GREEN CERAMIC TILES: THE SUSTAINABLE USE OF NATURAL RESOURCES AS BASIC REQUIREMENT

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1. ABSTRACT

In the present work, scrap packaging glass from urban separated collection (post-consumer waste) and industrial ceramic wastes (pre-consumer wastes) were used as secondary raw materials to prepare ceramic tile prototypes 100% green.

These innovative green ceramic products are sintered about 200°C lower than a traditional porcelain stoneware tile and maintain unchanged their performance in terms of flexural strength, Young modulus and Weibull modulus. Moreover, the green ceramic products are 100% recyclable within the ceramic process, avoiding their landfill disposal at the end of their life.

2. INTRODUCTION

The European Commission published the draft position paper "Circular Economy: a strategic European resource policy" (March 2015) in which a zero waste programme for Europe is envisaged through a circular economy strategy. Cerame-Unie expressed its views in this frame and stressed that resource efficiency requires an LCA approach, highlighting that the social and economic aspects of sustainability should always be considered in the EU legislation. Therefore, adequate access to raw materials, as well as separation and processing of waste, and a well-functioning market for secondary raw materials are needed.

Ceramic tile industries are already quite virtuous. The waste reuse factor of the Italian factories is always higher than BAT and Ecolabel limit [1] and, frequently, it is also higher than 100% indicating that factories also recycle waste from other industries.

Almost all of the industrial ceramic wastes are reused in the same process, in a closed loop cycle. Only exhausted lime from the fume abatement system is still landfill confined.

Until about 2005 the research demonstrated just a limited substitution of wastes [2-4]. Considering the post-consumer wastes, involving scrap glass such as packaging glass and cathode ray tube glass, their reuse in a traditional tile mix was noted to be up to 10% or up to 5%, respectively [5-11]. To boost these limits, the present research, developed within an EU Eco-Innovation project (WINCER), shows an example of best practice taking place in the ceramic industry.

The innovative idea is based on a new concept of the ceramic mix in which the traditional functions (plasticizing, tempering and fluxing) are performed by wastes instead of natural raw materials (clays, sands and feldspars, respectively).

The innovative approach goes beyond the partial substitution of natural raw materials and the strategy involves "wastes synergy". A selection of pre- and post-consumer wastes is opportunely balanced and mixed to obtain ceramic tiles made of 100% recycled materials.

3. MATERIALS AND METHODS

The chemical and mineralogical composition of wastes (green scrap tiles, exhausted lime and scrap glass) was determined with the use of inductively coupled plasma emission spectroscopy (ICP-OES Optima 3200 XL, Perkin-Elmer, USA), Table 1, and by X-ray diffraction analysis (XRD, PW3830, Philips, NL).

Two innovative body mixes containing 100% wastes, were formulated by using 40% green scrap tiles and 60% scrap glass (mix 1) with the addition of 1% exhausted lime (mix 2).

These mixes were prepared by milling the secondary raw materials in a porcelain jar mill for 30 minutes, with 33 wt% water and 0.6 wt% deflocculating agent.

The rheological behaviour of the ceramic suspensions was analysed by a rheometer (RS 50 HAAKE, D). The flow curves were obtained in the control rate mode, in order to evaluate the variation of viscosity in shear rate conditions.

To obtain powders suitable for shaping, the slips were dried overnight in an oven at 110°C, crushed and sieved to pass a 125 μm screen. The test specimens, in the form of disks and bars, were prepared by adding 6 wt% water to the dried powders, followed by uniaxial pressing at 52 MPa. Sintering was performed in a laboratory electric furnace at six different maximum temperatures, in the range 940-1040°C, adopting a heating rate of ~5°C/min and natural cooling to room temperature. The sintering behaviour of the fired specimens was evaluated on the basis of their linear shrinkage and water absorption determined according to the test methods recommended for ceramic tiles, set out in Standard EN ISO 10545-3.

The quantitative mineralogical compositions of the samples fired at their optimum temperature were determined by X-ray diffraction analysis (PW3830, Philips, NL). Powdered specimens, diluted with 10 wt% corundum NIST 676 as internal standard, were side loaded to minimize preferred orientation. Data were collected in the angular range 10-80 °2ϑ with steps of 0.02° and 5 s/step and the Rietveld refinements were performed using GSAS-EXPGUI software.

The microstructure of the fired materials was analysed by a scanning electron microscope, SEM, (Zeiss EVO 40, D) equipped with an energy dispersion X-ray attachment, EDS, (Inca, Oxford Instruments, UK), observing suitable specimens polished to a mirror-like finish.

The flexural strength of the fired specimens in the form of bars, 70x10x6 mm was measured by using a universal testing machine (10/M, MTS, USA), equipped with a three-point bending apparatus, 60 mm roller span, adopting a crosshead speed of 5 $mm \cdot min^{-1}$. The modulus of elasticity was also evaluated, via an extensometer applied in correspondence to the middle of the surface of the bars subjected to the tensile stress. The average flexural strength, σ, was calculated on twenty results of correctly fractured specimens and Weibull's modulus, m, was evaluated via the least squares method and linear regression analysis, adopting, as the probability estimator, $P_n = (i-0.5)/N$.

4. RESULTS AND DISCUSSION

The chemical and mineralogical compositions of the selected wastes are reported in Table 1.

The scrap glass is a completely amorphous soda-lime glass. Exhausted lime is a calcium-based waste and unfired scrap tiles have the typical composition of ceramic tiles.

The ceramic suspensions containing 100% wastes show quite a different rheological behaviour (Fig. 1). With respect to a previously studied typical porcelain stoneware suspension [REF], mix 1 shows a flow curve indicating an higher viscosity and mix 2 shows an high thixotropic behaviour that will create problems during the industrial process (mill emptying phase). Therefore, mix 2 cannot be used as a new recipe in the industrial process because it needs to be optimized from a rheological point of view.

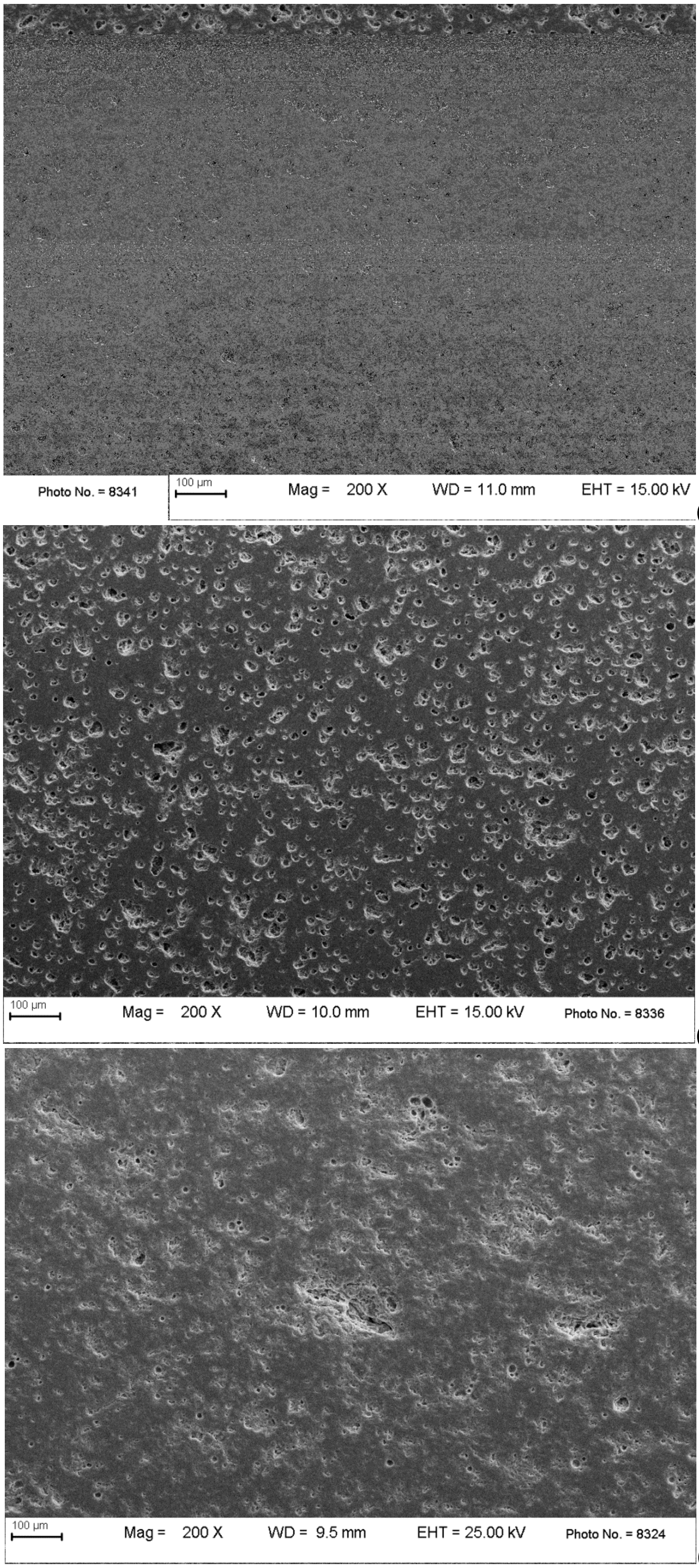
The firing behaviour of mixes 1 and 2 is reported in Fig. 2 with respect to a reference standard porcelain stoneware mix [5]. Both mixes show a significantly lower optimum firing temperature (960°C) compared to the standard mix (1160°C), which was fired in the same laboratory conditions in a previous study. The stability during firing, represented by the dotted lines in Fig. 2, is quite similar for all the samples. This is due to the incipient crystallization during the sintering process, especially in the new mixes 1 and 2, in which the synergy among wastes promotes the formation of wollastonite and plagioclase (Table 2).

The mechanical properties are reported in Table 3 with respect to a standard porcelain stoneware. All the fired samples 1 and 2 show flexural strength, σ, quite similar to that of the traditional porcelain stoneware fired at higher temperature. The Young modulus values, E, are significantly lower than that of the reference in both samples 1 and 2. This is an advantage because the materials are still mechanically resistant but are less rigid. The Weibull modulus, m, which is an index of the material's reliability, is quite high in all the fired samples. For some commercial porcelain tile this modulus can be significantly lower, till 5.

In fact the microstructure of the polished cross section of the samples shows some differences, especially in terms of porosity and pore size (Fig. 3).

Oxides	Scrap glass wt%	Exhausted lime wt%	Unfired scrap tiles wt%
SiO_2	71	-	69.81
Al_2O_3	4.31	0.10	18.85
TiO_2	0.10	-	0.58
Fe_2O_3	0.48	0.26	0.62
CaO	9.00	58	0.61
MgO	2.46	0.36	0.43
K_2O	0.83	0.42	1.56
Na_2O	11	0.36	2.16
SO_3	-	6.57	0.09
ZnO_2	-	0.15	-
L.O.I.	0.56	12.25	4.18
Mineralogical composition	Amorphous	Calcium hydroxide Fluorite Calcium sulphate	Quartz, Kaolinite, Illite, Microcline, Plagioclase

Table 1. *Chemical and mineralogical composition of the wastes.*



(a)

(b)

(c)

Figure 3. *SEM micrographs of the polished cross section of mix 1 (a) and mix 2 (b) both fired at 960°C, with respect to that of a standard porcelain stoneware sample fired at 1160°C (c).*

	Quartz	Mullite	Plagioclase	Cristobalite	Wollastonite	Glass
Mix 1	4.8±0.1	-	16.4±0.3	3.3±0.2	8.8±0.3	66.7±1.1
Mix 2	4.1±0.1	-	18.5±0.3	3.2±0.2	9.8±0.3	64.4±1.1
Standard [5]	21.4±0.1	5.3±0.5	3.4±0.4	-	-	69.9±1.2

Table 2. *Quantitative mineralogical composition of the fired mixes.*

	σ (MPa)	*E* (GPa)	*m*
Mix 1, 960°C	72.7±5.3	48.3±3.5	16.2
Mix 2, 960°C	72.6±7.5	47.8±3.0	11.6
Standard, 1160°C [5]	94.9±5.0	72.9±1.5	21.9

Table 3. *Mechanical properties of the fired mixes.*

5. CONCLUSION

The results showed that exhausted lime creates problems during the milling step and its reuse should be avoided unless there is a higher addition of expensive dispersant agents. At this time, that is not considered economically feasible.

In any event, it should be possible to industrialize the mix without exhausted lime (mix 1), which gives rise to a material quite similar to a traditional porcelain stoneware but fired about 200°C lower.

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