Recycling of CRT glass in plastering mortars

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Abstract. Landfilling of end-of-life CRT (cathode ray tube), from computers and other electric or electronic equipment, is an emerging environmental issue which require immediate actions. CRT glass waste represents over 50% of the weight of WEEE (Waste Electrical and Electronic Equipment). However, recycling techniques for CRT glass represent a major problem due to the different compositions of the glass used in CRT manufacturing, in particular due to the presence of lead in various amounts in the panel, funnel and neck tubing. The present paper investigates an alternative method for CRT glass recycling by using it as a substitute for natural fine aggregates in plastering mortars. Research has been carried out for both: analysis of glass chemical stability (assessing the interaction with water to simulate the behaviour of CRT glass in landfills or discarded WEEE in inappropriate areas), and leaching behaviour of the binding mortars with CRT glass as fine aggregate substitute. The results showed that the obtained mortars presented a good chemical stability, the concentration of lead being under the detection limit.

1. Introduction
The demand of electrical and electronic equipment (EEE) for consumer has been on increase in last decades around the world, especially the demand of televisions and computers. Rapid advances in technology and ready availability of newer and cheaper designs have determined the customers to discard EEE even before the end of their useful life. This has the effect of generating very large quantities of electrical and electronic equipment waste (E-waste or WEEE), to be managed by the relevant responsible. Finding a sustainable, technically feasible and economically viable strategy for WEEE management has been not easy, especially due to their numbers and the toxic materials in their composition.

A cathode ray tube (CRT) is a device used as video display components of televisions and computers. It is estimated that CRT glass accounts for approximately 50% by weight of commercial electronics and 30% by weight of data processing equipment and also contains metals such as lead, strontium, antimony and barium [1, 2].

According to the literature, CRT displays consist of 85% glass, in which about 65% is panel glass, 30% funnel glass and 5% neck glass [3]. A wide variety of studies of the CRTs toxicity have demonstrated that the funnel glass and neck glass are hazardous waste, while the panel glass presents a lower toxicity [4]. The chemical composition varies between the funnel glass and panel glass, which need to be treated as leaded glass and, respectively as lead-free glass [5].

CRT waste has an important environmental impact, and implicitly also on human health, arise mainly from the lead content. The heavy metals pollution represents an important global issue because of their extremely toxic effect even at low concentrations. One of the highest environmental
risk is the omnipresence of heavy metals due to their toxicity, persistence and lack of biodegradation [6-8]. The main environmental impact of lead is due to the leaching of lead from broken CRT glass when it's mixed with acid waters in waste landfills, thus polluting both soil, subsoil and groundwater. Lead can affect almost any human organ, including the nervous system, the kidneys and the reproductive system. The primary negative effect of lead toxicity is on the central nervous system.

Regulations require the CRT glass waste to be recycled or re-utilised for different purposes. The two principal ways of recycling the CRT glass are „closed-loop“ recycling and „open-loop“ recycling. When recycling CRT waste, recovered glass can be used in further manufacture of same product (closed-loop recycling) or into other different products (open-loop recycling). Some major industries that have potential to use recovered CRT glass in open-loop recycling system are glass industry, ceramic industry and construction materials industry [1].

The provision of CRT glass as raw material of well-controlled quality is difficult due to the variation of its composition, which is largely considered as a trade secret by the producers [9], and the knowledge of the composition of CRT glass is very important. Therefore, recycling of CRT glass into new products could become an obstacle due to the differences in composition between CRT glass and other glass products [10]. The use of CRT glass in the manufacture of new products can only be effective if the degree of leaching of heavy metals does not exceed the limits values laid down by the regulations in force [11].

A direction for recycling the CRT glass waste can be their use as a replacement for natural aggregates in the manufacture of mortars and concrete for construction materials industry. There are numerous studies [12-15] and most of the results have shown that particle size and shape, chemical composition of the glass, replacement ratio have a significant impact on the performance of concrete and mortar. Natural river sand is commonly used as a fine aggregate for the production of mortar. Reuse of CRT glass to replace river sand is possible due to the same chemical structure. Excessive sand exploitation cause serious environmental problems. The use of alternative sources to obtain inorganic binding materials will reduce the consumption of natural resources and improve the sustainability of the developed materials. Also, the need to landfill certain waste, such as CRT glass, will be eliminated, reducing the long-term impact to the environment and human health.

The research reported in this paper was focused on a recycling technique for CRT glass into cementitious materials, namely plastering mortars. Mortars are well homogenized mixtures of water, binder, aggregate and additives. The CRT glass is used as a substitute for natural fine aggregates.

2. Materials and methods
The research was focused on a recycling technique for CRT glass into cementitious materials by using it as a substitute for natural fine aggregates in plastering mortars. For this purpose, the chemical stability in aqueous media of the CRT glass was assessed prior to its use in plastering mortars to investigate its pollution potential.

To determine the leaching behaviour of CRT glass (funnel glass, panel glass and mixture of the two types of glass in ratio 1:1), in particular to simulate the behaviour of CRT glass on landfills, leaching tests were performed according to the international standard SR EN 12457/1− 4: Leaching – Compliance test for leaching of granular waste materials and sludge. Distilled water as leaching agent and liquid-solid ratios (L/S) of 2 l/kg and 10 l/kg were used. Leaching tests were carried out with Dissolution Tester (USP) TDT-08L ELECTROLAB, with continuous slow stirring.

The results were expressed in mg/kg dry matter (DM). Results of leaching tests were compared to the limits values for waste acceptance on inert waste landfills in accordance with the requirements of Order 95/2005, shown in the Table 1.

The plastering mortars were prepared using ordinary Portland cement (CEM I 52.5R) and sand aggregate (mixed with CRT glass - funnel glass and panel glass in ratio 1:1). To obtain cubic mortar specimens, different water/binder ratios were used. The sand had a particle size distribution of 0.1-1 mm. CRT glass was milled to particle size of 0.31 mm. Also, the percentage of CRT glass sand substitution was varied. The influence of the addition of lime to the mixture analyzed. Lime is used in
masonry mortars in order to reduce the corresponding costs of their manufacture. Molded samples were cured for 1, 2 and 7 days on water under normal temperature conditions (T = 20 ± 2°C) and humidity (U.R. ≈ 90%). The mortar paste was subsequently intercalated between two brick plates to determine the adhesion efficiency of the mortar paste to the brick. After 7 days of hydration, the two bricks were binded with the mortar. The following aspects were considered: mortars prepared with CRT glass waste to meet the requirements of typical mortars according to the field of use and the amount of CRT glass waste replacing the sand do not change the workability of the mortars.

| Indicator | L/S ratio = 2 l/kg | L/S ratio = 10 l/kg |
|-----------|-------------------|---------------------|
| Lead      | 0.2               | 0.5                 |
| Nickel    | 0.2               | 0.4                 |
| Zinc      | 2.0               | 4.0                 |

*Dry Matter

The oxide composition of the CRT glass used in the experiments mixture was determined by X-ray fluorescence spectrometry (XRF). Leaching test of the mortar specimens after 7 days of hydration was performed in order to to highlight the mortars capacity to encapsulate CRT waste.

3. Results and discussions

3.1. Chemical stability in aqueous media of the CRT glass

The results of lead leaching tests from CRT glass mixture, compared to the limit value for acceptance of waste on inert waste landfills in accordance with the requirements of Order 95/2005, are presented in Figure 1.

![Figure 1. Lead leaching from the CRT glass mixture.](image)

The concentration of lead in glass mixture CRT significantly exceeds the limit values for both L/S ratio (more than 37 times for a L/S ratio = 2 l/kg and more than 4.5 times for a L/S = 10 l/kg).

Heavy metal leaching tests, carried out separately for funnel glass and panel glass were performed at the L/S ratio = 10 l/kg and sampling was performed at certain time intervals.

The leaching results of lead and zinc from the funnel glass are shown in Figures 2 and 3:
Regarding the leaching behavior of the funnel glass, an increasing evolution of lead and zinc leaching can be observed. For nickel, the determined values were below the detection limit of 0.06 mg/kg. Since the nickel limit value provided by Order 95/2005 is 0.4 for the L/S ratio = 10 l/kg, we can consider that nickel is not a problem for the environment. The lead concentration exceeds the limit of 0.5 mg/kg after 45 minutes of leaching, after 26 hours exceeding 10 times the limit value. In the leaching time range of 0.25 - 26 hours, zinc had an increasing trend but it did not exceed the 4 mg/kg limit.

The results obtained for leaching of lead and zinc from the panel glass are shown in Figures 4 and 5.

Regarding the leaching behavior of the panel glass, an increasing evolution of lead and zinc concentrations can be observed. For nickel, the determined values are below the detection limit of 0.06 mg/kg. Lead had an ascending trend but did not exceed the limit of 0.5 mg/kg. The same situation is reported for zinc.

3.2. Recycling of CRT glass in plastering mortars

Oxide composition of raw materials used in this study (CRT glass mixture and ordinary Portland cement CEM I 52,5R) determined by X-ray fluorescence spectrometry (XRF) is shown in Table 2.

A total of ten mortar mixes including control mixtures were prepared (table 3). Crushed CRT glass was used in order to replace the river sand at levels of 10%, 20% and 30% by weight. The mortar samples composition (recipes) is shown in the Table 3.
Table 2. Oxide composition of the CRT glass mixture (funnel glass and panel glass in ratio 1:1) and Portland cement (CEM I 52,5R).

| Composition (%) | CRT mixture | CEM I 52,5R |
|-----------------|-------------|-------------|
| SiO₂            | 58.5914     | 21.8610     |
| Al₂O₃           | 2.7366      | 5.2005      |
| Fe₂O₃           | 0.2547      | 4.0178      |
| CaO             | 1.0816      | 60.6191     |
| MgO             | 1.3716      | 2.5269      |
| ZnO             | 0.2532      | 0.0434      |
| MnO             | 0.1116      | 0.0681      |
| K₂O             | 5.9835      | 0.7525      |
| Cl              | -           | 0.0509      |
| P₂O₅            | -           | 0.1397      |
| As₂O₃           | -           | 0.0843      |
| Cr₂O₃           | -           | 0.0858      |
| SO₃             | -           | 4.4945      |
| SrO             | -           | 0.0556      |
| Na₂O            | 9.4581      | -           |
| CuO             | 0.0488      | -           |
| SrO             | 5.1020      | -           |
| ZrO             | 1.0375      | -           |
| Sb₂O₃           | 0.1948      | -           |
| BaO             | 6.7123      | -           |
| PbO             | 7.0623      | -           |

Table 3. Plastering mortar recipes.

| Sample | Binder (%) | Aggregate (%) | Water/binder ratio |
|--------|------------|---------------|-------------------|
|        | CEM I 52,5R | Lime | Sand | CRT glass |               |
|        |             |       |      |           |               |
| M-0    | 100         | -    | 100  | -         | 0.45          |
| S10-0  | 100         | -    | 90   | 10        | 0.45          |
| M-1    | 100         | -    | 100  | -         | 0.5           |
| S10-1  | 100         | -    | 90   | 10        | 0.5           |
| S20-1  | 100         | -    | 80   | 20        | 0.5           |
| S30-1  | 100         | -    | 70   | 30        | 0.5           |
| MV     | 75          | 25   | 100  | -         | 0.5           |
| SV10   | 75          | 25   | 90   | 10        | 0.5           |
| SV20   | 75          | 25   | 80   | 20        | 0.5           |
| SV30   | 75          | 25   | 70   | 30        | 0.5           |

3.3. Leaching behavior of the plastering mortar

The results of the leaching tests for the mortar samples after 7 days of hydration, respectively the heavy metal concentrations in the leaching solutions are presented in Table 4.

Table 4. Plastering mortar recipes.

| Sample | Determined values (mg/kg D.M) – Quality indicators |
|--------|---------------------------------------------------|
|        | L/S ratio = 2 l/kg L/S ratio = 10 l/kg           |
|        | Lead | Nickel | Lead | Nickel | Lead | Nickel | Lead | Nickel |
| S10-0  | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> |
| S10-1  | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> |
| S20-1  | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> |
| S30-1  | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> |
| SV10   | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> | BDL<sup>a</sup> |
The leaching behaviour of the mortar specimens after 7 days of hydration revealed that the analysed samples do not present a pollution potential. The heavy metals (Pb, Zn, Ni) concentrations were under the limit allowed by the current legislation, namely for acceptance of waste on inert waste landfills.

4. Conclusions
The results of the leaching tests have highlighted that the CRT glass mixture is a hazardous waste, as the lead concentrations exceed the limit values for inert waste provided by OM 95/2005: 37 times for L/S ratio = 2 l/kg and 4 times for L/S ratio = 10 l/kg. The chemical compositions of the panel and funnel glass were different, the panel glass containing almost no lead, while the funnel glass containing high level of lead, therefore a mixture of 1:1 ratio was used. The leaching tests of mortar samples after 7 days of hydration have highlighted the fact that the materials do not present pollution potential, the results determined on the analyzed metals being under the limit allowed by the current legislation. The use of CRT glass waste as a partial replacement of sand represents an important step towards sustainable, ecological, energy efficient and technical-economic development of the construction materials industry.

5. References
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