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CATHODE RAY TUBE (CRT) LEAD GLASS: LEAD LEACHING STUDY AFTER A CHELATING AGENT TREATMENT

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Abstract

This study is focused on the removal of leachable lead present in CRT (cathode ray tube) glass employing different chelating agents, NTA (nitrilotriacetic acid) and ATMP (amino trimetilen phosphonic acid), and then on the evaluation of their extractive capability. The operating conditions are the following: T=80°C, t=1h, pH=10, solid/liquid weight ratio=1/10, reagent concentration= 0.1 M. Afterwards a number of leaching tests at controlled pH were performed in the 5-9 range for 48h at room temperature to define the lead leaching curves for CRT glass matrix and to evaluate the chelating process efficiency.
Experimental leaching curves showed a semi-U-shaped pattern, with maximum lead release at acid pH. Results demonstrated that NTA is able to remove the 66-80% of lead leachable at pH 5.

Key words: chelating agents, leaching tests, lead extractive method, WEEE lead-glass

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1. Introduction

Since the end of the 90s, the re-use of waste electrical and electronic equipment (WEEE) generated over the world has been of great interest. In recent years the replacement of TVs with Cathode Ray Tube (CRT) glass by flat-panel displays caused a drastic increase of WEEE characterized by a high lead content. Discarded computer monitors and television sets are identified as hazardous materials due to the high content of lead in their cathode ray tubes (CRTs). In particular, over 98% of lead is found in CRT glass. Directive 2002/95/EC, on the restriction of the use of certain hazardous substances in electrical and electronic equipment, is not applicable to every product, in fact there are some applications which are exempted from these requirements. An example is the glass from cathode ray tubes which contains PbO ranging from 12 to 25 wt% as protection from X-ray radiation (ICER, 2004).

Today, the disposal of lead-containing glass has become a serious environmental issue. High amount of obsolete electronics including TV and CRT monitors are in storage because appropriate e-waste management and remediation technologies are insufficient. Since leaching is of concern, heavy metals need to be removed before the residual inorganic materials can be disposed of in landfills or otherwise used.

Many approaches for the treatment of CRT glass have been performed mainly from 2009 up to now. Hydrothermal conditions have been applied (Miyoshi et al., 2004), C and CO (Chen et al., 2009; Nakada et al., 2008) and TiC and SiC are exploited to reduced lead to its elemental form (Yot and Méar, 2009). Leaching under acidic conditions was also used for lead recovery by removing lead from

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crushed funnel glass surface by means of nitric acid at 3–5% concentration (Ling and Poon, 2012).

Yuan et al. (2012, 2013) treated CRT glass mechano-chemically by ball milling and removed 92.5% of the lead by diluted nitric acid leaching. Wang and Zhua (2012) extracted lead oxide nanoparticles from cathode-ray tube (CRT) funnel glass using self-propagating high-temperature synthesis method.

Okada et al. (2012) removed most of the lead as metal by reductive melting and immobilized the remaining lead by oxidative melting in such a way that the treated glass passed Japanese legal criteria for recycling. Carboxylates and phosfonates as chelating agents can be used to extract lead from funnel glass (Barbieri et al., 2014; Sasai et al., 2008) and also methods of chlorides volatilization (Grause et al., 2014a, 2014b).

In this paper the effectiveness of two different chelating agents with different functional groups such as the phosphonate group amino trimetilen phosphonic acid (ATMP) and the carboxylate group nitrilotriacetic acid (NTA) was further investigated in order to develop an extraction process efficient and with low environmental impact with regard to both the procedure to be followed (temperature, time, cycles) and the reagents/solvents used.

In particular the study focuses on the definition of the lead leaching curves for treated and untreated CRT glass matrix at different pH. This was achieved by means of leaching tests at controlled pH in the 5-9 range, useful to simulate the real environmental leaching conditions. Lead concentration in eluates was determined through FA-AAS analysis.

The metal-sequestering properties of carboxylates and phosphonates are commonly employed in different products and applications, such as in household detergents, to prevent precipitation of bivalent ions from washing suds and thus avoiding scale deposition on both textiles and washing machine parts; but also in the water treatment, descaling of boilers, in the photography industry, in agricultural fertilizers, during pulp and paper production, for metal finishing and rubber processing, or in food, pharmaceuticals and cosmetics (Egli, 1994).

The development of a novel recycling process for spent lead glass is essential in order to increase the recycling rate with higher efficiency. Pb powder or Pb salts can be obtained from the leaching solution and the Pb-depleted solution reused into the leaching step (Zhang et al., 2013). At the end of the paper a regeneration process of spent chelating agent solution with formation of lead sulphide precipitate was further proposed.

2. Experimental

2.1. Materials preparation

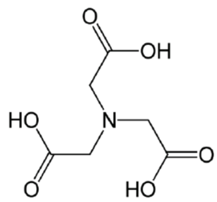
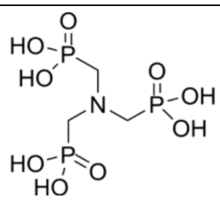
Waste funnel glasses of TVs and PCs monitors were provided by a treatment plant in North of Italy already cleaned from the coating and ground below 2 cm. The glass was firstly dry-ball milled and sieved in order to separate 0.5-1 mm and 1-4 mm particle sizes.

The chelating agents employed, 2,2',2''-Nitrilotriacetic acid NTA (≥99% purity) and Amino tris(methylene-phosphonic acid) ATMP (≥99% purity), were used as sodium salts. Their structures are reported in Table 1. For both the chelating agents a solution of 0.1 M was prepared keeping pH fixed around 10 with a buffer solution.

2.2. Total lead concentration of untreated funnel glass

The total lead concentration in funnel glass was determined by a strong acid digestion method. The digestion procedure followed is that indicated by Test Method CPSC-CH-E1002-08 "Standard Operating Procedure for Determining Total Lead (Pb) in Non-Metal Children's Products" (2009), that for the determination of lead in ceramic, glass, crystal and other siliceous materials refers to EPA Method 3052, "Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices" (1996). For the digestion of the funnel glass an Ethos Touch Control Advanced Microwave LabStation was used.

Table 1. Used chelating agents

Abbreviation	***Name***	***Structure***
NTA	2-[Bis(carboxymethyl)amino]acetic acid; 2,2',2''-Nitrilotriacetic acid	
ATMP	Amino tris(methylene-phosphonic acid)	

Lead concentration in digested funnel glass was determined by FA-AAS analysis (Perkin Elmer AAnalyst 400). The result is 186.02 ± 5.34 (mg/g), which is the mean values of three sample digestions. Considering that the PbO concentration in CRT glass shows a wide range of concentration which depends on the lot of sample (from 12 to 25%), this value could not be considered representative of the average lead content in CRT glasses from a treatment plant.

Total lead content in treated glass was not determined since, acting only on the surface lead content, and working with granular and not powdery samples, this was assumed remaining almost constant before and after the chelating agent treatment.

2.3. Chelating agent treatment at T=80°C

For each of the two lead glass particle sizes (0.5-1 mm and 1-4 mm) a treatment with NTA or ATMP chelating agent solutions (0.1 M at pH 10, conditions chosen by a previous work (Barbieri et al., 2014), which demonstrated that alkaline environment favors the reaction) was performed. The lead glass characterized by a specific particle size was sealed in container with chelating agent solution, employing a solid/liquid weight ratio of 1/10. The system was heated at 80°C for 1 h. The treated glass was separated from the chelating agent solutions by settling and washed with distilled water in order to remove any chelating agent traces. The cleaned glass was collected and dried in oven at 110°C overnight.

2.4. Lead leaching tests

A number of leaching tests at controlled pH were performed to evaluate the lead leaching properties of CRT funnel glass and the effectiveness of the chelating agent treatments. In order to simulate the leaching conditions to which CRT lead glass may be exposed to environmental scenarios, a pH range between 5 and 9 was considered.

Leaching tests were performed on both untreated and treated glass. Regarding untreated glass, only 1-4 mm particle size was employed in the tests. The samples were sealed in suitable polypropylene vessels with a solid/liquid weight ratio of 1/10. The system was kept in stirring for 48 h at room-temperature. Set a pH value, the instrument kept it within a narrow range (+/- 0.2). Control was achieved automatically by adding appropriate volumes of acid or base (HNO_3 0.1 M and NaOH 0.1 M) varying from 0.05 mL to over 1 mL. Leaching procedure is in compliance with CEN/TS 14997:2006. Lead concentration in eluates from leaching tests was determined by FA-AAS analysis (Perkin Elmer AAnalyst 400).

2.5. Microstuctural and semiquantitative analyses

The microstructural analysis before and after all the funnel glass treatments was performed by scanning electron microscopy (ESEM, Quanta-200 Fei, Oxford Instruments) equipped with EDS (microanalyzer Inca-350, Oxford Instruments) for the semiquantitative element analysis in particle surface.

In Fig. 1 a flow chart of the overall process is reported.

3. Results and discussion

3.1. Leaching test at controlled pH

The leaching tests results are reported in Fig. 2. Curves represent the lead release trends for different samples. The lead leachable was investigated in different pH in order to simulate the leaching conditions to which CRT lead glass may be exposed to environmental scenarios. For the treated glasses, the determination was performed at pH 5, 6, 8, 9, and the natural pH of water/glass equilibrium (about 7), whereas for untreated glass only pH 5, 9 and system equilibrium one were investigated.

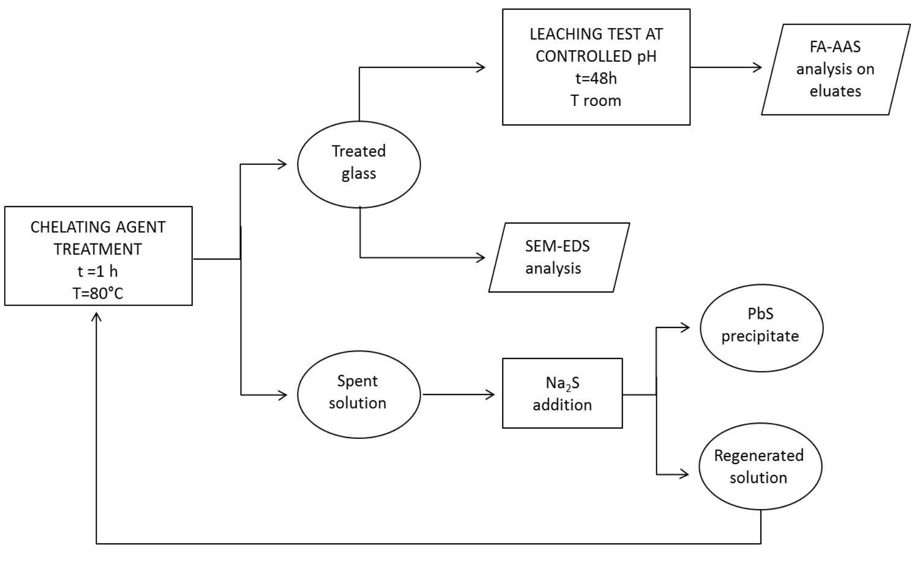


Fig. 1. Flow chart of the process

The experimental leaching curves obtained for glass matrices (Fig. 2) well retrace the theoretical characteristic curves for lead leaching at different pH reported in literature for other matrices. This trend shows a semi-U-shaped pattern, with maximum lead release at acid pH (Centioli et al., 2008, Popovici et al., 2013).

Fig. 2 shows that at pH 5, the pH of interest in the lead extraction as it promotes the higher release, the treatment with NTA produces a Pb leachable reduction of 66-80% depending on particle size (0.29 mg/g released by 1-4 mm treated glass and 0.53 mg/g by 0.5–1 mm treated glass against 1.56 mg/g of untreated glass).

This significant result, obtained using NTA as chelating agent, has not been achieved employing ATMP. In fact the Pb release values for samples treated with ATMP solution were comparable with those obtained for untreated glasses for the same particle sizes. This data suggest that, compared to ATMP, NTA presents a higher chelating capability towards lead in the considered matrix.

As regards the effect of the particle size some consideration should be made. It is noted that glass particle size is a significant factor affecting lead extraction, as the smaller is the particle size the forceful is the leaching, as observed for the glass treated with NTA.

For ATMP an anomalous trend is observable due to the ineffectiveness of the treatment with ATMP especially on the high particle size, so all the surface Pb amount was available from 1-4 mm glass matrix to be leached by the leaching test. On the opposite NTA appears to have been effective on both the particle sizes, and so with equal effectiveness of the treatment the fine particle size is that which released more.

3.2. Microstuctural and semiquantitative analyses

The results of SEM-EDS analyses on 0.5-1 mm treated glasses and untreated glass are reported in Fig. 3. Different areas of the funnel glass were analyzed to obtain the average percentage of surface lead content before and after the treatments. Results are consistent with those obtained from leaching tests. In fact starting from a lead content of 20% average in untreated glass, NTA treatment reduced it to 14.37% (with an extraction percentage of about 28%), where as ATMP did not go below 18.30%.

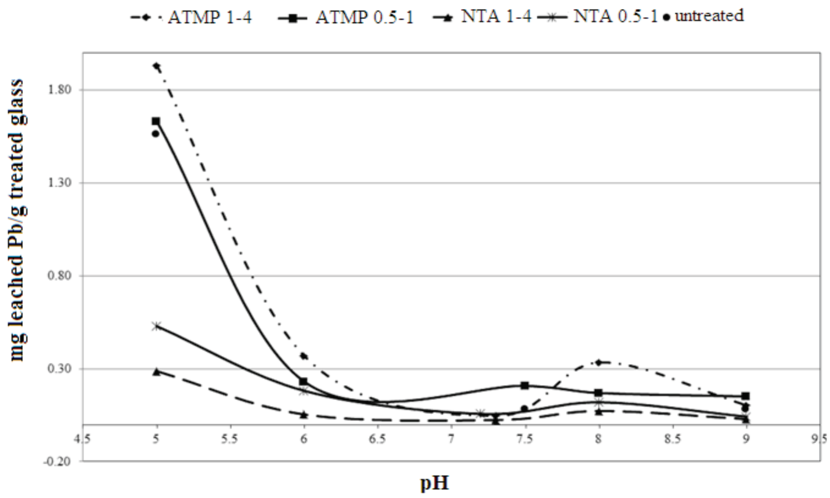


Fig. 2. Quantity of leached lead (mg) for unit of mass (g) of treated lead-glass at controlled pH after 48h

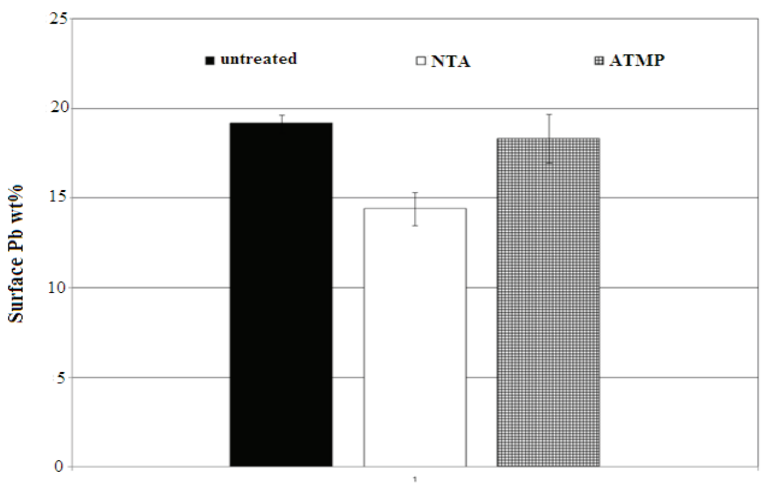


Fig. 3. Average percentage of surface lead content before and after the treatment for 0.5-1 mm particle size glasses

Furthermore, a single 1-4 mm glass grain that was previously treated with NTA (as it proved to be the best chelating agent) was lapped with sandpaper in order to remove the first superficial layers of the glass. SEM-EDS analyses were carried out on both the lapped area not exposed to the treatment and on the surface area directly exposed to the chelating agent solution. As expected, in the lapped area the lead concentration was higher than the un-lapped area (Fig. 4). In the SEM-EDS image reported in Fig. 4 the dividing line between the lapped area (on the right) and the un-lapped area (on the left) is clearly visible.

3.3. Chelating agent solution regeneration

At the end of the lead removal process a treatment of the spent chelating agent solution, the new waste obtained was developed. It allows both the exhausted solution regeneration and the recovery of extracted lead as lead sulphide precipitate. The study of the regeneration process was developed only for NTA solution, since it proved to be more effective in the removal of lead from the funnel glass than ATMP.

Lead was precipitated by adding to the solution an appropriate quantitative of sodium sulphide (Na_2S), a highly water-soluble salt (470 g/l at 10 °C). The reaction that occurs is the following (Eq. 1).

$$NTA\text{-}Pb + Na_2S \rightarrow NTA\text{-}Na + PbS_{(s)} \quad (1)$$

Lead sulphide gradually settles and its high insolubility (K_{ps}=3.4*10^{-28}) favours the reaction proceeding. PbS was separated from NTA solution by filtration. In Fig. 5 the XRD spectrum of lead sulphide precipitate is reported.

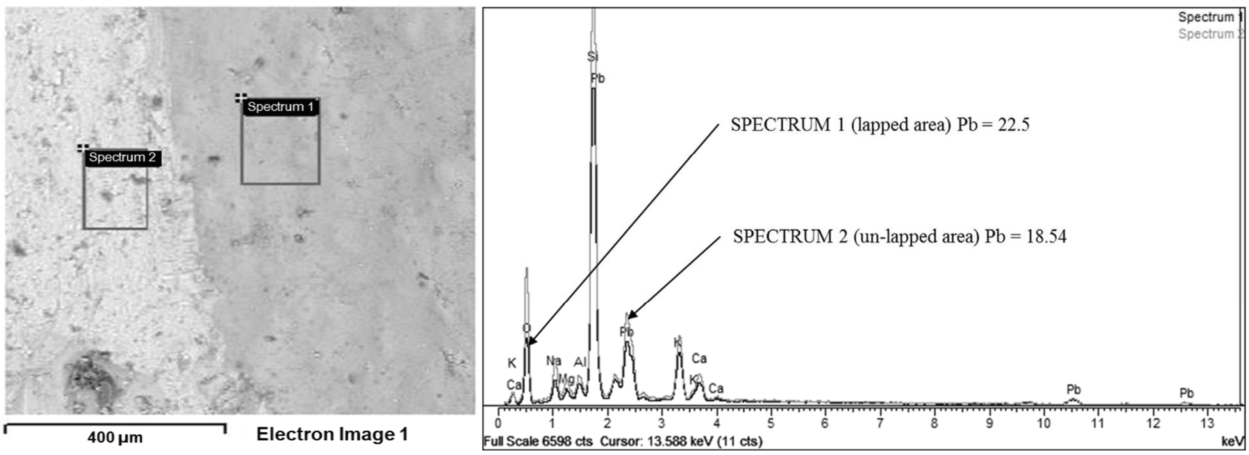


Fig. 4. SEM image and EDS spectra of a 1-4 mm glass grain treated with NTA and lapped with sandpaper

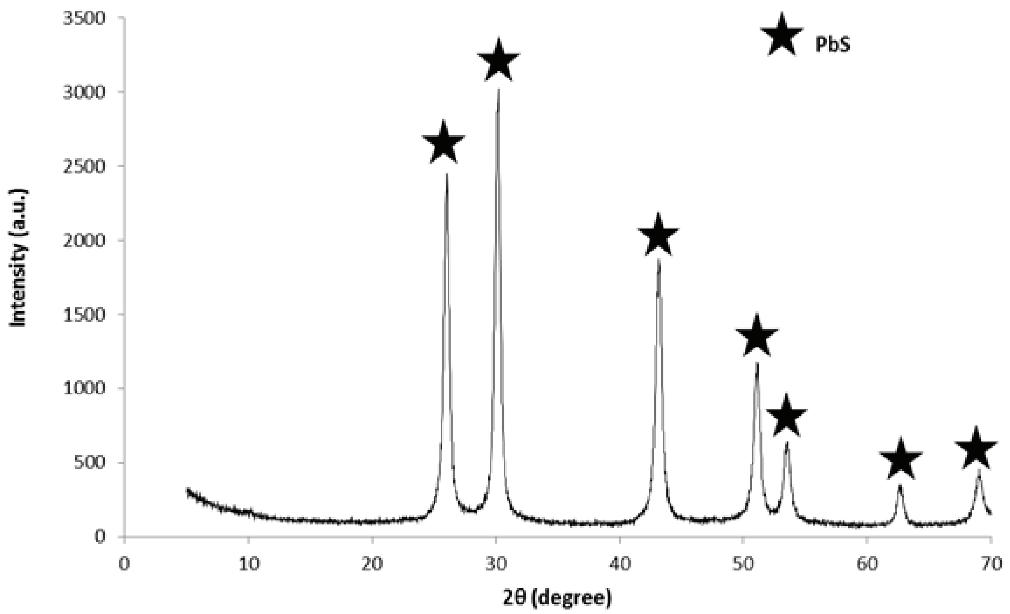


Fig. 5. XRD spectrum of PbS precipitate

4. Conclusions

In the present study the lead leaching from CRT glass was investigated before and after a chelating agent treatment by means of leaching tests at controlled pH for 48h at room temperature. In particular, the 5-9 pH range was considered in order to simulate different environmental scenarios. In accordance with the theoretical characteristic curves for lead leaching at different pH reported in literature for other matrices, the experimental leaching curves obtained for CRT glass showed the higher release at acid pH. Through a comparison of the results obtained for treated and untreated glass, it was found that NTA is an efficient chelating agent in the removal of lead from funnel glass network, since after the treatment at 80°C for 1h at pH 10 lead leachable at pH 5 was reduced for 66-80% depending on particle size (0.29 mg/g released by 1-4 mm treated glass and 0.53 mg/g by 0.5-1 mm treated glass against 1.56 mg/g of untreated glass). On the other hand, ATMP proved to be ineffective in lead removal from WEEE glass.

In terms of benefits, it should be noted that the chelating agent treatment developed is eco-friendly, since the process doesn't need high temperatures (T=80°C) or long time of reaction (t=1h); the solvent utilized is water; NTA is easily biodegradable by various groups of bacteria; considering that the chelating technique maintains the glass natura of the powder, the solid leaching glass residues obtained after Pb removal could be used for the preparation of building materials such as foam glass, glaze, ceramic tiles, cement.

Further aspect of sustainability, the regeneration of the solution by means of Na_2S allows the obtainment of PbS precipitate as secondary product and the solution can be used for new treatment of the glass.

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