTs rather costly for scrap dealers. The challenge of an environmental friendly disposal arises from the difficulty of selling leaded glass. Few companies employ such material in the manufacture of new products.

Lead oxide is added to the glass composition for inhibiting the electromagnetic radiation from the acceleration of electrons, which later form the images on the screen, from hitting the users. Lead is considered a toxic agent to human health and the environment. As a result, CRT monitors and CRT televisions are considered hazardous electronic waste in accordance with various government agencies (ENVIRONMENT AGENCY IRLAND, 2008).

The tube CRT is composed of three types of glasses with different chemical compositions - the neck glass, the funnel glass and the panel glass. The funnel glass has a layer of iron oxide in the inner surface and a layer of graphite carbon in the outer surface.

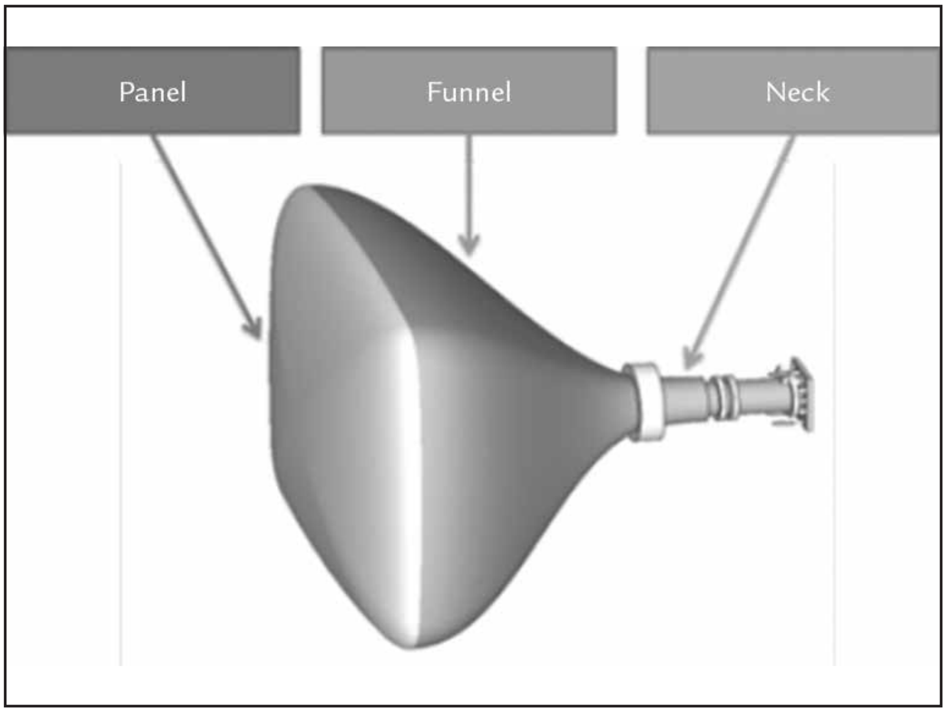

Figure 2
CRT tube and the three types of glasses.

Initially, it was expected that the lead found in the glass matrix remained immobilized within, since the immobilization in an inert material is a technique widely used for the disposal of hazardous waste. However, the lead present in the tube surface may suffer solubility in acidic environments (pH = 4), especially if the glass is broken (JANG, 2003).

According to literature (MUSSON, 2008), lead is leached from the CRT tubes with values greater than those permitted by NBR 10004. Thus, the CRT tube is considered a residue class I–dangerous in accordance with NBR 10004 (ABNT, 2004).

Recycling of the CRT monitors can be designed into a *closed-loop* system, where the CRT glass returns to the manufacturer and is used in the manufacture of new CRTs. However, this conception of *closed-loop* is difficult to perform, since the manufacture of CRTs is declining and the logistics costs would be high, especially for countries where there are no manufacturers.

In an *open-loop* system, the CRT glass is used in the manufacture of other products. This alternative is more conceivable economically and in logistical terms. Alternatives such as mixing aggregates in concrete or asphalt, the manufacture of foam glass and even the lead or copper smelter are possible (XU, 2012; ICER, 2004). However, the concentration of lead initially present in such materials can render them unfit for reuse or recycling.

The process of extraction of lead from the glass matrix involves hydrometallurgical and pyrometallurgical routes. As an example of the hydrometallurgical routes, we can cite the work of Pruksathorn and Damronglerd (2005), which claims to remove the lead from the glass matrix using leaching and electrodeposition procedures. In the leaching step, there was a 95% removal of lead using 0.1N HNO_3 and 0.5N acetic acid in a ratio of 0.5% by weight of solid to liquid. The electrodeposition of lead from this solution had a yield of 95%. The pyrometallurgical process was developed to obtain nanoparticles of lead (XING, 2011). Nanoparticles of lead were obtained using a carbon reducing agent, in a vacuum of 500–2000 Pa, with a temperature of 1000°C for 2 hours.

The possible redox reactions in the system are:

(1) $$PbO_{(s)} + C_{(s)} \leftrightarrow CO_{(g)} + Pb_{(g)}$$

(2) $$2\ PbO_{(s)} + C_{(s)} \leftrightarrow CO2_{(g)} + 2Pb_{(s)}$$

(3) $$PbO_{(s)} + C_{(s)} + O_{2(g)} \leftrightarrow PbCO_{3(s)}$$

In reaction 1, lead can be reduced with carbon according to equation (CHEN, 2009):

$$\Delta G_r = 289427\text{-}481.88T + 2RT\ln\rho\ (328 - 885\ ^0C)$$

If the pressure is 101,325 Pa (1 atm), the temperature at which the reaction becomes spontaneous is 724.10°C. For a pressure of 1333 Pa, the temperature decreases to 525.86°C. Regarding volatilization temperature, for a 1 atm (101325Pa) pressure, lead volatilizes at 1737ºC. While for a 1333Pa pressure, lead volatilizes at 1167ºC (OSTERMAN, 2010).

However the removal of lead is not well studied. The main studies verify the possibility of using the CRT glass for other purposes. In the pioneer work developed by Mear (2006), he proposed the use of CRT funnel glass as a raw material for manufacturing foam glass. Production parameters such as reaction time, temperature and amount of reducing agent added were established. However, in a later work, it was found that foams made from this material where leachable at levels of 13 mg/L of lead (YOT, 2011).

In another study, the use of leaded glass as a fluxing material was proposed because of the fact that many metal smelting operations use sand as a fluxing agent for removing impurities. In copper smelters, zinc precious metals, and the leaded glass from the CRT monitor may be used as a fluxing agent (ICER, 2004).

Recently, the use of leaded glass in the manufacture of clay bricks and tiles was developed. Additions of up to 5% by weight of lead glass were performed in bricks and tiles. Mechanical strength, water absorption, porosity, and density were analyzed. It was concluded that addition of 2% by weight of lead glass brings no significant changes in the properties of the bricks and tiles. However, the addition of 5% causes undesirable effects, mainly on the mechanical properties (DONDI, 2009).

This study aims at the removal of lead from the glass matrix using a thermal redox process alternating the atmospheres, temperatures, reducing agents, and reactions times.

2. Materials and Methods

Several samples of CRT monitors were collected at the service center in Porto Alegre, RS, Brazil. The monitors were segregated, their components separated, and weighed. The different types of CRT glasses tubes were separated using a tool designed for cutting glass with a diamond cutting disk. Then the glass was ground in hammer mills into particle sizes of less than 60 mesh and dried at 60°C for 3 hours.

The samples of CRT glass of different models and brands were then analyzed by X-ray fluorescence spectroscopy in a Shimadzu model XRF-1800 device to determine the initial concentration of lead in the three types of glass, as well as the concentration of other oxides. From this data, the lead recovery rate was calculated as the difference between the initial and final concentrations.

The glass that had the highest concentration of lead was funnel glass, so the samples from the funnel glass were used in thermal treatment processes in a Sanchis model Tube Furnace (MUSSON, 2000). Figure 3 presents the three type of schemes.

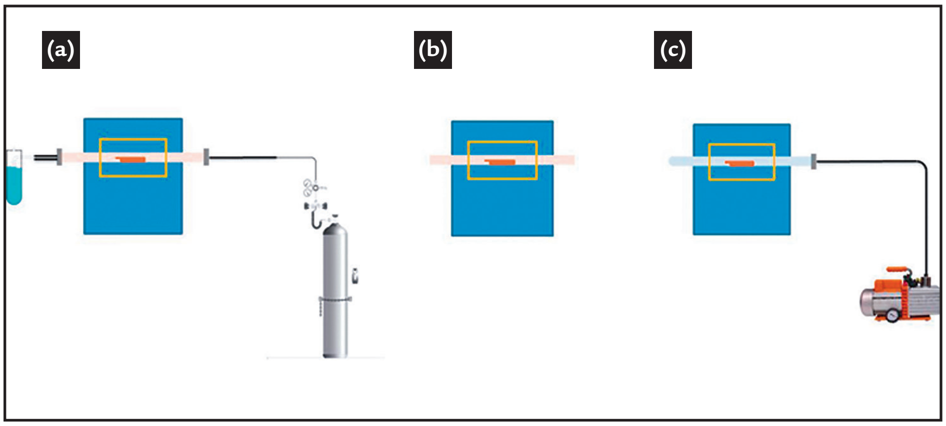

Figure 3
Schematic design of the experiments.
a) Systems with gases
b) System with open atmosphere
c) System with low pressure

Three thermal processes were established for the removal of lead from the glass matrix. The first process - A and B - uses gas and a reducing agent. The second process - C and D - was performed in an open system in ambient atmosphere, with and without the addition of a reducing agent. The third process - E and F - employs a vacuum, with and without the addition of a reducing agent. The reducing agent employed was 99.99% carbon graphite with particle size of 325 mesh. The gas flow was 10 L/min in all gaseous processes. In each experiment 20 grams (glass + reducing agent) were used. The conditions for each test are presented in Table 1.

Sample	Temperature (°C)	Atmosphere	Reducer Agent (% p/p)	Reaction Time (h)
A1	1200	Argon gas	9	1
A2	1200	Argon gas	9	2
A3	1200	Argon gas	9	4
A4	1200	Argon gas	9	6
A5	1200	Argon gas	0	6
A6	1200	Argon gas	2	6
A7	1200	Argon gas	5	6
B1	1200	Carbon dioxide gas	9	1
B2	1200	Carbon dioxide gas	9	2
B3	1200	Carbon dioxide gas	9	4
B4	1200	Carbon dioxide gas	9	6
B5	1200	Carbon dioxide gas	0	6
B6	1200	Carbon dioxide gas	2	6
B7	1200	Carbon dioxide gas	5	6
C1	1200	Ambient atmosphere	0	2
C2	1200	Ambient atmosphere	0	6
C3	1200	Ambient atmosphere	0	10
C4	1200	Ambient atmosphere	0	14
C5	1200	Ambient atmosphere	0	20
D1	1200	Ambient atmosphere	5	2
D2	1200	Ambient atmosphere	5	6
D3	1200	Ambient atmosphere	5	10
D4	1200	Ambient atmosphere	5	18
D5	1200	Ambient atmosphere	5	24
E1	800	Vacuum – 1,3kPa	0	2
E2	800	Vacuum – 1,3kPa	0	4
E3	800	Vacuum – 1,3kPa	0	10
E4	800	Vacuum – 1,3kPa	0	18
E5	800	Vacuum – 1,3kPa	0	24
F1	800	Vacuum – 1,3kPa	5	2
F2	800	Vacuum – 1,3kPa	5	6
F3	800	Vacuum – 1,3kPa	5	10
F4	800	Vacuum – 1,3kPa	5	18
F5	800	Vacuum – 1,3kPa	5	24

Table1
Parameters used in the thermal processes.

After thermal processing, the solid samples were analyzed by X-ray fluorescence spectroscopy to determine the final amount of lead in each sample. In this work the gases generated during the process were not collected for analysis.

3. Results and discussion

The first stage of work was the chemical characterization of glass types present in cathode ray tubes. This characterization was performed with the milled glass (325mesh) by X-ray fluorescence and is shown in Table 2.

Table 2
Main oxides of three types of glasses.

Mass percentage

Oxides	Neck	Funnel	Panel
BaO	nd	0.17	6.25
SiO_2	59.3	56.2	66.5
PbO	19.6	22.1	0.03
K_2O	6.98	6.69	6.65
Na_2O	5.78	5.55	7.38
CaO	3.4	3.28	1.57
MgO	1.95	1.83	0.35
Al_2O_3	1.77	1.79	1.79
Fe_2O_3	0.83	1.39	0.38
SrO	0.06	0.08	6.79

nd - non detectable

It can be noticed that only the funnel and the neck glass have lead in their composition. The panel glass is free of lead, which can facilitate recycling, since it is separated from the other types of glasses. The funnel glass presented the highest level of lead, and thus, this glass was chosen for the thermal process to remove lead.

The aim of the thermal process is to promote a redox reaction of the lead oxide to metallic lead or any other lead compound that can be removed in the gas phase, using carbon as a reducing agent. This reaction depends mainly on the temperature, pressure, time, quantity of reducing agent, mass diffusion of the reagents and products, and type of atmosphere in the furnace (CHEN, 2009).

Different atmospheres were used because of their chemical interaction with the redox reaction. Carbon dioxide was used to saturate the atmosphere and force the redox reaction towards the reactants preventing the reaction of carbon and oxygen. Argon gas was also passed on, because this is an inert atmosphere for the redox reaction, so the effect of the addition of the reducing agent could be better analyzed. The ambient atmosphere was applied to evaluate how the redox is affected by the furnace atmosphere. Vacuum was used because redox reaction is favored at low pressures.

Figure 4 presents the variation of lead removal with time for reactions A and B. In these experiments, the temperature (1200°C) and the reducing agent (9% of carbon) were held fixed.

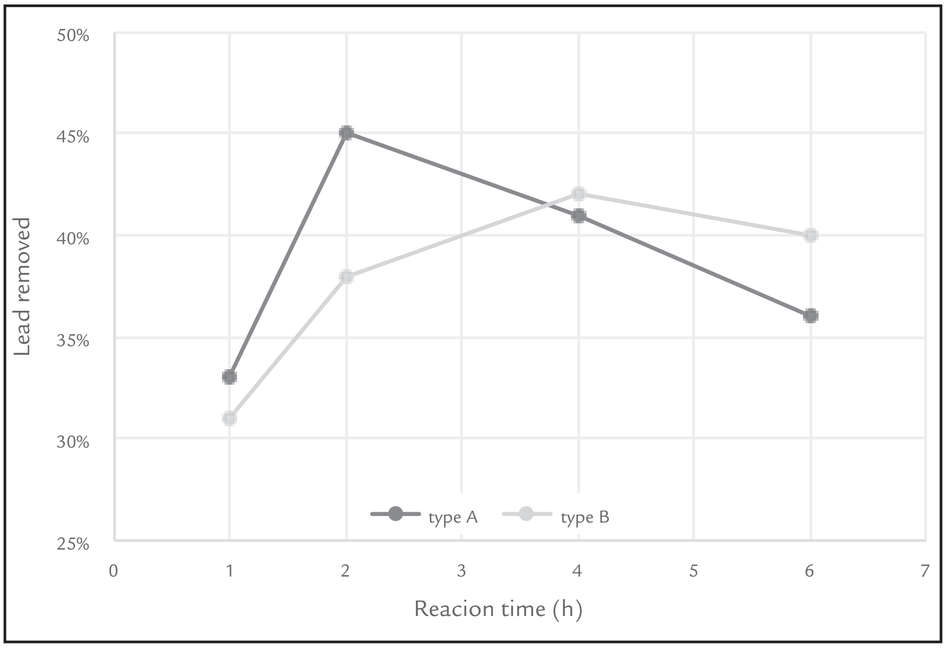

Figure 4
Relationship between
lead removal (%) and time
reaction (h) in the first process
for A and B samples at1200°C and 9% of C.

The expected relationship between the reaction time and the amount of lead removed is a linear ratio. However, in the A and B series, there is a non-linear increase during the first hours of the test, followed by a decline in the removal of lead. The best result (45%) was obtained with sample A2 at 2 hours. For the type B, sample B3 presented the maximum amount of lead removal (42%).

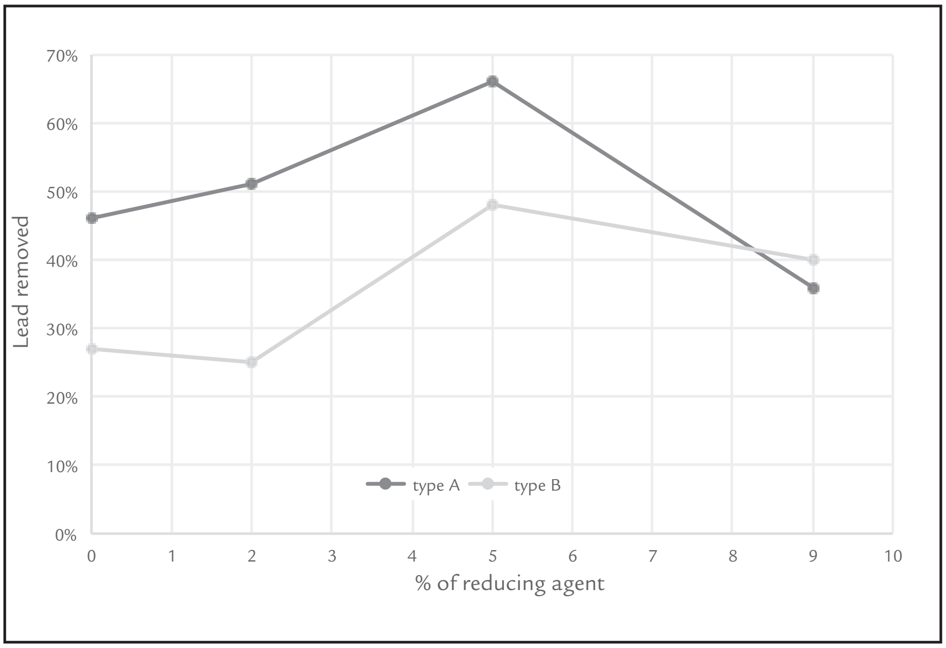

Figure 5
Relationship between
lead removal (%) and reducing agent (%)
in the first process, A and B samples.

Figure 5 shows the variation of the reducing agent (carbon content) for the A and B series. It is possible to note that 5% of carbon is the optimum amount for removing lead. Above this value, there was a significant reduction in the lead removal. A linear relationship between the amount of carbon and amount of lead removed was expected. However, this behavior was not obtained. This fact can be explained by the diffusion of carbon into the glass matrix. Even mixing the reducing agent (carbon) to the samples, the lead present in the CRT glass is much more homogeneous than carbon.

The carbon/lead oxide ratio, for the optimum amount of reducing agent, is 4.65 times greater than that of the stoichiometric reaction.

For reactions under atmospheric pressure (A, B, C and D), it is seen that at 1200°C, the vapor pressure of lead is 2146 Pa and this value is far below atmospheric pressure (101325 Pa). Thus, the tendency of the lead is to remain in the liquid phase. However, due to the complexity of the samples (glass containing numerous other oxides), lead can react and be removed in other chemical forms.

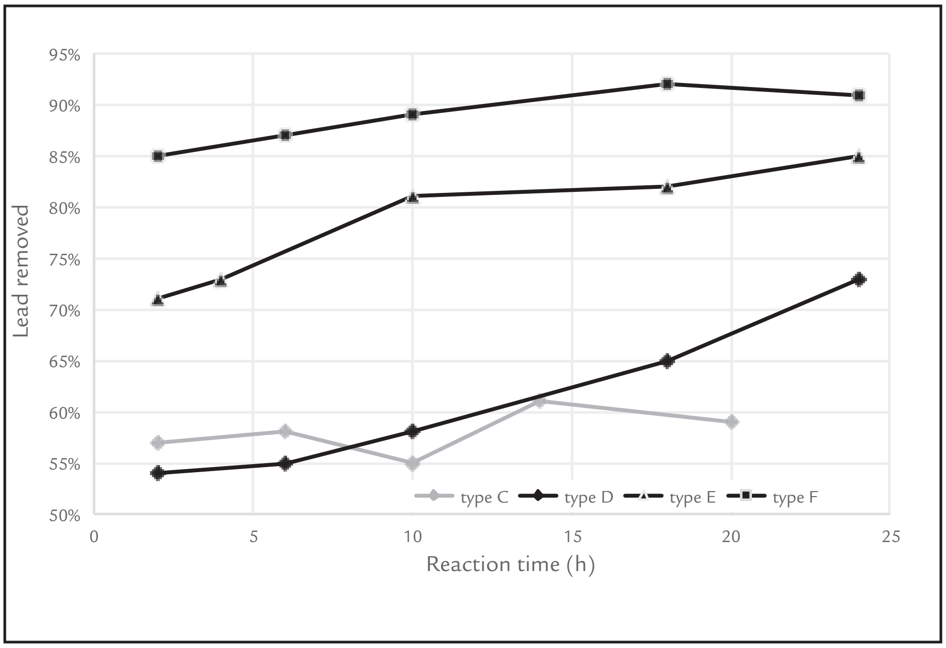

Figure 6
Relationship between
lead removal (%) and time reaction
(h) for the C, D, E and F processes.

Figure 6 show the lead removal for the C, D, E and F process. These types of reactions were performed with greater reaction times than those of type A and B reactions. The proportion of 5% of reducing agent was used (except type C), because it was evaluated as the optimum amount of reducing agent in the type A and B reactions.

The type C reaction was performed to observe the lead removal without the addition of a reducing agent and without the passage of any gas. Clearly, the removal of lead can be accomplished only by heating the glass to a temperature of 1200°C. However, the removal occurred until a rate of 61% (sample C4). The lead removal rate did not have an appreciable variation between reaction times 2 and 24 hours.

The type D reactions were also performed in ambient atmosphere. However, the reducing agent was added in the proportion of 5% (wt%) in each sample. The addition of the reducing agent increased the rate of lead removal, especially in reactions D4 and D5, corresponding to a reaction time of 18 and 24 hours, respectively. The highest removal rate of these reactions was the D5 sample, which showed a 73% removal of lead.

In Figure 6, it was also possible to see that for the D, E and F series, there was a direct relationship between the reaction time and amount of lead removed. The vacuum pressure of 1333 Pa (used in E and F series) is higher than the vapor pressure of lead at 800°C (7.54 Pa). However, this series of experiments, performed under low pressure, obtained significantly greater amounts of lead removal than those performed at atmospheric pressure. This means that, under low pressure, lead remains liquid, but is probably reacting more intensely with the other glass components and is removed.

The type E reactions showed a percentage of lead removal greater than 70%, reaching 85% with sample E5 (24 hours). However, the sample E3 had a rate of 81% lead removal in a reaction time of 10 hours, which is significantly lower than the sample E5 (24 hours of reaction time). This short reaction time decrease the energy cost of the process without significantly affecting the lead removal efficiency.

The type F reactions showed the best results of all the samples. The removal of lead attained 92% in sample F4 (18 hours). There are no large variations of lead removal with the reaction time. Sample F1, which remained in the furnace for 2 hours, showed a removal rate of 85%, while sample F5, which was 24 hours in the furnace, had a rate of 91%.

4. Conclusions

Initially, it was concluded that not all of the glass present in the cathode ray tube has lead in its composition. Panel glass, since separated from other, can be easily recycled. The funnel and the neck glass have, respectively, between 20% - 28%, and 25% - 30% of lead oxide in their composition.

For this study, the thermal processes performed for lead removal from the glass showed promising results. The use of inert atmosphere - argon (type A) and carbon dioxide (type B) for lead removal showed lower rates (66 and 48% respectively) than those listed under the influence of ambient atmosphere (type C). It was expected that these atmospheres (A and B) interact with the sample in the furnace and promote better lead removal rates, but the results did not confirm this expectation. In these experiments (type A and B reactions), it was determined that the best percentage of reducing agent (carbon) was 5%.

It was also concluded that only the heating of the funnel glass to temperatures of 1200°C (ambient atmosphere) promotes the removal of lead from the glass matrix (reaction type C), since there is already carbon on the surface of the glass (present in the coating) and it can act as a reducing agent. In the type D reaction, an agent reducer (5%) was added and the removal rate increased after 8 hours of experiments, reaching a removal of 73% with 24 hours.

The best results for lead removal occurred under low pressure with 5% of carbon as the reducing agent (type F reactions). The vacuum reduces the temperature at which lead can be removed by increasing the vapor pressure, thereby facilitating the lead removal. Under these conditions, it was possible to remove 92% of the lead in the glass of CRTs using a thermal process.

Thus, it is was concluded that it is possible to remove the lead from the glass matrix of CRTs using thermal processes, allowing reuse and/or recycling of glass in a more environmentally safe disposal.

5. Acknowledgments

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6. References

ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. ***Norma NBR 10004:*** Resíduos Sólidos - Classificação. Rio de Janeiro, 2004.

—. ***Norma NBR 10005:*** Lixiviação de Resíduos. Rio de Janeiro, 2004.

—-. ***Norma NBR 10007:*** Amostragem de Resíduos. Rio de Janeiro, 2004.

CHEN, MENGJUN, ZHU, JIANXIN. Lead recovery and the feasibility of foam glass production from funnel glass of dismantled cathode ray tube through pyrovacuum process. ***Journal of Hazardous Materials***, v. 161, p. 1109–1113, 2009.

De OLIVEIRA, C.M., BERNARDES, A.M., GERBASE, A.E. Collection and recycling of electronic scrap: A worldwide overview and comparison with the Brazilian situation. ***Waste Management***, v. 32, p. 1592-1610, 2012.

De OLIVEIRA, E.L., RICHTER, G.M., VEIT, H.M. Leaching of Cathode Ray Tubes as a justification for recycling. In: CONGRESSO INTERNACIONAL DE TECNOLOGIAS PARA O MEIO AMBIENTE, 3., 2012, Bento Gonçalves. ***Anais eletrônicos.*** Bento Gonçalves: FIEMA, 2012.

DONDI, M. et al. Recycling PC and TV waste glass in clay bricks and roof tiles. ***Waste***

Management, v. 29, p. 1945–1951, 2009.

ENVIRONMENT AGENCY IRLAND. Consolidated European Waste Catalogue. Environment Agency Hazardous Waste. 2008.

ICER. Materials recovery from waste cathode ray tubes (CRTs). ***The Waste & Resources Action Programme***, 2004.

JANG, Y., TOWNSEND, T.G. Leaching of Lead from Computer Printed Wire Boards and Cathode Ray Tubes by Municipal Solid Waste Landfill Leachates. ***Environmental Science & Technology,*** v. 37, p. 4778–4784, 2003.

KIM, D. et al. Encapsulation of lead from hazardous CRT glass wastes using biopolymer cross-linked concrete systems. ***Waste Management***, v. 29, p. 321–328, 2009.

MÉAR, F., YOT, P., RIBES, M. Effects of temperature, reaction time and reducing agent content on the synthesis of macroporous foam glasses from waste funnel glasses. ***Materials Letters***, v. 60, p. 929–934, 2006.

MUSSON, S. et al. Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure. ***Environmental Science and Technology,*** v. 34, p. 4376-4381, 2000.

NNOROM, I.C. et al. Global disposal strategies for waste cathode ray tubes. ***Resources, Conservation and Recycling,*** v. 55, p. 275-290, 2011.

OSTERMAN, V. et al. Critical Melting Points and Reference Data for Vacuum Heat Treating. Solar Atmospheres Inc., 2010. Available at: http://solarmfg.com/wp-content/uploads/2011/01/Critical-Melting-Point1.pdf

PRUKSATHORN, K., DAMRONGLERD, S. Lead recovery from waste frit glass residue of electronic plant by chemical-electrochemical methods. ***Korean Journal of Chemical Engineering,*** v. 22, p. 873–876, 2005.

ROCHA, H.T.R. et al. Diagnóstico da geração de resíduos eletroeletrônicos no Estado de Minas Gerais. Fundação Estadual do Meio Ambiente, 2009.

XING, M.F., ZHANG, F.S. Nano-lead particle synthesis from waste cathode ray-tube funnel glass. ***Journal of Hazardous Materials,*** v. 194, p. 407–413, 2011.

XU, QINGBO, et al. Cathode ray tube (CRT) recycling: current capabilities in China and research progress. ***Waste Management***, v.32, p. 1566–1574, 2012.

YOT, PASCAL, G., MÉAR, FRANCOIS, O. Characterization of lead, barium and strontium leachability from foam glasses elaborated using waste cathode ray-tube glasses. ***Journal of Hazardous Materials***, v. 185, p. 236–241, 2011.

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