Development of a method for recycling of CRT funnel glass

Tung-Chai Ling and Chi-Sun Poon*
Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong.

Abstract
Finding better solutions to manage and recycle cathode-ray tube (CRT) glass is crucial for reducing the environmental threats due to the disposal of the glass. In this paper, the results of a laboratory study on developing a method for removing lead from crushed funnel glass surface and re-utilizing the treated glass in cement mortar are presented. The results demonstrate that nitric acid at 3% to 5% concentration levels can be used to remove most of the lead from the crushed funnel glass surface and render it as non-hazardous waste based on TCLP testing. It is noted that the particle size of glass and number of treatment cycles are significant factors affecting lead extraction. The study further demonstrated that it is feasible to utilize up to 100% of treated funnel glass as a replacement for natural sand for producing cement mortar.

Keywords: Cathode ray tubes, recycled funnel glass, lead extraction, nitric acid, cement mortar.

1. Introduction
The disposal of cathode ray tube (CRT) based monitors from old computer and television sets has become a major environmental concern due to the rapid development and introduction of LCD/LED display models [1-3]. In Hong Kong, about 6 million sets of computers are currently being used and about 20% of the stocks are replaced annually [4]. Some of them are discarded even before the end of their useful life and the discarded number is expected to keep increasing in the coming years. The traditional management solution of CRT waste in Hong Kong is landfilling; however, it is environmentally not desirable since the toxic constituents (e.g. Pb) could be leached to the environment [1, 5].

With rising awareness of the problems caused by lead leaching from CRT glass, the disposal of CRT at landfills is strongly discouraged [6]. The reuse of outdated sets by redistribution may slow down or delay the rate of CRT disposal, but treatment at the end of their life cycle remains a major issue in modern society. Also, the potential to reuse CRT glass in the assembly of new units is not high due to the shrinking market demand for CRT worldwide. In some countries, such as Sweden, abandoned CRT glass is crushed and sent to lead smelting [7]. This application is preferable to landfilling, but the problems of high processing cost and the potential volatilization of constituents (e.g. PbO) need to be addressed. In
Italy, a direct-sintering of powdered CRT glass process has been successfully implemented to produce new dense glass-based products [8]. Since the technology only require processing at a relatively low temperature, making this approach more feasible. In most cases, however, extraction and purification are carried out to ensure that the recycled glass is non-toxic [9].

It is well-known that CRT funnel glass contains a significant amount of lead (22-25% wt) [10-11]. A number of studies have been conducted to investigate the effectiveness of using distilled water, alkali and acid solutions as an extraction fluid for lead recovery and other heavy metals removal from crushed the CRT glass [12-14]. Foresman and Foresman [12] found that a 3% (wt) solution of alkali hydroxides can remove lead on the surface of pulverized glass at 70°C. Similar findings were also reported by Goforth et al. [13], and they proved that Pb can be extracted from a CRT funnel glass sample with a carbonate/bicarbonate buffer (pH 9). To further enhance the lead removal efficiency, Stephen et al. [15] have suggested grinding the glass into finely ground powder instead of using coarsely crushed glass, but this would ultimately increase the cost of the whole treatment process. Saterlay et al. [16] have proposed a simple method using a combined chemical and ultrasound method. The ultrasonic vibration has been found to accelerate the leaching process over the conventional stirring method, allowing removal of over 90% of the leachable lead after only 1 h of sonochemistry-leaching. The effects of adding silicon carbide and titanium nitride as reducing agents have also been investigated [17-18]. Silicon carbide has been proven to be more effective in reducing Pb(II) and Pb(O) than that of titanium nitride. Chen et al. [19] also found that 98.6% recovery rate of lead can be achieved at the right conditions. They further noted that the recovered funnel glass can be re-used for the production of new foam glasses.

In finding an alternative to the current CRT glass disposal method, encapsulating the Pb-containing glass particles in a polymer concrete composite had been studied [20], and the results showed the polymer concrete system could considerably decrease the lead leachability.

In this study, we attempted to i) develop a method for removing the leachable lead from crushed CRT funnel glass (to examine the influence of crushed glass size, acid solutions and treatment cycles on lead removal) and ii) evaluate the feasibility of re-utilizing the treated CRT funnel glass to produce cement mortar (to examine the influence of glass content on the fresh and hardened properties, potential leaching of lead, and the potential use as mortar as a shielding material for x-ray radiation).

2. Removal of lead from crushed CRT funnel glass surface
Removal of leachable lead from discarded CRT glass is the goal of the present study. It is known that the concentration of lead within CRT funnel glass is much higher than other parts of the CRT [1, 21]. Therefore, only CRT funnel glass was investigated in this study and it was sourced from a local CRT recycling facility. The initial characterization of CRT glass was the determination of “total” metal concentrations and their leaching behaviour.
2.1. “Total” lead concentration of CRT funnel glass (ground powder)

The “total” concentration of lead metal in funnel glass was determined by using a strong acid digestion method. Dismantled CRT funnel glass was first crushed and then ground into fine powder for “total” lead metal analysis. Together with standards and blanks, triplicate samples of about 0.25 g of the glass powder were digested with a mixture of concentrated nitric and perchloric acids in a 4:1 volume ratio. The powder was digested at 65, 90, 115, 135, 160 and 185°C until dry. The remaining residues were finally leached for one hour in 10 ml of 5% nitric acid. The leachates were then centrifuged at 3500 rpm for 10 min and analyzed for total lead content using induction coupled plasma atomic emission spectroscopy (ICP-AES). The “total” lead concentration of CRT funnel glass is presented in Table 1. The results reported are the mean values of 3 measurements (the range is within ±5%).

Table 1. “Total” lead concentration of tested CRT funnel glass.

<table>
<thead>
<tr>
<th>CRT funnel glass</th>
<th>Lead (Pb) (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinded glass powder</td>
<td>13000</td>
</tr>
</tbody>
</table>

2.2. Leachable lead from crushed funnel glass surface – Toxicity characteristics leaching procedure

The metal leaching properties of crushed CRT funnel glass were examined by the standard toxicity characteristics leaching procedure (TCLP). The TCLP test, originally developed by the U.S. Environmental Protection Agency (EPA) is a standard procedure carried out to determine if waste is hazardous or otherwise [22]. The test was carried out at room temperature of about 20 °C. The leaching fluid with a pH value of 2.88 was prepared by diluting 5.7 mL of glacial acetic acid in 2 L of distilled water. Then the extraction was done by putting 20 g of the glass sample in 400 ml of the prepared extraction fluid and the mixture was tumbled for 18 h in a rotary mixer.

As can be seen in Table 2, the leachable Pb concentration from samples with a particle size of 2-5 mm was about 37 mg/L. This value increased by approximately 10-fold to 330 mg/L when the particle size of glass was reduced to below 2 mm. This is consistent with the results of previous studies [10, 16], reporting that more lead was leached from samples with smaller particle size, probably due to more surface area being exposed. The Pb concentration, however, did not change much for the sample size of <0.6 mm. The values detected were all above the U.S. EPA regulation concentration (5 mg/L) for Pb and thus funnel glass should be classified as a hazardous material.

Table 2. TCLP results of crushed CRT funnel glass with different particle sizes

<table>
<thead>
<tr>
<th>Particle size</th>
<th>Pb concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-5 mm</td>
<td>36.8</td>
</tr>
<tr>
<td>0.6-2 mm</td>
<td>328.0</td>
</tr>
<tr>
<td>&lt;0.6 mm</td>
<td>332.0</td>
</tr>
</tbody>
</table>
2.3. Influence of nitric acid solutions and glass size on the removal of leachable lead from crushed funnel glass surface – preliminary laboratory trial

It is known that the particle sizes of funnel glass and nitric acid solutions (strength of extraction) are contributing factors to the variability in lead leaching levels. Three different particle sizes (2-5 mm, 0.6-2 mm and <0.6 mm) of glass were assessed. Three different nitric acid solutions (1%, 3% and 5%) were used to extract Pb from the crushed funnel glass surface at a solid:liquid ratio of 1:5. The concentrations of lead in the acid solutions after the extraction process are given in Tables 3 and 4.

As seen in Table 3, the Pb concentration detected did not show a direct relationship with strength of the acid used, regardless of the particle size of glass. However, there was a general increase of Pb concentration in the extracts with decreasing glass particle size.

Table 3. Pb concentration after extraction by different acid solutions

<table>
<thead>
<tr>
<th>Acid solutions</th>
<th>1% HNO₃</th>
<th>3% HNO₃</th>
<th>5% HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle sizes (mm)</td>
<td>2-5</td>
<td>0.6-2</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Extracted Pb (mg/L) from crushed funnel glass surface</td>
<td>365</td>
<td>405</td>
<td>475</td>
</tr>
</tbody>
</table>

Table 4. TCLP results of treated glass.

<table>
<thead>
<tr>
<th>Acid treated glass</th>
<th>1% HNO₃</th>
<th>3% HNO₃</th>
<th>5% HNO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle sizes (mm)</td>
<td>2-5</td>
<td>0.6-2</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Pb (mg/L)</td>
<td>58.2</td>
<td>16.8</td>
<td>4.30</td>
</tr>
</tbody>
</table>

The leachable lead from the funnel glass after being treated with different acid solutions is presented in Table 4. It is important to note that the funnel glass treated with 1% HNO₃ failed the TCLP test (> 5 mg/L) in all but one case. This result suggested that 1% nitric acid might not be able to remove all the easily removable lead from the glass surface in the treatment process. On the other hand, both 3% and 5% nitric acid treatments achieved the necessary acid removal efficiency as the TCLP leachates from the respective treated funnel glass were all below 5 mg/L. Therefore, nitric acid treatment at a concentration of 3% or 5% was proved to have sufficient ability to remove most of the lead from the funnel glass surface and render it non-hazardous waste. After taking cost, time and operational considerations (treatment cycles per acid solution) into account, it was recommended that CRT funnel glass be crushed down to < 5 mm and treated with a 5% nitric acid concentration. Based on the above results, the following treatment train was designed and tested in the laboratory.

2.4. Removal of leachable lead from CRT funnel glass – a laboratory pilot-scale test

Based on the above findings, crushed funnel glass with a particle size of 0.6-2 mm and nitric acid concentration of 5% were chosen for further investigation. A 20-cycle treatment scheme was tested in the
laboratory to predict the lifetime of acid solutions in the treatment beakers. The following describes the treatment procedures for the funnel glass under a laboratory pilot-scale test and the details are shown in Figure 1.

2.4.1. Treatment process

2.4.1.1. Acid treatment. 0.6-2 mm crushed funnel glass was immersed in a 5% nitric acid solution for about 3 h to extract lead from the glass surface. The glass was stirred every hour for a minute so that all glass surfaces were exposed to the acid solution. Acid-washed glass inside the stainless steel container was then removed from the beaker and the carryover acid retained between the glass particles was removed by free draining for about 15-30 min. The recovered glass was subjected to water soaking and the acid solution was retained for the next round of glass treatment. At the end of the process, the Pb-containing acid solution which was regarded as a hazardous waste was sent to a local chemical waste treatment plant for further treatment and disposal.

Figure 1. Flow diagram of the treatment procedure.
2.4.1.2. **Soaking process.** The acid-treated glass from the acid beaker was placed in the soaking beaker (beaker) so that the remaining acid on the glass surface could be washed away. The glass was soaked for 1.5-2 h and stirred for a minute at the beginning and at the end of the treatment period. The soaked glass was then recovered with a free draining approach. The recovered soaking solution was retained for the next soaking cycle.

2.4.1.3. **Rinsing process.** The soaked glass from the previous treatment steps was rinsed using clean tap water. The soaked glass was washed with flowing water for approximately 10 min (approximately 36 L). The rinsed glass was recovered and dried overnight before being subjected to the TCLP procedure to assess whether the treated glass is still classifiable as hazardous waste. Samples of the rinsing water were collected during the process to monitor water quality as well.

2.4.2. **Findings**

The solutions from all beakers (acid beaker, soaking beaker and rinsing beaker) were analyzed for Pb concentration after the treatment cycles and the results are summarized as follows. All the data reported in Figures 2-4 were within the two standard deviations of the mean.

2.4.2.1. **Lead concentration in acid beaker.** The results of extracted lead from 0.6-2 mm crushed funnel glass contained in the 5% nitric acid beaker up to 20 treatment cycles are shown in Figure 2. As can be seen in the Figure, the Pb concentration increased to approximately 14000 ppm at the end of 20 cycles in the acid beaker, with an average increasing rate of 700 ppm per cycle.

![Figure 2. Pb concentration after treatment cycles.](image-url)
2.4.2.2. Lead concentration in soaking beaker. Figure 3 shows that the Pb concentration in the soaking beaker reached about 2000 ppm after 20 cycles of soaking, with a 100 ppm increase/cycle on average.

![Graph showing the lead concentration in soaking beaker](image)

Figure 3. Pb concentration of soaking water after treatment cycles.

2.4.2.3. Lead concentration in rinsing beaker. The Pb concentrations in the effluent was determined. As shown in Figure 4, the rinsing water displayed a Pb concentration that was within the government sewer discharge limits of <2.5 ppm. Thus, the wastewater from the rinsing beaker can be normally discharged without treatment.
Figure 4. Pb concentration of rinsing water after treatment cycles.

2.4.2.4. **TCLP results of treated funnel glass**

At the end of the three-step treatment process, the treated funnel glass was dried in air and then subjected to the TCLP test. As observed in Figure 5, all the treated glass could be classified as non-hazardous waste as the leachable Pb concentrations were below the 5 ppm limit. This result shows that the leachable lead from the crushed CRT funnel glass can be effectively removed by the developed treatment method.

Figure 5. Pb concentration in TCLP leachates of treated CRT funnel glass.
3. Use of treated CRT funnel glass in cement mortar

3.1. Producing CRT-based cement mortar

The feasibility of using the treated glass as 25%, 50%, 75% and 100% replacements of river sand in cement mortar was investigated. The particle size of natural river sand and the treated funnel glass used was both < 5 mm. ASTM Type I ordinary Portland cement and fly ash complying with ASTM class F ash were used as the cementitious materials. The mix proportion designed for the control mortar mix (without CRT glass) was 0.75:0.25:2.5:0.45 (cement:flyash:sand:water). After measuring the fresh properties, three types of samples using steel moulds were cast, (i) 40×40×160 mm for flexural strength test, (ii) 25×25×285 mm for alkali-silica reaction and (iii) 5×100×100 mm for X-ray radiation shielding/attenuation ability. The prepared samples were demoulded after 1 day and placed in the water curing tank (at 27°C) until the day of testing.

3.2. Testing for CRT-based cement mortar

The flow table test was used to determine the workability of the fresh mortar mix as described by ASTM C1437 [23]. The hardened density of mortar was determined by using a water displacement method according to ASTM C642 [24]. A three-point flexural strength test in conformity with ASTM C348 [25] was performed at 1, 7 and 28 days on the prism specimens (40×40×160 mm). The 25×25×285 mm mortar bar specimens were used for the alkali-silica reaction (ASR) test in accordance with ASTM C1260 [26]. In order to assess the leaching potential of lead from the crushed CRT-based cement mortar samples, the TCLP test was conducted on the fractured prism samples after the flexural strength tests. A typical diagnostic X-ray tube and radiation monitor controller were used to assess the radiation shielding/attenuation ability [27].

3.3. Results of CRT-based cement mortar

The fresh and hardened properties as well as the lead leaching of the crushed mortar samples and radiation shielding properties test results of all CRT-based cement mortar mixes are shown in Table 5.

3.3.1. Fresh properties

The flow table results of CRT-based mortar mixes shown in Table 5 indicate that the inclusion of CRT treated funnel glass in the mortars significantly increased the flow values. The increase of fluidity may be due to the impermeability and the smooth surface of the glass compared to that of sand [28]. The flow table value increased by about 17.5 mm for every 25% funnel glass replacement.

3.3.2. Hardened density

As shown in Table 5, the hardened density increased with increasing funnel glass content. 100% funnel glass-based mortar gave the highest density of 2,472 kg/m³, whereas 0% funnel glass-based mortar gave the lowest density of 2,208 kg/m³. The increase in density of the mortar specimens is attributed to the relatively high specific gravity of funnel glass compared to sand due to the presence of lead inside the glass.
Table 5. Experimental testing results of CRT-based cement mortar.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Flow value, mm</th>
<th>Density, kg/m^3</th>
<th>Flexural strength, MPa</th>
<th>ASR, %</th>
<th>TCLP, mg/L</th>
<th>Attenuation coefficient, mm^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>After mixing</td>
<td>28d</td>
<td>1d</td>
<td>7d</td>
<td>28d</td>
<td>14d</td>
</tr>
<tr>
<td>CRT0-mortar</td>
<td>120</td>
<td>2208 (±13.1)</td>
<td>3.3 (±0.11)</td>
<td>6.2 (±0.17)</td>
<td>7.1 (±0.32)</td>
<td>0.015 (±0.004)</td>
</tr>
<tr>
<td>CRT25-mortar</td>
<td>143</td>
<td>2289 (±24.4)</td>
<td>2.9 (±0.05)</td>
<td>5.8 (±0.41)</td>
<td>6.9 (±0.15)</td>
<td>0.024 (±0.004)</td>
</tr>
<tr>
<td>CRT50-mortar</td>
<td>160</td>
<td>2365 (±9.8)</td>
<td>2.7 (±0.06)</td>
<td>5.5 (±0.31)</td>
<td>6.2 (±0.33)</td>
<td>0.043 (±0.002)</td>
</tr>
<tr>
<td>CRT75-mortar</td>
<td>175</td>
<td>2422 (±6.0)</td>
<td>3.1 (±0.09)</td>
<td>4.9 (±0.48)</td>
<td>5.5 (±0.22)</td>
<td>0.048 (±0.004)</td>
</tr>
<tr>
<td>CRT100-mortar</td>
<td>190</td>
<td>2472 (±6.7)</td>
<td>2.8 (±0.30)</td>
<td>4.3 (±0.52)</td>
<td>4.3 (±0.11)</td>
<td>0.086 (±0.000)</td>
</tr>
</tbody>
</table>

Note: n.d. – not detected.

3.3.3. Flexural strength
The 1, 7 and 28-day flexural strength of the mortar mixes are illustrated in Table 5. The results show that control mortar without funnel glass showed the highest strength at all test ages and a gradual reduction in strength was observed with increasing funnel glass content. At 100% glass content, the 28-day flexural strength dropped from 7.1 MPa to 4.3 MPa, which indicated an average of 39.4% reduction in strength as compared to the control mortar. The decrease in strength is mainly attributed to the weak adhesion bond between the smooth surface funnel glass and the cement paste [29]. However, all the CRT mortars met the minimum requirements of ASTM C 1329 [30] for cement mortar Type M, S and N. Therefore, it can be concluded from these results that CRT-mortar can be used for building constructions.

3.3.4. Expansion due to alkali silica reaction
An accelerated mortar test method was used to assess the risk of deleterious expansion due to ASR. As expected, the association of funnel glass had a negative effect on the ASR expansion of the mortar mixes. It was noticed that the increase in funnel glass content caused expansion due to ASR (see Table 5). However, the expansions were controlled within the permitted limit of 0.1% at 14 days by the use of fly ash in the mixes. This could be understood by the fact that the pozzolanic reaction of fly ash could reduce the alkali hydroxide concentration in pore solution [31], resulting in less expansion ASR in the CRT-based cement mortar.
3.3.5. Lead leaching of crushed CRT-based cement mortar
The potential of in-service lead leaching of CRT-based mortar was examined by the TCLP test. The TCLP test results of crushed CRT-based mortars affirmed that the leaching of lead is below the detection limit of 0.06 ppm. Apparently, when the CRT funnel glass is incorporated in cement mortar, the cementitious matrix effectively solidifies the glass and immobilizes the lead by the alkaline environment in cement [32].

3.3.6. Radiation shielding properties
The x-ray radiation shielding test was performed in an x-ray laboratory designed for medical diagnostic examination. The results (Figure 5) show that the attenuation coefficient (shielding properties) of the cement mortars increased from 0.069 to 0.167 (per mm thickness) with an increase in CRT funnel glass content from 0% to 100%. This is because the lead contained within the funnel glass can actively interact with x-rays, thus reducing its energy and the depth of radiation penetration [33]. The half-value layer (HVL) was computed and it was found that the HVL provided by the mortar with 100% CRT funnel glass was about 4.2 mm which was around 50% more than the attenuation provided by the cement mortar without funnel glass. This proved that the CRT-based cement mortar is effective in shielding against x-ray radiation.

4. Conclusions
This study has demonstrated that the leachable lead of crushed CRT funnel glass particles can be effectively removed by an acid extraction method rendering the treated glass non-hazardous waste based on the TCLP test. Increasing the concentration of nitric acid solution up to 5% enhanced the removal ability of lead from the glass surface.

The study also has successfully demonstrated that treated funnel glass can be reutilized to replace up to 100% of the sand in cement mortar production. Incorporating the funnel glass increased the workability (flow table value) and hardened density but gradually reduced the flexural strength due to the weaker bonding between the smooth glass surface and the cement paste. All the CRT-based cement mortars showed innocuous ASR behaviour when fly ash was added. In addition, incorporating funnel glass in cement mortar greatly enhanced the radiation shielding properties, making it a potential construction material for use in the construction of radiation diagnostic rooms.

Acknowledgments
The authors would like to thank Environment and Conservation Fund, Woo Wheelock Green Fund and The Hong Kong Polytechnic University for funding support.

References


[22] U.S. Environmental Protection Agency, Test Method 1311, Toxicity Characteristic Leaching Procedure (TCLP), Specifications of the Committee on Analytical Reagents of the American Chemical.