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CERAMIC GLAZES FOR WALL TILES WITH DIFFERENT GLASS WASTES

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ABSTRACT. Ceramic glazes are thin coatings which enhance the aesthetical aspect, increase the mechanical strength and chemical stability, and waterproof of the support. The glaze composition contains an important quantity of frit for decreasing the melting point. In this study, the frit is replaced by the different glass wastes and the properties of resulted glazes were evidenced. Various compositions of glazes were formulated. The oxide compositions, the particle size distribution of glass wastes were determined. The glazes were prepared and applied on wall tiles biscuit and thermal treated at 1100˚C for three hours. Using optical and scanning electron microscopy the glazes microstructure and the intermediate layer between the glaze and ceramic support were analysed. The linear thermal expansion coefficient of the glazes and chemical stability in acid/alkaline solutions were determined.

Keywords: *ceramic glaze, waste glass, composition, microstructure*

INTRODUCTION

Ceramic wall tiles are porous products made from clay mixed with sand, limestone and other raw materials. Due to their high porosity, the tiles are not used as such, the ceramic support being covered by a thin coating of glaze. As a result, the porous tile becomes waterproofed, the mechanical strength and chemical stability increase, and last but not least a higher possibility of cleaning is obtained.

Research into exploitation and recycling of industrial wastes for the manufacturing more value-added materials is very important and necessary for an eco-friendly environment [1]. Waste electronic and electronical equipment (WEEE) contains a high amount of reusable materials such as plastics, metals and glass, which can be used as secondary raw materials [2].

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In the past years the recycling process of WEEE has become an alternative to reduce the cost of materials mainly oxide materials by replacing some expensive raw materials with these wastes. Another advantage resulted by using the glass wastes is to minimize energy consumption in obtaining the fluxes (frit for glazes) and to diminish environmental impact (avoid the landfill disposing of cathode ray-tubes - CRT, due to hazardous elements in composition) [1].

Different studies showed that a wide variety of industrial wastes can be used, in different types of ceramic products like glass and glass-ceramics [2,12], roof tiles [3], floor tiles [4], porcelain stoneware tiles [5], for substitution of non-plastics materials.

A great practical interest, due to their compositions, represents end of life (EOL) CRT panels presents several options for reuse [1,6].

CRT's constitutes approximately 65% of the weight of the television or computer monitor. CRT's are composed of glass components, each of different composition: the panel (65%) – barium-strontium glass, the funnel (35%) – lead glass, the frit – lead glaze, and the neck (5%) a reach lead glass [7, 8]. Several toxicity studies showed that the funnel and neck are hazardous wastes, and the panel shows very little toxicity [9, 10].

Also due to the fact that the recycling of WEEE is not yet fully automated, it remains labor intensive, and requires efforts to make the process profitable, to increase the consumption of WEEE instead of natural raw materials [11].

Because CRT panel composition is similar to glazes, the reuse of these wastes is appropriate for ceramic glazes production, particularly as substitute for ceramic frits (fluxing agent) [7, 13]. A great variety of glazes can be obtained by varying the content of waste in the composition.

The aim of this study is to develop and characterize several compositions of glazes made of different glass wastes, frit and natural raw materials.

RESULTS AND DISCUSSION

Raw materials characterization

Chemical composition

The chemical composition determined by wet chemistry analyses on the frit and glass wastes are presented in Table 1.

The usual frit for wall tiles is mainly consisting of silica, aluminum oxide, calcium oxides besides of alkali and small quantity of ZnO. The CRT glass waste has a similar content in silica, small quantity of alumina and calcium oxide but an increased content in barium oxide and alkalis. The green and transparent glass wastes are very similar in composition having a higher content in silica then frit and CRT glass, high content in calcium oxide and alkalis.

The chemical composition of the glass wastes and the other raw materials is very important for the formulation of a proper glaze, depending on use of the glaze.

Table 1. Oxide composition of frit and glass wastes

Sample / Oxide [%]	Frit	CRT glass	Green glass (bottle)	Transparent glass (jar)
SiO_2	58,2	60.73	71.10	69.98
Al_2O_3	10,30	4.23	3.26	2.80
Fe_2O_3	0,08	0.01	0.03	0.04
CaO	6,86	3.01	8.23	10.97
MgO	1,27	0.98	2.66	2.94
Na_2O	5,00	8.00	14.00	12.00
K_2O	1,00	7.00	0.50	0.50
BaO	-	15.05	-	-
ZnO	3,44	-	-	-

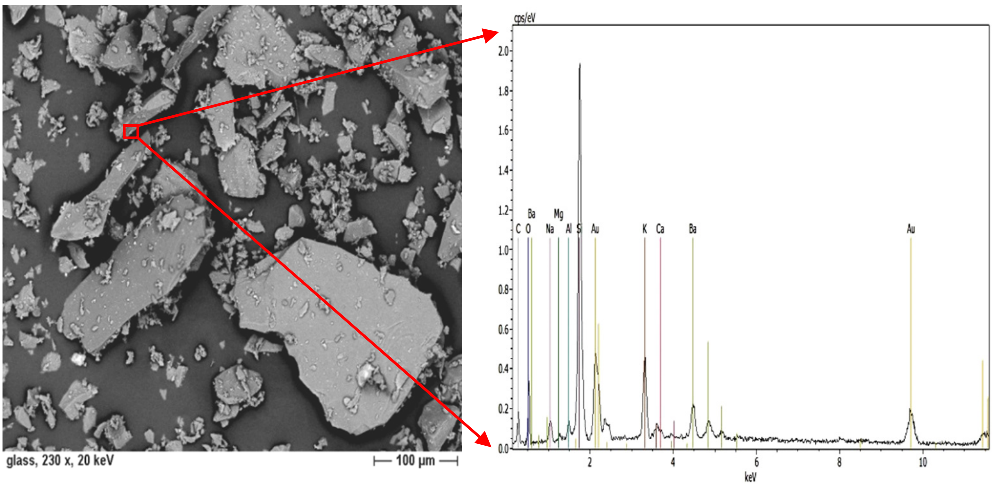

Figure 1. SEM image with EDS spectra of CRT glass

CRT glass wastes come from scrap computer monitors, which were previously separated from plastic/wooden enclosure, and after divided into two parts: - the front (the panel - part without lead), and - the back (the cone – part which contains lead). The CRT glass used in this study was the panel, glass without lead. In the Figure 1 is presented an image of crushed CRT glass wastes with EDS spectra for a small pieces. The elements identified by EDS spectra are similarly with those from chemical oxide analyses.

The green and the transparent waste glasses are selected from households. Their composition being very similar with a ceramic frit they are frequently used in low temperature glazes.

Particle size distribution of the glass wastes

The melting temperature of the raw glaze depends of the type of ceramic support mainly of its sintering temperature. The wall tiles have the firing temperature about 1000 ºC, so at this temperature the glaze mixture has to be completely melted. Therefore, the grain sizes of the compounds is recommended to be very small, mainly micrometer sizes, under 60 μm. The tested glass wastes were milled in a laboratory ball mill and their grain size distributions are presented in Figure 2.

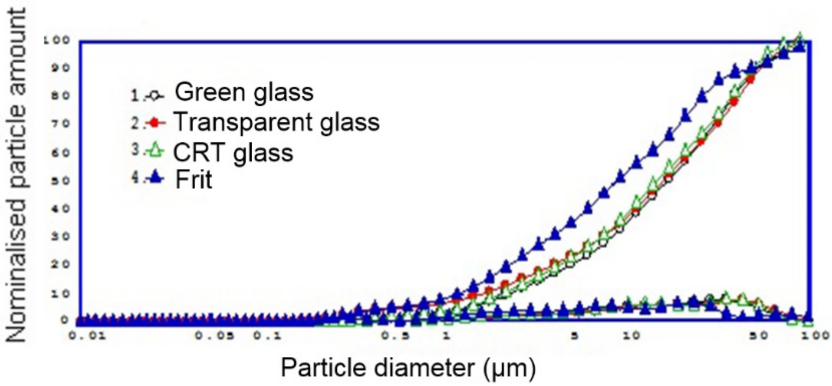

Figure 2. Grain size distribution of studied glass wastes and frit

For all the samples the size range is between 179 nm and 90 μm. In the case of the frit, 92 % grains have a size smaller than 55 μm; the CRT glass waste has about 95 % grains below 58 μm; the sizes of grains for transparent and green glass wastes are very similarly, majority smaller than 58 μm (about 93 %).

Bentonite

Clay and kaolins are usually used in slurry composition for maintaining the solid phase in suspension. In experiments the Romanian bentonite with composition presented in table 2 was tested.

Table 2. Oxide composition of bentonite

Oxide	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
[%]	70,92	0,18	12,66	1,32	3,5	1,4	0,45	1,27	8,4

In all experimented compositions the zirconium silicate, $ZrSiO_4$, having micrometer sizes (1-5 μm) was used as opacifier.

For coloring the glazes a ceramic pigment based on cobalt oxide was used.

Characterization of the glaze slurry

Density of the slurries

For obtaining an adequate raw layer on the ceramic support the density of the slurry is necessary to be around the 1400 g/l. The slurries prepared with water in the laboratory are the density between 1380 g/l and 1450 g/l.

Characterization of the fired glazes

Thermal expansion coefficient, acidity index and surface tension

A ceramic glaze can be considered a glass on a porous support and its thermal expansion coefficient has to be closely to the ceramic support. If these values are very different on the glaze surface appear defects like crazing or peeling. For a good compatibility of the glaze with ceramic support the glaze thermal expansion coefficient should be slightly below the ceramic body.

The calculated acidity index (AI) of the glazes must be between 2 and 3. In the case of index AI smaller than 2 the glaze cannot be formed on the surface of the ceramic body due to the lack of glass forming oxides (SiO_2). An index AI bigger than 3 induces crystallization of some oxides from glaze composition.

The surface tension of a glaze is very important for obtaining an uniform coating on the ceramic body and its value should be around 300 dyne/cm^2. The thermal expansion coefficients α, in the temperature range 20 – 600 ºC, acidity index AI and surface tension of the studied glazes are presented in Table 3. From this point of view all glazes are suitable, except glaze 1.1 which has an acidity index AI smaller than 2. The experimented thermal expansion coefficient for the ceramic support is 8.8×10^{-6} C^{-1}.

It can be noted some differences between calculated and experimented thermal expansion coefficient which is attributed to the manufacturing of the samples. The highest value of thermal expansion coefficient is for glaze 1.1 with 90 % CRT glass waste followed by glaze 1.2 and 1.3. By partially replacing of the frit with glass wastes (60 %), the thermal expansion coefficient is decreasing. The value of glaze 2.2 is slightly under the one of ceramic body and the glaze 3 which contains only ceramic frit (90%).

Table 3. Thermal expansion coefficients, acidity index and surface tensions of studied glazes

Sample	Thermal expansion coefficient [C^{-1}] $\alpha*10^6$		Acidity index AI	Surface tension [dyne/cm^2]
	calculated	experimented		
Glaze 1.1	9.66	13.6	1.71	319.24
Glaze 1.2	8.88	12.1	2.09	334.08
Glaze 1.3	8.45	10.9	2.12	341.57
Glaze 2.1	7.27	10.6	2.00	326.48
Glaze 2.2	7.03	7.8	2.19	333.90
Glaze 2.3	8.82	9.9	2.20	337.65
Glaze 3.0	4.94	9.9	2.25	333.72

It can be concluded that glass wastes can be used as flux in the wall tiles glazes partially replacing the usual frit.

Glazes microstructure

The optical study in polarized light realized on the thin sections of glazed wall tiles allows evidencing some structural-textural characteristics.

The fine texture of the glazed wall tiles is illustrated in polarizing optical microscopy images (Figure 3). A high amount of quartz of various sizes and shapes and closed pores within a relatively homogeneous vitreous matrix in the ceramic support can be noticed.

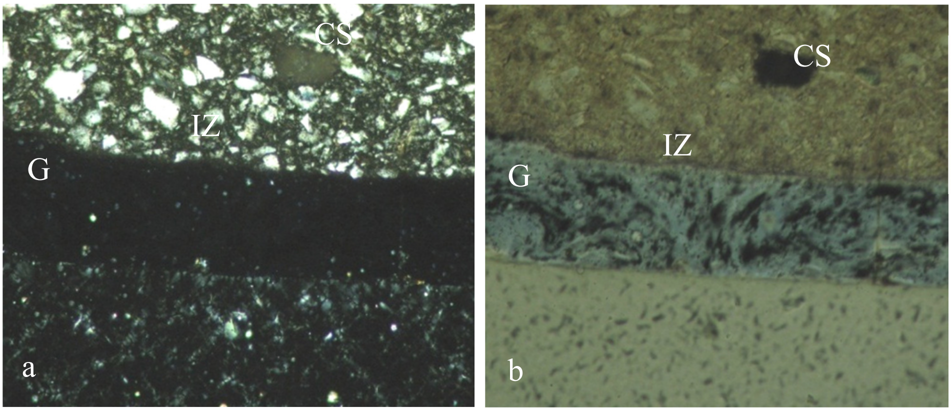

Figure 3. Optical microscopy images of glaze 1.1, (a) N+ (45x); (b) 1N (45x); (CS - ceramic support; G - glaze; IZ - intermediary zone)

Also only partly solubilized large quartz grains, as well as an incomplete homogenization of the blue ceramic pigment in the glaze are visible.

Scanning electron microscopy (SEM)

The SEM image (Figure 4) of the glazed wall tiles evidences a well intermediary layer between ceramic body and glaze. It can be seen that the glaze entered into the pores of the ceramic support, making a very strong glass-ceramic bond.

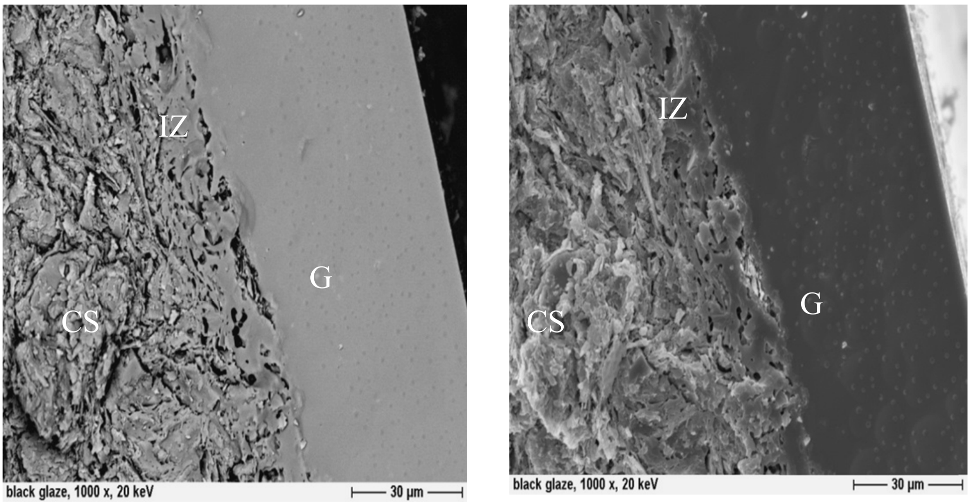

Figure 4. SEM images of glaze 1.1 with 90% CRT (CS- ceramic support; G-glaze; IZ-intermediary zone)

Also small ceramic pigment spots can be observed in the glaze layer.

Chemical stability in acid/alkaline solutions

The glazes presented a very good chemical stability to acid and alkaline corrosion. The weight losses in solutions of 3 % hydrochloric acid respectively natrium hydroxide after 96 hours are presented in Table 4. It can be noted that the weight losses of the glazes are almost insignificant.

This good behavior of the glazes can be attributed to a well-balanced composition of the glazes.

Table 4. Weight losses during the acid/alkaline attack

Attack Solution	Glaze	Weight before attack [g]	Weight after attack [g]	Weight losses [%]
HCl 3%	1.1	18,6841	18,6835	0,003211
	1.2	17,2675	17,2627	0,027806
	1.3	16,0848	16,0808	0,024874
	2.1	18,0898	18,0840	0,032073
	2.2	17,0259	17,0176	0,048773
	2.3	19,4195	19,4150	0,023178
	3	16,6697	16,6626	0,042610
NaOH 3%	1.1	18,3778	18,3778	0
	1.2	18,5901	18,5779	0,065669
	1.3	16,9851	16,9808	0,025323
	2.1	16,8766	16,8733	0,019558
	2.2	17,5218	17,5187	0,017695
	2.3	20,1967	20,1879	0,043590
	3	16,6039	16,5989	0,030122

CONCLUSIONS

Glazes with CRT, and household glass wastes can be obtained by combining the glass wastes with frit, and natural raw materials in various proportions. Also, even if the recycling of CRT glass is not simple because of the varying composition, glazes with CRT show an excellent glaze-ceramic compatibility, with an excellent chemical resistance.

The glaze-ceramic thermal compatibility is very well revealed with the SEM and optical microscopy. A continue intermediary layer between glaze and ceramic support are formed. No defects in glazes were evidenced.

In conclusion, the green and transparent glass wastes and CRT wastes can partially replace the usual frit in the wall tiles glaze compositions.

EXPERIMENTAL SECTION

The glaze suspensions are formed of different raw materials, which can be divided into: non-plastics (frits, oxides, pigments), plastics (clays) and additives (opacifiers, binders).

The experimented compositions are presented in Table 5.

Table 5. The experimented ceramic glaze compositions

Raw materials [%] / sample	CRT glass waste	Transparent glass waste	Green glass waste	Frit	Ceramic pigment	$ZrSiO_4$	Bentonite
1.1	90	-	-	-	4	2	4
1.2	-	90	-	-	4	2	4
1.3	-	-	90	-	4	2	4
2.1	60	-	-	30	4	2	4
2.2	-	60	-	30	4	2	4
2.3	-	-	60	30	4	2	4
3	-	-	-	90	4	2	4

The first group of glazes is formed from the compositions 1.1, 1.2 and 1.3 in which the frit is totally replaced by de CRT glass waste, transparent glass waste and green glass waste. In the second group formed from the compositions 2.1, 2.2 and 2.3 the wall tile frit was partially replaced (60 %) by the above mentioned wastes. For comparing the results, the composition with 90 % frit usually used in manufacturing of wall tiles was formulated.

The raw materials weighed according to the reciepe were milled in a laboratory mill (type Pulverisette 6) for 45 minutes, at a rotation speed of 250 rpm.

The glaze, kept under continuous stirring in order to avoid sedimentation, was deposited on the moistened ceramic tile, by dipping into the glaze slurry.

After a short drying time the samples were thermal treated in a Nabertherm laboratory kiln. The firing rate was of 10°C/min up to maximum temperature (1100°C), for 30 minutes at this temperature.

The grain size distribution of the frit and glass wastes were studied by using a Counter Coulter WING-SALD 7101 granulometer and the thermal expansion coefficient with a Linseis Horizontal dilatometer L75Hx1400.

From the fired ceramic glaze R 1.1 it has obtained 25-30 micrometers thin sections that were used for the optical study with polarized light under a Nikon Eclipse E200 microscope.

Chemical stability was tested by immersing the glazed samples in solutions of 3 % hydrochloric acid respectively natrium hydroxide.

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