POSIBILITĂȚI DE VALORIFICARE A UNOR DEŞEURI DE STICLĂ PROVENITE DE LA TUBURILE CINESCOAPE
POSSIBILITIES FOR RECOVERY OF SOME GLASS WASTE FROM CATHODE RAY TUBES

VASILICA DIMA*, MIHAI EFTIMIE, ADRIAN VOLCEANOV, GEORGETA VOICU, RAMONA DINCĂ
[1]*Universitatea POLITEHNICA Bucureşti, Str. G. Polizu, nr. 1, sector 1, 011061, Bucureşti, România*

This paper presents experimental results on cathode ray tubes – CRT - glass waste for recovery in glazes. We characterized the CRT glass waste and we obtained frits from it.

We determined the density, the hydrolytic stability, the wetting ability against temperature and the thermal expansion curves, both on waste and obtained glasses.

Glazes were prepared and applied on ceramic support (terracotta and sandstone) in laboratory. SEM micrography was performed to support-glazes interface.

Lucrarea prezintă rezultatele experimentale privind valorificarea în glazuri a deşeurilor de sticlă provenite de la tuburile cinescoape. Deşeurile de sticlă au fost caracterizate şi au fost obținute frite din acestea. S-au determinat densitatea, stabilitatea hidrolitică, capacitatea de umectare şi curbele de dilatare termică, atât pe deşeurile de sticlă cât şi pe sticle obținute cu deşeuri.

Au fost preparate în laborator glazuri şi au fost aplicate pe un suport ceramic(taracota şi gresie). S-au realizat micrografii SEM la interfața glazură – suport ceramic.

Keywords: *CRT glass waste, glazes, recovery*

1.Introduction

The limited resources and the continuously increasing rate of the global economic activity development require a serious ecological approach and a careful and coherent re-evaluation concerning the industrial waste recovery, in order to obtain viable capitalization and recycling processes.

9 million tons waste electrical and electronic equipment (WEEE) are obtained at the European level *. Recent estimations showed that by 2020, it will be produced an average of 12.3 million tons WEEE / year.

Glass components are contained, in a smaller or greater percentage, in many of these equipments. Many EU Member States have studied and analyzed the WEEE situation [1-3, 5-7].

There are already techniques for recycling electronics, metal, plastics, while for the glass components the situation is much more difficult because of their different compositions. Their recovery would mean significant savings in raw materials and energy and also reducing of the environmental pollution [1-8].

Among WEEE waste a special interest present the TV and computer monitors that allow the separation of kinescope tube, a component representing 2/3 of the whole weight of these types of equipment and consists of 85% glass (65% is the screen, 30% the conical part and 5% the cylindrical part – the neck).

The composition of different types of glasses used for the cathode ray tube is in agreement with technical specifications that must be accomplished during the functioning of the device

The *screen*, front panel, is made of a silicate glass containing strontium and barium, and represents about two thirds from the whole cathode ray tube. The *conical* part is a glass with lead oxide and the *cylindrical* part that seals the electronic tube is a glass with high content of lead oxide. The frit (glass for soldering of the screen and the cone) is a glass based on lead oxide, having a low melting temperature and is comprised only into the colored cathode ray tubes [1-10].

The compositions of different types of glasses forming the kinescope tube contain valuable oxides like SiO_2, SrO, BaO, PbO, CaO, Al_2O_3 , which manufacture means large amounts of row materials and which exploitation and processing represent a source of environment breakdown and energy consumption.

Many of these oxides are to be found in glaze compositions. In this context, the industry of glass and ceramics are the best consumers of this glass waste when carefully selected from screen, monitors and displays.

The glass waste resulting from cathode ray tube processed accordingly can be used in different areas such as: admixtures at brick manufacturing, foam glass, tableware glass, glass fibers and in a more extensive way for glazing ceramics. The use

* Autor corespondent/Corresponding author,
Tel. + 40 21 4023996, e-mail: vasilica.dima@gmail.com

of glass waste from cathode ray tubes to obtain ceramic glazes represents a valuable and effective alternative in this circumstance. Literature data has recorded the attempts made in different countries for study and potential application of cathode ray tube glasses for ceramic glazing.

Our experiments on the waste glass recovery resulted from cathode ray tubes have the following objectives:

1. Characterization of CRT glass waste;
2. Obtaining of melts from waste and the characterization of the obtained glasses;
3. Preparation of frits / glazes for different ceramic products.

2. Glasses and waste characterization

The following properties were determined for both waste and re-melted glass (see section 2.2):

- density, using hydrostatic weighing method;
- hydrolytic stability, through the conductivity method;
- wetting ability, through the wetting angle measurement technique;
- thermal expansion, performed with the differential type dilatometer from which was calculated the linear thermal expansion coefficient, glass transition temperature and softening temperature, as well.

Chemical composition of the glasses was determined through EDAX spectra of samples (Table 1) obtained with a Hitachi S 2600 N equipment.

From EDAX spectra and Table 1 result the following facts:

Table 1

Chemical composition of glasses
Compoziţia chimică a sticlelor

Oxide/ Glass *Oxid / Sticlă* %	Panel Glass *Sticlă panou frontal*	FunnelGlas *Sticlă partea conică*	M Glass *Sticlă din amestec*
SiO_2	54.34	41.96	55.75
K_2O	23.86	7.25	15.41
BaO	20.35	0.00	9.57
PbO	0.00	30.52	12.92
Na_2O	0.88	4.69	3.04
SrO_2	0.00	7.87	0.49
Al_2O_3	0.57	7.00	2.03
MgO	0.00	0.71	0.27
Fe_2O_3	0.00	0.00	0.52
Total	100.00	100.00	100.00

- The glass obtained from the panel waste is a silicate glass with a high content of barium oxide (BaO) and alkali (K_2O).
- The glass obtained from the funnel waste is characterized by very high lead oxide (PbO) content.
- M-Glass is obtained by melting a mixture of waste: 65% panel waste, 30% funnel waste and 5% neck waste, according to the proportion of each component within the cathode ray tube.

2.1. Density determination

Density was determined by the hydrostatic weighting method, which consists of samples weighting in air and then in water. The results are shown in Figure 1.

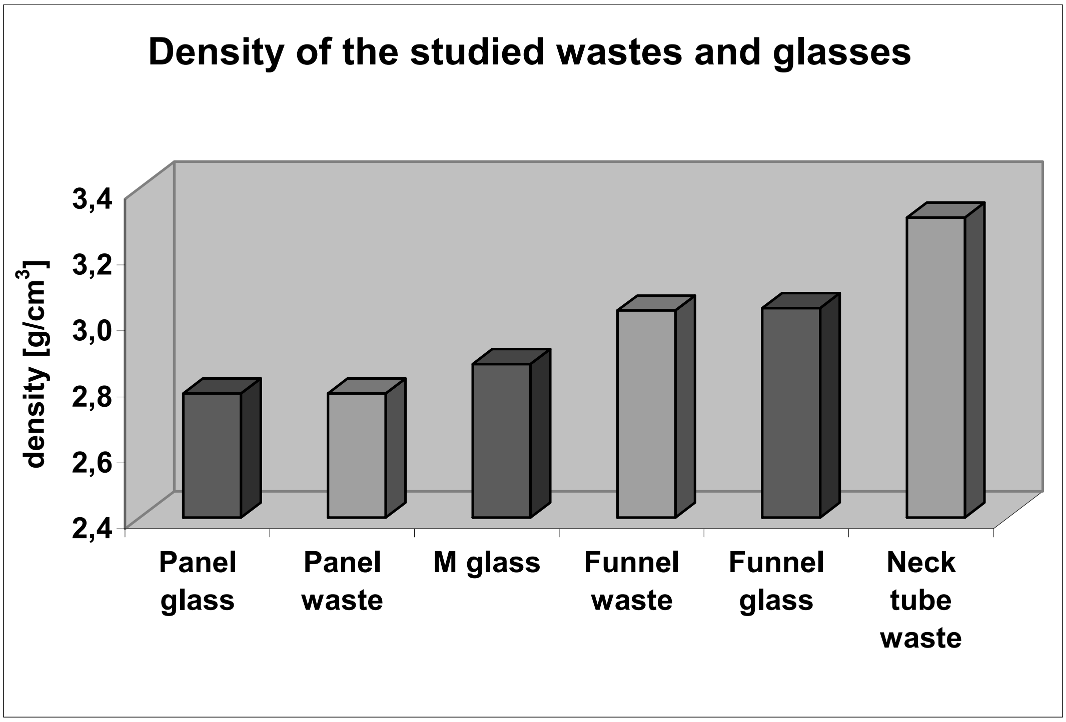


Fig. 1 - Graphic representation of the samples density /*Reprezentarea grafică a densităţii probelor.*

One can observe that the density of samples is correlated with the heavy metal oxide content. Thus, in Figure 1 it can be seen that the glass from funnel and neck waste containing PbO, with a high specific weight (d_{PbO} = 9.64 g/cm^3), has a higher density compared to panel glass, that does not contain PbO.

It was also to notice that glass density is lower than waste density. It has been widely reported [3] that glasses containing heavy metals are characterized by a large amount of dissolved gases directly from the manufacturing process, such glasses being not extensively refined.

2.2. Hydrolytic stability determination

The hydrolytic stability of samples was determined by measuring electrical conductance variation of the glass powder, in water, in time. The method has the advantage that it provides qualitative information on the kinetic process of glass - water interaction, emphasizing if this process stops in time or evolves continuously, without stopping (etching process). Figure 2 shows the conductivity value of glass powder suspension of the studied samples after 3 hours.

It was found that the re-melting of glass samples leads to a higher conductivity (lower hydrolytic stability) compared to the waste ones, the fact being explained by the less compact structure as resulted after re-melting. A major influence may also have the different thermal history of waste glass in comparison with the re-melted glass.

At the same time is to be noticed a continuous increase in time of the suspension samples conductance, but having different evolution, which means that is possible the ion exchange and reaction processes in water of the weakest linked ions in the network (Na^+, Ba^{2+}, Sr^{2+}) to take place.

Figure 2 shows that the sample from the panel has a higher conductance than funnel and neck samples, so exhibiting a lower stability to water. This behaviour could be assigned to the higher alkali content (23.86%) in comparison with the other two samples.

Conductivity values recorded over a period of 3 hours is quite low (below 30 µS), thus suggesting a good chemical stability, as a general behaviour of these type of glasses and waste, as well.

2.3. Determination of wetting ability against temperature

To be used as frits/glazes the following two leading properties of glass are important:

- adhesion to the ceramic substrate;
- thermal expansion coefficient able to ensure conditions for a good glaze – ceramic substrate mismatch at a convenient firing temperature.

Wettability is involved in several stages of glass and glaze fabrication process. During the glazing of ceramic products, at glaze - ceramic substrate contact, adhesion can be enhanced by heating glass until the wetting angle, θ, becomes small enough. The wetting angle is used as a measure of wettability and it represents the angle between the tangent at the liquid-gas separation surface with the solid-liquid separation surface, always containing the liquid phase. The wettability increases with the decrease of the wetting angle.

For this purpose the wetting angle at 1000^{0}C was selected (Figure 3), the temperature being the one at which are fired the glazes on a ceramic terra-cotta coated substrate, sandstone, tile etc.

Determination of the samples wetting ability was performed on both waste and re-melted glass. Each sample was placed on a sandstone

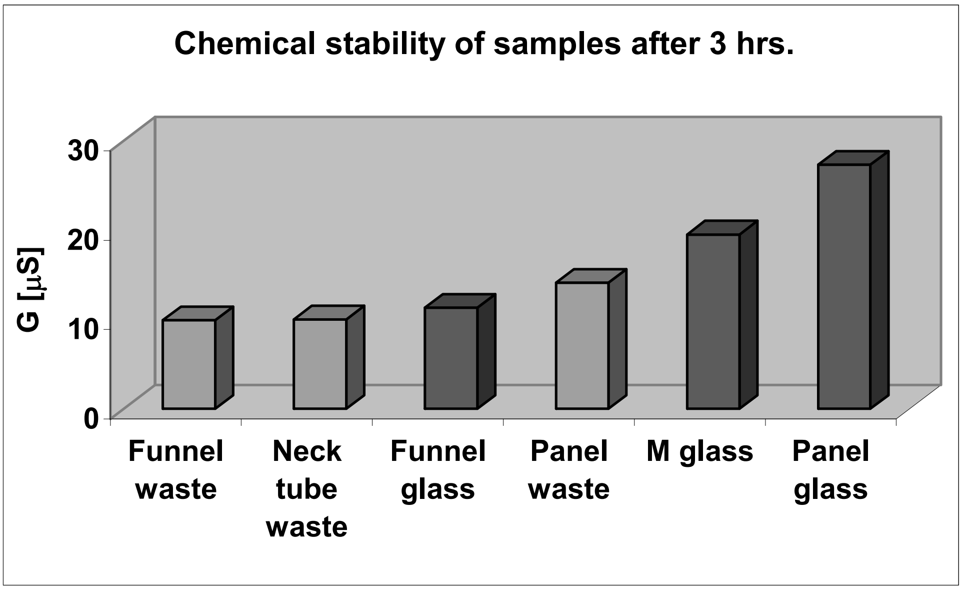


Fig. 2 - Plotting of the samples hydrolytic stability after 3 hours/ *Stabilitatea hidrolitică a probelor după 3 ore.*

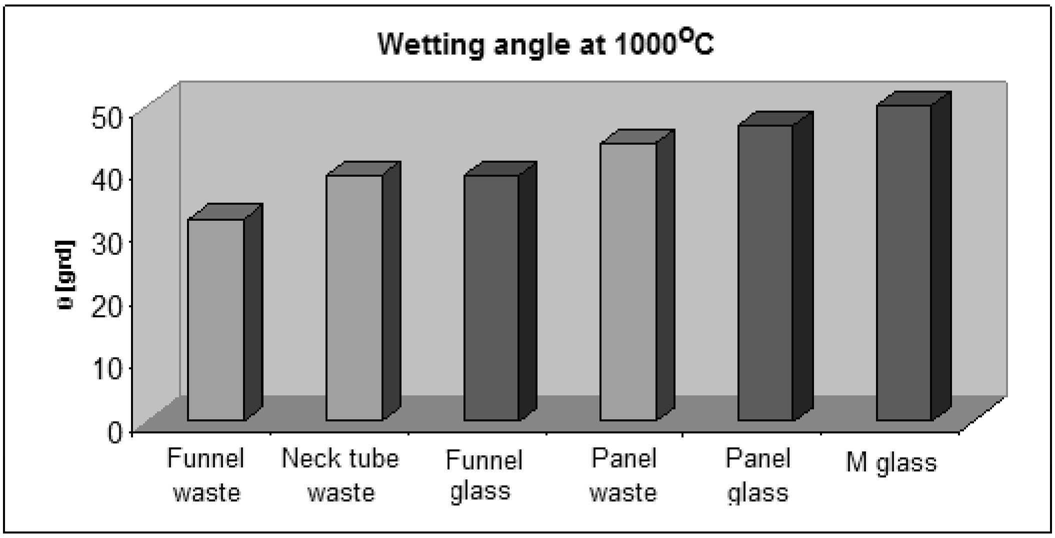


Fig. 3 - Representation of the wetting angle at 1000 °C/ *Reprezentarea unghiului de umectare la 1000°C.*

ceramic substrate, placed in a refractory tube of a horizontal electric furnace, specially designed for this purpose. The wetting angle θ was recorded for each step of 10°C up to 1000°C.

As regard the wettability assessed through the wetting angle, it results:

- Both waste and re-melted glass has relatively good wettability at 1000°C, the wetting angle values being in a narrow range: 32-50 degree.
- The best wetting ability (lowest wetting angle, 32 degree) is presented by the funnel waste, which actually has the highest PbO content (30.52%), with a positive influence.

2.4. Determination of thermal expansion curves

For determination of the thermal expansion curves of samples a rate of temperature increase of 3°C/min was used.

The processing of information provided by the dilatometer curves allowed one to determine: glass transition temperatures, dilatometer softening temperature and linear thermal expansion coefficients, as well (Table 2).

The analysis of the thermal properties presented in Table 2 emphasized the relatively high values of the linear thermal expansion coefficients in the temperature range of 20-300°C, comparable to the lead oxide glasses, around of 100 • 10^{-7} K^{-1}.

Table 2

Thermal properties samples/ *Proprietăţile termice ale probelor*

Sample / *Proba* — Property / *Proprietate*	Waste /*Deşeu*			Glass / *Sticlă*		
	Panel *Ecran*	Funnel *Con*	Neck *Cilindru*	Panel *Ecran*	Funnel *Con*	M *Amestec*
Thermal expansion coefficient, *Coeficient de dilatare termică,* α •10^7K^{-1}	103.40	98.56	102.10	104.57	105.47	104.19
Glass transition temperature *Temperatura tranziţiei vitroase, Tg , °C*	537	464	461	513	473	480
Lower annealing temperature *Temperatura inferioară de recoacere, TIR , °C*	500	430	450	498	456	471
Upper annealing temperature *Temperatura superioară de recoacere, TSR , °C*	559	479	469	519	484	483
Softening temperature *Temperatura de înmuiere dilatometrică, Td , °C*	588	514	505	554	514	537

Specific to these compositions, waste or glass, is the presence of the alkaline oxides in pretty high concentrations (23.86%), but also is that of lead and barium oxides, which contribute to the growth of the thermal expansion coefficient.

Taking into account that some ceramic substrates (sandstone, terra-cotta etc.) have similar expansion coefficients, it is possible that this waste to be of interest for glazes manufacturing [1-8]. The literature [1-3] reports good results for using glazes of CRT- waste up to a content of 20-30%.

3. The elaboration of melts

In order to obtain the melts, the waste was crushed in a porcelain crucible to a grain size of about 2-3 mm.

Three samples were prepared:

- Panel glass obtained by melting of the panel waste;
- Funnel glass, obtained from funnel waste;
- M-glass, obtained from a mixture of 65% panel waste, 30% funnel waste and 5% neck waste, which is the percentage of cathode ray tube component [1].

For M-glass, the crushed waste was weighed and homogenized.

The melts were obtained in refractory crucibles, in an electric furnace with kanthal resistors as heating elements. After the temperature reached 1400°C, it was maintained for 2 hours to allow the melt to achieve chemical and thermal equilibrium. After the heat treatment homogeneous, clear and fluid melts resulted, exhibiting a very good machinability, thus allowing a quite easy casting in a graphite die. The samples were obtained as rods with 40-50 mm length and diameter of about 8-10 mm.

Annealing was performed at temperature of 500°C for 60 minutes and then stopped, leaving the samples inside the oven to cool slowly for 12 to 14 hours.

After brushing of green terra-cotta and sandstone substrate with the slurry, the samples were dried at room temperature in lab environment for about 18 hours and then were fired following a heat treatment curve with a heating rate of 200^0C/h and a soaking time of 1 hours at 1000^0C (Figure 4).

The samples were analyzed by Hitachi S 2600 N at coating –support interface, confirming the role of the interface to ensure the fit of the glaze to ceramic support. SEM images are in figure 5 a) and b).

The analysis of SEM micrographs reveals a well defined interface that makes a strong bonding between the crystalline ceramic substrate and the glaze.

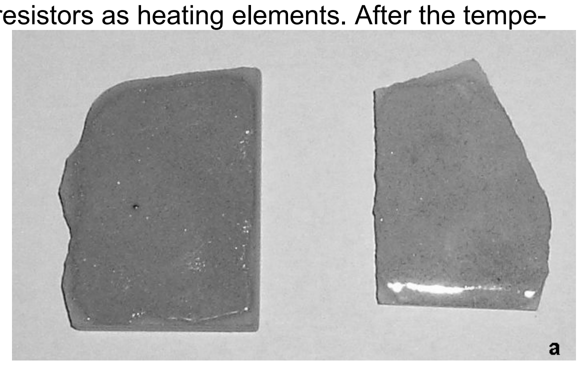
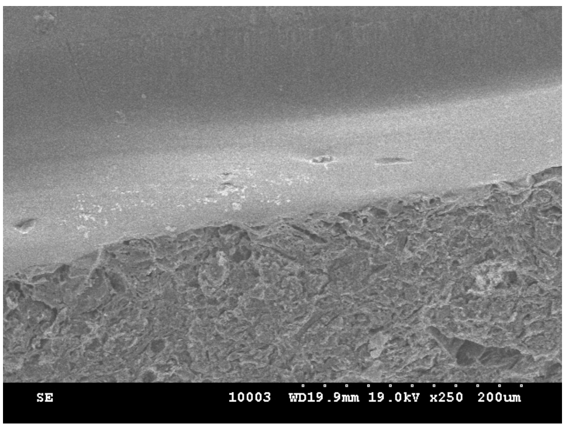
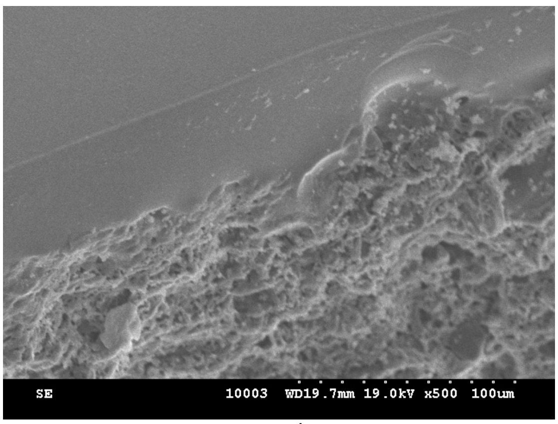


Fig. 4- Aspect of glazed samples: a) sandstone substrate; b) terra-cotta substrate/ *Aspectul probelor glazurate:a)suport de teracotă; b) suport de gresie.*



a



b

Fig. 5 - SEM images of glaze – ceramic substrate a)-terracotta, b)-sandstone interface/ *Micrografii SEM la interfața glazură-suport* ceramic *a)suport de teracotă; b) suport de gresie.*

The vitreous phase is dense, continuous, without crystals and adherent to support.

4. Conclusions

There were elaborated melts from waste and the obtained glasses were characterized in order to estimate their use as frits / vitreous glazes for various ceramic products.

The obtained results and their correlation with literature data made possible to draw the following conclusions:

- density of glass is correlated with heavy metal oxide content;
- the hydrolytic stability of re-melted glass samples was found to be lower than that of the waste. This can be explained by the less compact structure resulting after waste re-melting. A major influence may also have the different thermal history of waste glass compared to waste re-melted glasses;
- hydrolytic stability is influenced by the chemical composition, particularly by the presence and concentration of the alkali - glass panel, which has higher alkali content than that of the other two samples and therefore it has the lowest stability;
- the wetting angle presents relatively small values in a narrow range (32 - 50 degrees) at temperature of 1000^0C and therefore the wettability is likely to positively influence the adherence to a ceramic substrate;
- as thermal properties, there were outlined the relatively high values of the linear thermal expansion coefficients in the temperature range of 20-300°C, comparable to the lead oxide glasses, being of the order of $100 \cdot 10^{-7}$ K^{-1};
- Specific to these compositions, both waste and glasses, is the presence of enough high alkali concentration, but also for lead and barium oxides which contribute to the higher value of the thermal expansion coefficient.

For this reasons, the research on using these types of glasses in frits for glazes is very laborious and has to be performed with great care regarding the thermal expansion coefficient, in order to ensure a good compatibility between glaze and substrate.

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