



Effect of Temperature and Time on Lead Recovery from Waste Cathode Ray Tube Funnel Glass by Pyrovacuum Reduction Technique

Prof. Dr. Muna K. Abbass¹, Assit. Prof. Dr. Abdulkaliq F. Hmood², Salam Z. Abbas³

Dept. of Production Engineering and Metallurgy, University of Technology, Baghdad, Iraq

Abstract: The disposal of cathode ray tubes (CRT) represents a major challenge because of their toxicity and volume. There are several methods to separation lead from this glass and take advantages of the residue. In this study, the metallic pure lead was recovered from waste (CRT) funnel glass by a modern and effective process known as pyrovacuum reduction process. The parameters of this process are holding time (1, 2, 3, 4 & 5 h) and temperature (700, 800 & 900 °C) with other fixed conditions such as pressure (10^{-1} mm Hg) and carbon adding amount (9 %). The maximum pure lead recovery has reached 99 % at 900 °C and 5 h (best conditions). It was shown that the purity of recovered lead was 99 % in pyrovacuum process.

Keywords: CRT, Funnel Glass, Pyrovacuum Reduction, Recovery of Lead

I. INTRODUCTION

In the past decades, the treatment of waste (CRT) glass has attracted special attention because liquid crystal display (LCD) and light emitting display (LED) technologies are replacing old (CRT) glass, therefore, the disposal of cathode ray tube (CRT) monitors and televisions increases each year, generating very large quantities of scrap containing many types of materials [1]. In addition to the stopping of the recycling industry (closed loop) of scrap(CRT) to new (CRT) [2]. Several countries, such as Taiwan, China, and United states, discard yearly almost 1 million, 5 million, and 3.2 million Pieces respectively. The (CRT) televisions and monitors consist of three main parts, namely CRT tube, polymeric frame, and circuit board [3]. The (CRT) tube is made up of three components namely, screen (front panel), funnel, and neck (electron gun) as shown in **Figure 1**.

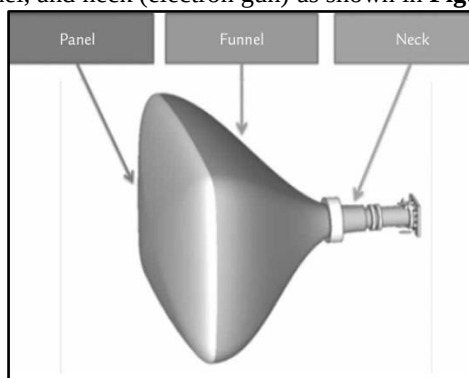


Figure1: The parts of cathode ray tube glass [4]

The panel glass contains barium oxide but does not contain lead oxide while, the funnel and neck glass contains lead oxide to absorb x-ray radiation and UV emitted from the electron gun [4]. Funnel glass is the biggest part of (CRT) glass representing about one-third from all weight of (CRT). This part is considered as toxic waste because it contains high quantity of lead (20 – 25 % of lead oxide) [5]. Lead is a toxic metal and its effects to human health and its impact on the environment have been a great concern to the society for a long time, perhaps more than the other metals [6]. The most serious case, the direct disposal of lead glass in the landfills has become one of the most dangerous things, because it will contaminate the soils and therefore would contribute to the environmental pollution [7]. The lead separation from funnel glass is impossible to complete the lead recovery by traditional acid leaching methods, because the extremely stable structure of this type of glass [8]. In a previous study, the researchers used the reduction melting process at normal atmospheric pressure. This process is simple and does not require complex equipment. The researchers concluded that the highest recovery rate was 96 % at 1400 °C, however, this method is economically expensive and needs large amount of energy to separate the metallic lead from CRT glass [9]. In other studies, the researchers studied the effect of chlorinating volatilization process on scrap funnel glass for detoxification. After testing various parameters on the lead separation from this glass, the study concluded the best operating conditions of temperature, time, and pressure which were 1000 °C, 2 h, and 600 ± 50 Pa respectively and the maximum evaporation rate was 99 % [10]. The aim of this work is to

study the effect of pyrovacuum reduction process parameters (temperature and holding time) on the lead recovery from (CRT) funnel glass , the possibility of transfer the residue glass in this process to other industries such as foam glass, glass matrix composites, and glass ceramics, in addition to the environmental safety was evaluated.

II. MATERIALS AND METHODS

A. Sample Preparation

Cathode ray tube (funnel glass) sample was prepared from the waste (old television). Then the funnel glass was dismantled from the other (CRT) glass of the glass parts such as screen and neck, and the glass coatings was removed by wet - scrubbing .The funnel glass was crushed into smaller particle sizes (around 3cm) by using jaw crusher type (Retsch – BB200 rostfrei) . Then grinding the funnel glass by using dry ball mill type (Retsch – PM 100) was done , rotation speed was 250 rev/min for 5 min and it was repeated for three times . Sieving process was carried out by using auto sieve shaker type (Impact, ISO 3310-1:2000) , in order to get the desired particle size (-53 μm) for the glass powder .The sample of the glass was analyzed by x-ray fluorescence (XRF) type (SHIMADZO,EDX-7000), in order to determine the initial lead concentration before starting the pyrovacuum process as shown in **Table 1**. The main steps of sample preparation was shown in **Figure 2** .

Table 1: Chemical composition of CRT funnel glass by XRF after sieving process to size (-53 μm)

Oxide	SiO ₂	PbO	K ₂ O	Na ₂ O	Al ₂ O ₃	SrO	BaO	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	ZrO ₂
wt%	48.68	24.45	9.78	5.22	4.40	2.10	1.96	1.81	1.28	0.20	0.08	0.05

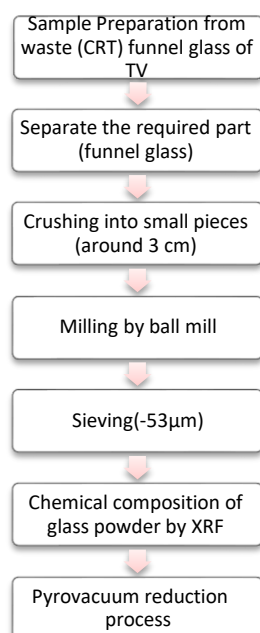


Figure 2: Illustrating the experimental steps of sample preparation used in this study .

B. Pyrovacuum Process

The process of pyrovacuum reduction was carried out in a special system designed and built up for this purpose as shown in **Figure 3**. The system consists of tube chamber which does the following processes :reduction, evaporation and condensation .

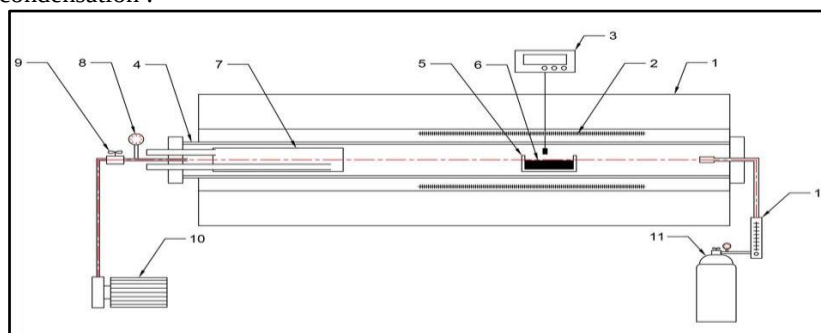


Figure 3: Schematic diagram of the lead recovery system: 1. block of the system, 2. spiral heaters, 3.thermal control device, 4. vacuum tube, 5. crucible, 6. funnel glass powder, 7. air cooling device, 8.vacuum gauge, 9. screw valve, 10. vacuum pump, 11. argon gas, 12. flow meter .

A (5 g) of glass powder was mixed with carbon powder of particle size ($-53\ \mu\text{m}$) as a reducing agent . The mixture of glass powder and carbon was dried at $100\ ^\circ\text{C}$ for 24 h. After drying the mixture was placed in a special crucible (looks like a boat) and placed in a tube chamber and closed this tube. Before starting the vacuum process, argon gas was pumped into the tube and then discharge it, to expel the air from the system .The temperature was raised for various temperatures ($700, 800,$ and $900\ ^\circ\text{C}$) , for various holding time (1, 2, 3, 4 and 5 h) , in order to determine the best parameters (temperature and time) at constant pressure ($10^{-1}\ \text{mm Hg}$) and constant carbon adding amount (9 %) . After the end of the testing time, the system was cooled down to room temperature, then the tube chamber was released to the ambient pressure . **Figure. 4** shows the mechanism of pyrovacuum reduction process . The redox reaction between lead oxide and carbon powder as shown in equation 1[11] .

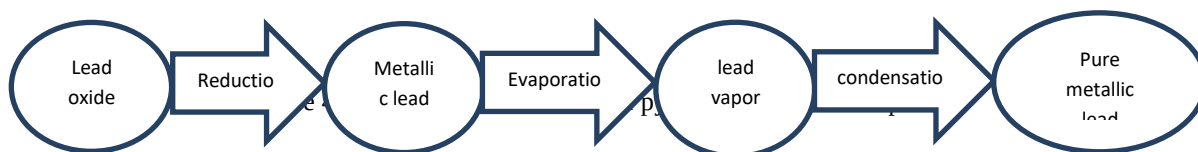
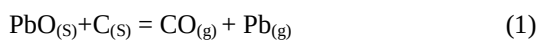


Figure 4: Steps for the mechanism of pyrovacuum reduction process .

III. RESULTS AND ANALYSIS

Physical and chemical tests were conducted for the recovered metallic lead and the residue of funnel glass . Characterization of the metallic lead was done by X-ray diffraction (XRD) using (Rigaku MiniFlex™ II diffractometer) with CuK α radiation of $\lambda=1.540$, current $t = 15\ \text{mA}$, voltage = $30\ \text{kV}$. **Figure.5** illustrates that no phase except metallic lead could be observed in the (XRD)analysis . The result was (99 %) of the metallic lead analysis by atomic absorption type (Phoenix - 986) . Also the atomic absorption type (Phoenix - 986) has shown that the lead content in the residue varies from (11.2 %) at $700\ ^\circ\text{C}$ for 1 h to (0.22 %) at $900\ ^\circ\text{C}$ for 5 h, according to the experimental conditions . **Figure.6** shows image taken by the Scanning Electron Microscopy (SEM) type (T ScanVEGA3LMU), image of the residue illustrates the porous form as raw material for the industry of foam glass, especially when the glass became a non-toxic material.

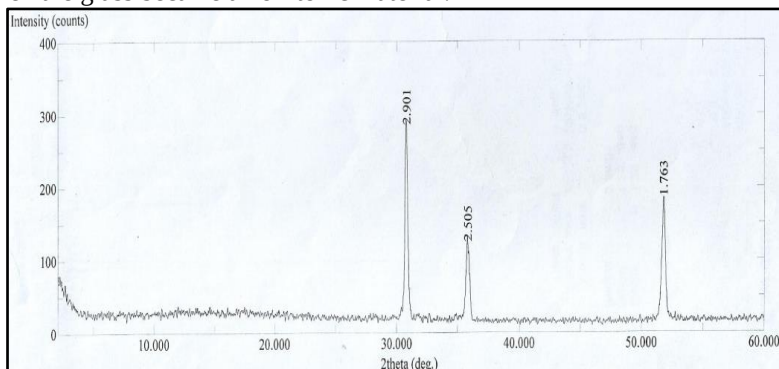


Figure 5: XRD pattern of the recovered metallic lead .

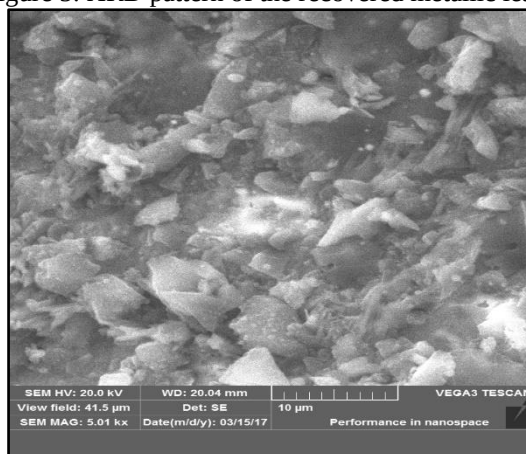


Figure 6: SEM image of the residue funnel glass after pyrovacuum reduction process .

IV. RESULTS AND DISCUSSION

A. Effect of Temperature on Lead Recovery

Table 2 shows the time and temperature variables and their effect on the rate of lead recovery. Temperature is a very effective factor in reduction of lead oxide, evaporation of lead metal and then condensation of this vapour. **Figure 7** illustrates that increasing the temperature has a very positive effect on the rate of lead recovery especially above 800 °C, where the lead recovery was increased from 75.67 % at 700 °C to 98.28 % at 800°C. This is because the reduction process of lead oxide was started at (380 °C), subsequently the lead oxide found in glass powder has been completely transformed into metallic lead at (800 °C). This result is consistent with reference [11]. In addition to the vapour pressure of lead element (saturation pressure= 10^{-1} mm Hg or 13Pa) is almost equal to operation pressure at 800 °C [12]. The lead recovery rate was calculated according to lead concentration in the funnel glass before and after the pyrovacuum process as shown in equation 2. [11].

$$\text{Lead recovery \%} = \frac{C_1 - C_2}{C_1} \times 100\% \quad (2)$$

Where C_1 : Lead concentration in the funnel glass before the thermal reduction process.

C_2 : Lead concentration in the residue of funnel glass after the thermal reduction process.

Table 2: Effect of time and temperature on the lead recovery rate with constant pressure (10^{-1} mm Hg) and constant carbon amount adding (9 %).

Temperature °C	Time h	Lead % in residue	Recovery rate %
700	5	5.51	75.76
800	5	0.39	98.28
900	5	0.22	99.03
900	4	0.28	98.76
900	3	0.30	98.67
900	2	0.42	98.14
900	1	0.49	97.84

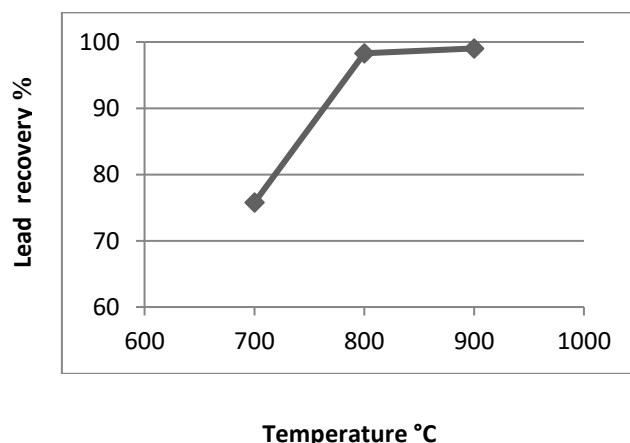


Figure 7: Relationship between lead recovery and temperature, other conditions: holding time = 5 h, carbon adding amount = 9 %, pressure = 10^{-1} mm Hg.

4.2 Effect of Time on Lead Recovery

The increase of time significantly affected the lead recovery ratio as shown in **Figure 8**. It was noticed that the rate of recovery increased with increasing time. This result is consistent with references [3,11]. It is clear from **Figure 8** that the holding time at 5 h gives a lead recovery rate of 99.03 % which is the highest ratio, so the holding time 5 h is optimum when other conditions are fixed.

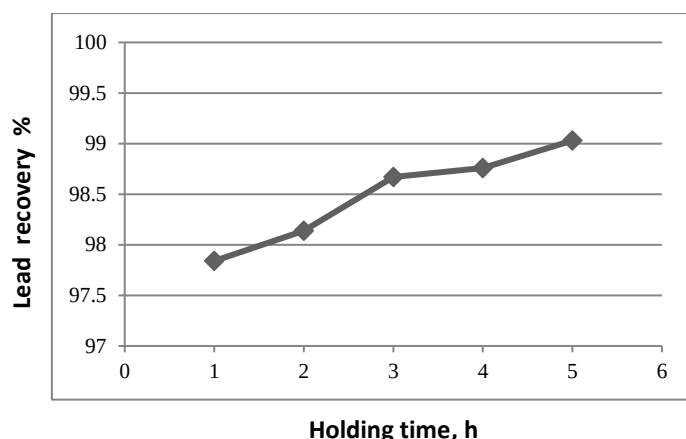


Figure 8: Relationship between lead recovery and holding time, other conditions : temperature = 900 °C, carbon adding amount = 9 %, pressure = 10^{-1} mm Hg.

V. CONCLUSION

It is clear that the effect of the pyrovacuum reduction process on removing the toxicity and lead recovery was successful. The optimum conditions were: temperature (900 °C) and holding time (5 h), the maximum lead removal reached 99.03 %. The recovered metallic lead was (99 %) where it can be used in many industries . The glass residue has become non-toxic material and it is possible to utilize it in foam glass industry and other fields .The most important aspect is to protect the environment and especially the soil from the lead toxicity .

REFERENCES

- [1] W.Meng, X.Wang, W.Yuan, J.Wang, G.Song. The recycling of leaded glass in cathode ray tube (CRT). *Procedia Environmental Sciences*, vol.31, pp.954-960, (2012) .
- [2] T.Okada, S.Yonezawa. Energy efficient modification of reduction melting for lead recovery from cathode ray tube funnel glass. *Waste Management*, vol.33, pp.1758-1763, (2013).
- [3] H.M.Veit, E.D.Oliveira, G.Richter. Thermal processes for lead removal from the funnel glass of CRT monitors. *Metallurgy and materials*, vol.68, pp.287-294, (2015).
- [4]]New approach to cathode Ray Tube (CRT) recycling, Report prepared by ICER for DTI, GW-12.10-130, (2003).
- [5] X.Lu, K.Shih, C.Liu, F.Wang. Extraction of Metallic Lead from Cathode Ray Tube (CRT) Funnel Glass by Thermal Reduction with Metallic Iron. *Environmental Science and Technology*, vol.47, pp.9972-9978, (2013) .
- [6] J R.J.Sinclar. *The Extractive Metallurgy of Lead*. Australasian Institute of Mining and Metallurgy, (2009).
- [7] N.Hiroyoshi, H.Prin, Y.Takaya, M.Ito. Application of Reductive Melting Process of CRT Glass for Recovering Valuable Metals from PCB Waste. *Resources Recycling. The 11th International Conference on Mining, Materials and Petroleum Engineering*, pp.33, (2013).
- [8] W.Yuan, W.Meng, J.Li, C.Zhang, Q.Song, J.Bai, J.Wang, Y.Li. Lead recovery from scrap cathode ray tube funnel glass by hydrothermal sulphidisation. *Waste Management and Research*, pp.1-7, (2015) .
- [9] T.Okada, H.Inano, N.Hiroyoshi. Recovery and immobilization of lead in cathode ray tube funnel glass by a combination of reductive and oxidative melting processes . *Journal of the Society for Information Display*, vol.20, pp.508-516, (2012).
- [10] A.Erzat, F.S.Zhang. Detoxification effect of chlorination procedure on waste lead glass. *The 8th International Conference on Waste Management and Technology*, vol.16, pp.623-628, (2014).
- [11] M.Chen, F.S.Zhang, J.Zhu. Lead recovery and the feasibility of foam glass production from funnel glass of dismantled cathode ray tube through pyrovacuum process . *Journal of Hazardous Materials*, vol.161, pp.1109-1113, (2008).
- [12] N.Yoshimura. *Vacuum Technology*. Springer, (2008).