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End of Life-Materials: WEEE Glass Recovery in Construction Sector

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ABSTRACT

In this work was investigated the feasibility to use Waste Electrical and Electronic Equipment (WEEE) glasses in construction sector as secondary raw material. WEEE glasses were used in different percentages as a function of the product obtained: 30-40wt% for glaze formulations, about 40wt% for glass-ceramics and 5wt% in brick bodies. The laboratory and industrial scale up results demonstrated that it is possible to produce a glazed tile with a glaze containing fluorescent lamps glass instead of commercial ceramic frits. Glass-ceramics composed by nepheline ($(Na,K)AlSiO_4$), akermanite ($Ca_2Mg(Si_2O_7)$) and celsian ($BaAl_2Si_2O_8$) were obtained at low temperature and short time (T = 900°C and t = 60 min) with panel glass as component. Besides, small amounts of panel glass were added in brick bodies because this glass is suitable as fluxing agent only at high temperatures; at brick manufacturing temperatures (around 1000°C), the glass viscosity does not enough contribute to the sintering process.

INTRODUCTION

For a new environmental sustainable economy, wastes are to be considered as a real opportunity to produce clean secondary raw materials. The situation is that: recycling has priority over disposal/deposition on landfill sites; use of secondary raw materials reduces costs and conserves resources; processing of waste materials into utilisable, quality-assured secondary raw materials is a necessity. In this context electronic waste is an emerging problem as well as a business opportunity of increasing significance, given the volume of e-waste being generated and the content of both toxic and valuable material in it. Electronic waste, e-waste, e-scrap, or Waste Electrical and Electronic Equipment (WEEE) describes loosely discarded, surplus, obsolete, broken, i.e. end of life, electrical or electronic devices. The processing of WEEE in developing countries causes serious health and pollution problems due to the fact that electronic equipment contains some very serious contaminants such as mercury, lead, cadmium, beryllium and brominated flame retardants. Even in developed countries recycling and disposal of e-waste involves significant risk for examples to workers and communities and great care must be taken to avoid unsafe exposure in recycling operations and leaching of materials such as heavy metals from landfills and incinerator ashes. Rapid technology change, low initial cost, and short operative life have resulted in a fast-growing surplus of electronic waste around the globe: in

Europe it constitutes the fastest growing waste stream (around 14 kgWEEE/inhabitant/year produced), with a growth rate almost three times higher than that of average Municipal Solid Waste (MSW, 3-5% annually)[European Environment Agency, 2003]. Technical solutions are available, but in most cases a legal framework, a collection system, logistics, and other services need to be implemented before a technical solution can be applied. In response, the European Commission adopted three directives: 2002/95/EC on restrictions of certain hazardous substances used in electrical and electronic equipment (RoHS); 2002/96/EC and 2003/108/EC on WEEE disposal; and 2005/32/EC on the eco-design of energy using products (EuP). In Italy the creation of e-waste collection and treatment centres gives the opportunity to have cleaned material useful for an open-loop recycling. This is the case of glass derived in particular from cathode ray tubes (CRT) of television sets and of computers (85 wt%) and from fluorescent lamps (90 wt%). It is important to underline that although liquid crystal displays are rapidly replacing cathode tubes, the 'long wave' of TV and PC waste is to be faced in the forthcoming decade; therefore, recycling on an industrial scale is the preferable solution. WEEE glasses are very different in chemical composition and treatments (coatings) so if they are crushed and mixed together they cannot be recycled as cullet, for instance for industrial glass production such as container glass, tableware glass, TV glass, etc. On the other hand, if the different components are separated and cleaned from the coating and other pollutant elements by applying suitable treatments belonging to some specialised companies, it is possible to obtain a secondary raw material of great quality. For instance, colour CRT glass is composed by: Panel (the front part, a very homogeneous barium strontium glass, of a greenish-blue colour, whose weight is about 2/3 of the whole CRT), Funnel (the hidden part, a lead glass, whose weight is about 1/3 of the whole CRT), connected by a low melting lead glaze (frit), and Neck (a lead rich glass, more than 25%, that covers the electron gun).

A typical fluorescent lamp is composed by a glass tube phosphor coated by different blends of metallic and rare-earth phosphor salts with electrodes located at both ends of the tube. Light tubes are generally made by a soft sodium calcium glass whereas the materials on the ends which are connected to the light cap are made of hard glass with higher lead content. The EOL lamps are classified among the WEEE which contain dangerous substances (CER 20 01 21*) and the majority of which are disposed by landfilling. The principal environmental hazard associated with these lamps is the small mercury content (normally less than 5 mg in accordance with RoHS Directive).

Since recent investigations have proposed porcelain stoneware tiles [Raimondo 2007, Andreola, 2008] [Andreola, 2007], radiation protection tiles [Boccaccini, 1997] and glass–alumina platelets composite materials [Minay, 2003] as possible applications for recycled PC and TV glasses, in this work some examples of possible application of cleaned end of life (EOL) e-waste glass (CRT panel and fluorescent lamp glass) in the construction sector will be show.

CASE STUDIES

CRT glass in bricks

Brick means a ceramic product having coloured body, porous, with a crystalline structure obtained by the firing of iron minerals-containing clays at temperatures usually below 1000°C. The composition of the natural body (extracted from clays deposits near the respective productive sites) can be divided in: clayey fraction, organic fraction, fluxing material and inert part. Heavy clays ceramics as bricks, are being produced from natural raw materials with a very wide–ranging overall chemical and mineralogical composition. In the last years is generally accepted the concept for which the use of recycled materials is environmentally preferable to that of virgin raw materials, in agreement with EU wastes Directive. For this reason, more brick body compositions are prepared using different types of industrial wastes with different effect as a function of their properties (features). The wastes can be divided in three main categories: (i) fuel wastes, (ii) fluxing wastes, (iii) plasticity reducing or plastifying wastes. The use of residues is especially interesting for many reasons as the energy saving, the quality conferred to the end products and the recycling of materials that otherwise would disposed in dump. Nevertheless, it is necessary, due to the large heterogeneity of residues, to carry out preliminary experimental tests for every typology of residue, before expecting their industrial employment.

In this study CRT panel glass was added to a commercial brick body for external facing bricks in amount raging from 0.5 to 3.0 wt%. The glass was ground in a laboratory ball mill to < 75 μm in size. Laboratory bricks samples were obtained by extrusion, mixing the materials with 22 wt% of water, the extruded bars samples (50mm x 150mm) were dried for 8 h with a drying cycle using circulation of forced air at variable temperature (40-75°C) and then fired in an industrial camera kiln with a heating rate of 100°C / h (13 h total time, Tmax: 1020°C and 3 h soaking time). The dried and fired specimens were characterized following the UNI technical rules. Linear shrinkage and flexural strength after drying and linear shrinkage, water absorption (24-hour immersion), weight loss, flexural strength, colorimetric measures and efflorescence after firing were determined in the obtained materials and compared to the standard one.

Table 1- Technological properties of the fired bricks samples

Technological property	Standard body	Body+0.5% panel glass	Body+1.5% panel glass	Body+3% panel glass
Linear shrinkage (%)	-0,08	-0,07	0,02	0,16
Weight loss (%)	15,72	14,96	14,91	14,62
Water absorption (%)	13.97	15.19	15.05	14.18
Flexural strength (MPa)	14.64	14.25	14.50	13.86

Table 1 shows that the properties obtained in the e-waste glass-added samples are in accordance to the industrial tolerance values regarding shrinkage, weight loss and flexural strength values. Instead a slightly increase of water absorption is observed.

Since CRT glass is lowmelting features (T softening: 855°C; T melting: 1115°C), it can play the role of sintering promoters through the formation of a viscous phase at high temperature [Matteucci, 2002; Tucci, 2004; Andreola, 2008]. Similar behaviours have already been observed in clayey bodies containing glass as raw material [Matteucci, 2002; Tucci, 2004, Ortelli, 1983; Palmonari, 1985; Cava, 2000; Pontikes, 2004]. The results obtained are in accordance with those of other authors [Dondi, 2009] and show that the addition of CRT panel glass, does not improve the mechanical and microstructural properties but not even worsens them with respect to the standard one. The study highlights that the glass is not involved in the solid state reactions developed during firing. This behaviour is due to the fact that at the firing temperatures of bricks the panel glass has a viscosity (around 10^4 dPa.s) which is not enough to contributes to the sintering process, so the glass does not act as a fluxing agent, filling the open porosity of the brick silicate matrix.

For this reason this kind of glass is suitable for bricks bodies that use enough plastic clays because it acts as plasticity-reducing agent.

CRT glass in glass-ceramics

Panel CRT glass was also used in the production of sintered glass-ceramics, which are fine-grained polycrystalline materials (50-98 vol% crystalline) formed when glasses of suitable composition are heat treated hence undergone to controlled crystallisation (devitrification). These materials have improved technological properties with respect to the parent glasses.
Two compositions were formulated by dry mixing 50 wt% of panel glass with different amounts of dolomite ($CaMg(CO_3)_2$) and alumina (Al_2O_3) in order to favour the crystallisation process or to improve the chemical resistance and hardness of the glass, and here named P5F2 and P6F2 (higher alumina or dolomite content, respectively). The sintering process was carried out on glassy frits obtained by prior melting (vitrification) of the waste mixtures at 1450°C in silicoaluminate crucibles and subsequent quenching in water. Glass powders have been dry-grounded to obtain a particle size less then 180 μm, checked by sieving. The samples were subjected to the sintering tests in the temperature range 700°-1000°C for times of 30, 60 and 120 min.

By the DTA curves performed on the quenched glasses three thermal events were carried out: an inflection point (Tg near 650°C) corresponding to glass transition temperature, an exothermic peak (Tc near 950°C) indicating the crystallisation and an endothermic event (Tm near 1150°C) related to the melting. P5F2 glass showed a more refractory behaviour, with respect to P6F2 sample, visible as higher Tg, because it contains a higher amount of Al_2O_3.

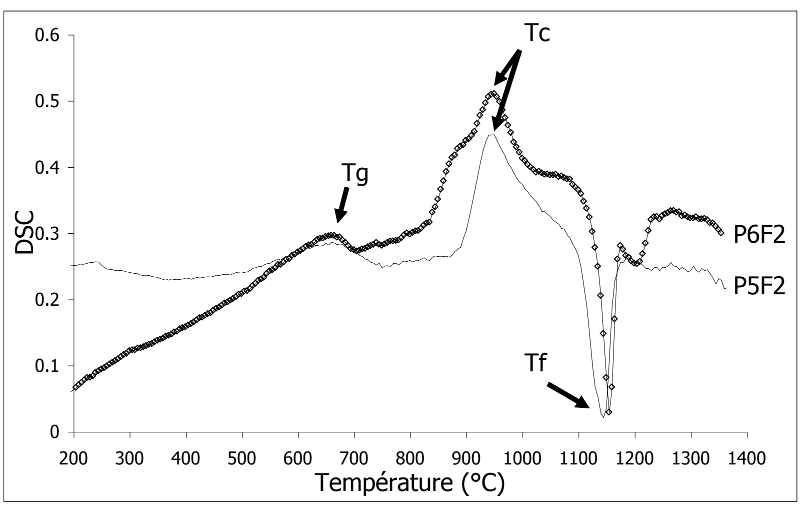
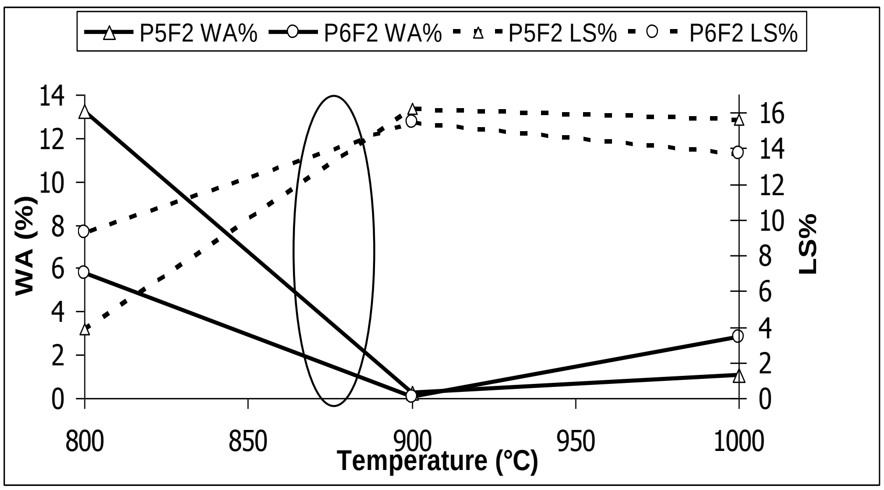


Fig. 1- DTA curves of the prepared glasses

The optimum sintering conditions were established to be T = 900°C and t = 60 min (as evidenced by Figure 1), because at these temperature and time the linear shrinkage is high and the water absorption is low (close to 0%). The decrease in water absorption by means of thermal treatment is caused by the decrease of open porosity resulting from the liquid-phase sintering process. The glassy phase melts forming a wetting liquid which penetrates between grains and exerts an attractive force pulling them together. Densification results from particles rearrangement under the influence of capillary forces and the filling of pores by liquid phase.The density values confirmed these mechanism being density 1.22, 1.42g/cm^3 at 800°C and 1.63, 1.68 at 900°C for P5F2 and P6F2, respectively. A further confirmation of this behaviour is given by the SEM analysis: at 800°C, necks between the grains powder are formed corresponding to the beginning of the sintering process, but the material presents a structure of compact powder and not a dense body; at 900°C a compact material with isolated spherical porosity is formed; at 1000°C the samples show a complete devitrified microstructure with corresponding higher intragranular porosity.

(a)



(b)

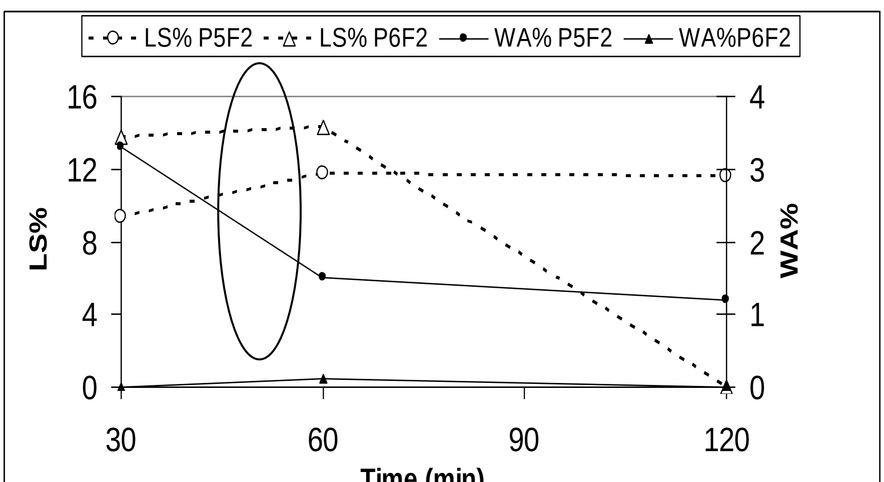


Fig. 2- Linear shrinkage (LS%) and water absorption (WA%) as a function of (a) temperature for t_{const} = 30 min and (b) time at T_{const} = 900°C.

XRD analysis showed different situations: at 800°C the sintered samples of both the compositions are amorphous, while at 900°C a considerable crystallisation degree, which further increases at 1000°C, is evident. Number and kind of phases developed at 900°C depend on the chemical composition. In both the compositions studied the main crystalline phase identified at 900°C is nepheline ($(Na,K)AlSiO_4$), which is the only phase formed in the sample P5F2. Differently, in the P6F2 glass-ceramic the highest amount of Ca, Mg, related to the higher content of dolomite, and Ba leads to the formation of akermanite ($Ca_2Mg(Si_2O_7)$) and celsian ($BaAl_2Si_2O_8$.) already at this temperature.

Fluorescent lamps glass in engobes/glazes

EOL (end of Life) Fluorescent lamps glass was used in order to formulate in laboratory scale compositions of ceramic engobes as substitute to industrial frit. An engobe is a thin layer of fluid clay based applied to a ceramic support in order to improve both the aesthetical and technical properties.

As stated above, this glass is a typical sodium (~16wt%)-calcium (~5wt%) silicate glass and shows a tendency to not crystallize with a low melting nature, confirmed by low softening and transition temperatures (respectively T_s: 567°C, T_g: 480°C) and high thermal expansion coefficient (α=9.7 10^{-6} $*$°C^{-1}). These characteristics are similar to some industrial frits with high expansion coefficient, so the recovery of this e-waste glass into engobes formulations was tested. Before the addition it was necessary to carried out a pre-treatment of the glass by sieving in order to separate pollutants such as bakelite, insulators, metallic conductors (5-6%). Engobe compositions were prepared using three glass fractions: as-received (VS), fraction above 1mm and hand cleaned (VL), residue fraction below 1mm without hand cleaned (VR). Besides, with the aim to compensate the absence into the glass composition, zircon ($ZrSiO_4$) was added in different percentages VL1(10wt%), VL2(5wt%), VL3 (3wt%) to improve the material brightness. From these considerations we can assume that the substitution of EOL lamp glass does not affect the final engobe particle size distribution and it will not cause changes on the related parameters (already industrially optimized) such as: fluency during application, porosity, drying time, etc. Thermal results have shown that the formulation containing e-waste glass has a more refractory behaviour in firing (ΔT=60°C) because the zircon added is not chemically bonded in the frit. From the aesthetic point of view colorimetric measurements evidenced that on the glazed final products, the presence of e-waste glass causes a slight decrease of the L* value (VL sample); this worsening is overcome by the addition of 5% of zircon which brings values closer to the standard (VL2). Another subject evaluated by L* values is the cleanliness effect of the glass; the data evidenced that as the purity degree decreases with L* decreases (VR2).

Starting from this laboratory screening, the research has been extended to industrial scale originating a commercial ecological product. In fact, a glazed porcelainized stoneware tile which uses a glaze containing EOL fluorescent lamps glass (40 wt%) has been produced. Notwithstanding the use of a secondary resource, the manufactured good has shown techno-logical properties similar to commercial ceramic floor and/or wall tiles. The developed technology, named Relux, consists in the production of innovative tiles with reduced environmental impact by implementing an environmentally ethical management system. Relux technology has been applied to improve environmental performance in five key areas: reducing the use of raw materials, reducing transport, reducing energy consumption, recycling high-quality materials and reducing waste processing.

Table 2- Colorimetric parameters for the different engobe compositions compared to the standard one. L* (lightness), a* (+a: expresses red;-a: expresses green), b* (+b: expresses yellow;-b: expresses blue), ΔE* (tolerance).

SAMPLE	**L***	**a***	**b***	**ΔE***
STD	92,37	0,05	2,45	0
VL	91,55	- 0,04	2,15	0,87
***VL*2**	92,27	- 0,28	1,78	0,75
***VR*2**	89,98	0,19	1,77	2,48

CONCLUSIONS

In the last 30 years there has been a common awareness, particularly in the industrialized countries, of the potentially ravaging effects towards the environment of hazardous waste such as WEEE, whose production is continuously growing. The work proposes different case studies for validating the use of e-waste, where the vitrification and the sintering processes have been used to obtain suitable products for building sector. The valorisation of WEEE glass, is towards the fabrication of marketable construction products, such as glass-ceramics, tiles and bricks. The challenge will be produce materials possessing the technical, mechanical and aesthetical properties required by the specific application.

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