Innovative Ceramic Tile Mixes: 100 % Green

E. Rambaldi, S. Fazio, F. Prete, M. C. Bignozzi

In the present work, scrap packaging glass coming from urban separated collection (post-consumer waste) and industrial ceramic waste (pre-consumer waste) were used as secondary raw materials to prepare prototypes of ceramic tiles 100 % green (100 % made of recycled materials). Opportunely balanced mixes of waste are able to synergically interact during the thermal cycle, giving rise to innovative materials able to sinter about 200 °C lower than a traditional ceramic tile mix, maintain good performances in terms of flexural strength, Young's modulus and Weibull's modulus.

Introduction

The European Commission published in December 2015 the position paper "Closing the Loop – an EU Action Plan for the Circular Economy" in which a zero waste programme for Europe is envisaged through a circular economy strategy. The proposed actions will contribute to "closing the loop" of product lifecycles through greater recycling and re-use, and bring benefits for both the environment and the economy.

The revised legislative proposals on waste set clear targets for reduction of waste and establish an ambitious and credible long-term path for waste management and recycling. Key elements of the revised waste proposal include, among others, a common EU target for recycling 75 % of packaging waste by 2030, a binding landfill target to reduce landfill to maximum of 10 % of all waste by 2030, a ban on landfilling of separately collected waste, promotion of economic instruments to discourage landfilling, economic incentives for producers to put greener products on the market and support recovery and recycling schemes.

Cerame-Unie expressed its views in this frame and stressed that resource efficiency requires an LCA (Life-Cycle Assessment) 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 well-functioning market for secondary raw materials are needed.

Ceramic tile industries are already quite virtuous. The waste re-use 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 recycle also waste coming from other industries. Almost all of the industrial ceramic waste are re-used in the same process, in a closed loop cycle. Only exhausted lime coming from the fume abatement system is still landfill confined.

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

Tab. 1 Chemical and mineralogical composition of the waste

Oxide	Scrap Glass [mass-%]	Exhausted Lime [mass-%]	Unfired Scrap Tile [mass-%]
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

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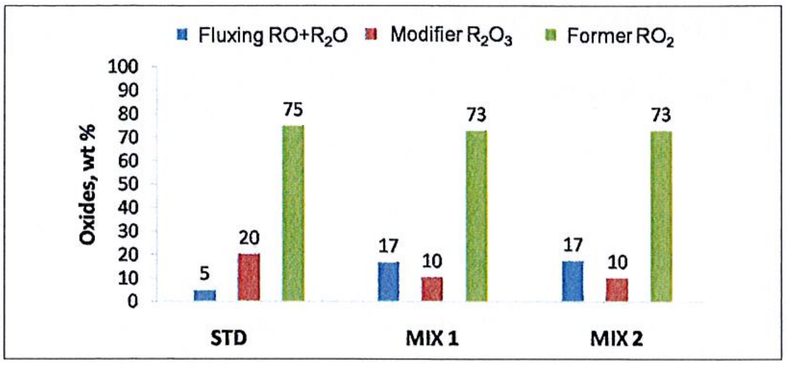

Fig. 1 Chemical composition of Mix 1 and Mix 2 in respect to the standard one (STD)

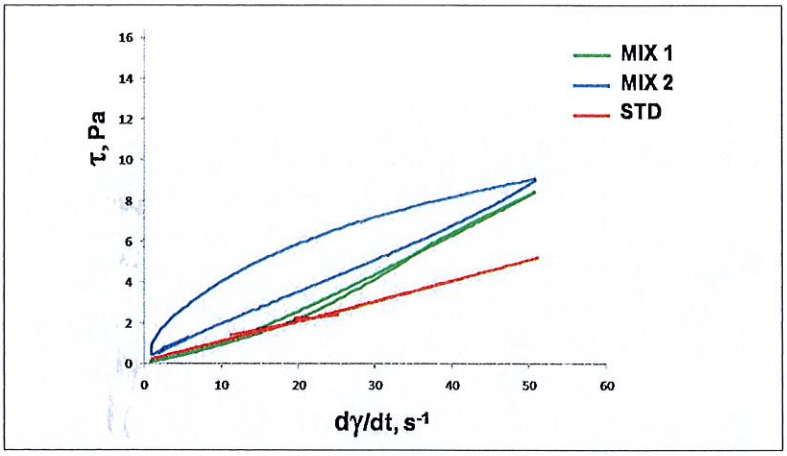

Fig. 2 Flow curves of the ceramic suspensions Mix 1 and Mix 2 in respect to a standard porcelain stoneware mix [6]

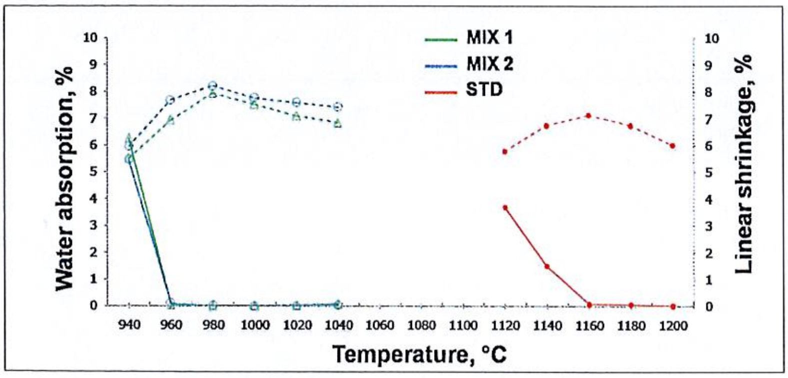

Fig. 3 Water absorption and linear shrinkage of Mix 1 and Mix 2 in respect to a standard porcelain stoneware mix [5]

The innovative idea is based on a new concept of ceramic mix in which the traditional functions (plasticizing, tempering and fluxing) are exerted by waste 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 concerns the "waste synergy". A selection of pre- and post-consumer waste is opportunely balanced and mixed to obtain ceramic tiles made of 100 % by recycled materials.

Materials and methods

The chemical and mineralogical compositions of waste (unfired scrap tiles, exhausted lime and scrap glass) were determined with the use of inductively coupled plasma emission spectroscopy (ICP-OES Optima 3200 XL, Perkin-Elmer/US; Tab. 1), and by X-ray diffraction analysis (XRD, PW3830, Philips/NL).

Two innovative body mixes containing 100 % of waste, were formulated by using only unfired scrap tiles and scrap glass (Mix 1) with the addition of 1 mass-% of exhausted lime (Mix 2). These mixes were prepared by milling the recycled raw materials in a porcelain jar mill for 30 min, with 33 mass-% water and 0,6 mass-% deflocculating agent. The rheological behaviour of the ceramic suspensions was analysed by a rheometer (RS 50 HAAKE/DE). 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 at 125 µm screen. The test specimens, in form of disks and bars, were prepared by adding 6 mass-% water to the dried powders, followed by uniaxial pressing at 52 MPa. Sintering was performed in a laboratory

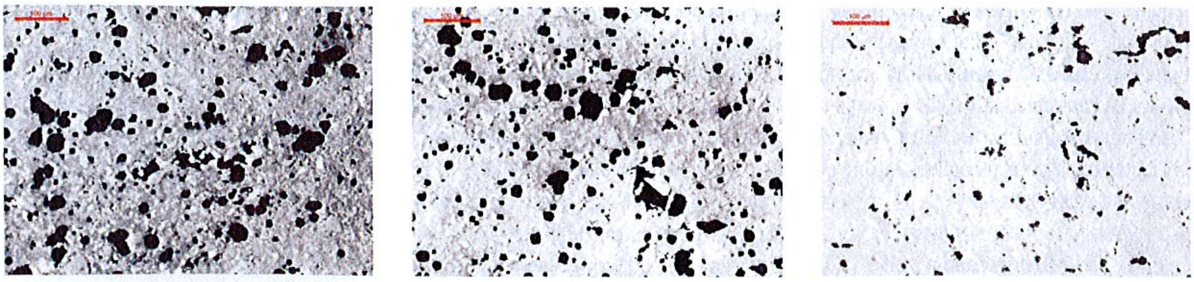

Fig. 4 OM micrographs of the polished cross section of Mix 1 (left), and Mix 2 (middle), both fired at 960 °C, in respect to a standard porcelain stoneware sample fired at 1160 °C (right); the scale is 100 µm

electrical furnace at 6 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 method recommended for ceramic tiles reported in EN ISO 10545-3.

The quantitative mineralogical composition of the samples fired at their optimum temperature was determined by X-ray diffraction analysis (PW3830, Philips/NL). Powdered specimens, diluted with 10 mass-% of corundum NIST 676 as internal standard, were side loaded to minimize preferred orientation. Data were collected in the angular range 10–80° 2 ϑ with steps of 0,02° and 5 s/step; the Rietveld refinements were performed using GSAS-EXPGUI software [12].

The microstructure of the fired materials, polished to mirror like finishing, was observed both with an optical microscope (OM, Leica/DE DM-LM). The closed porosity was determined by image analysis (Leica/DE, LAS v. 3.8) on the basis of at least 10 optical microscope images for each sample fired at its optimum sintering temperature.

The flexural strength of the fired specimens in form of bars of 70 mm × 10 mm × 6 mm was measured by using an universal testing machine (10/M, MTS/US), equipped with a 3-point bending apparatus, 60 mm roller span, adopting a crosshead speed of 5 mm/min. 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 20 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 $P_n = (i–0,5)/N$.

All results of the characterization of Mix 1 and Mix 2 were compared with those of a standard porcelain stoneware material already studied and published [5].

Tab. 2 Quantitative mineralogical composition of the fired mixes

	Mix 1	Mix 2	Standard [5]
Quartz	4,8 ± 0,1	4,1 ± 0,1	21,4 ± 0,1
Mullite	–	–	5,3 ± 0,5
Plagioclase	16,4 ± 0,3	18,5 ± 0,3	3,4 ± 0.4
Cristobalite	3,3 ± 0,2	3,2 ± 0,2	–
Wollastonite	8,8 ± 0,3	9,8 ± 0,3	–
Amorphous phase	66,7 ± 1,1	64,4 ± 1,1	69,9 ± 1,2
Crystalline Index	**0,37**	**0,35**	**0,07**

Tab. 3 Closed porosity (P) and mechanical properties of the fired mixes

	P [%]	σ [MPa]	E [GP]	m
Mix 1, fired at 960 °C	14 ± 3	72,7 ± 5,3	48,3 ± 3,5	16,2
Mix 2, fired at 960 °C	15 ± 3	72,6 ± 7,5	47,8 ± 3,0	11,6
Standard, fired at 1160 °C [5]	6 ± 3	94,9 ± 5,0	72,9 ± 1,5	21,9

Results and discussion

The chemical and mineralogical composition of the selected waste are reported in Tab. 1. Scrap glass is a soda-lime glass completely amorphous. Exhausted lime is a calcium-based waste and unfired scrap tiles have the typical composition of ceramic tiles.

The chemical composition of the different mixes is shown in Fig. 1 in terms of former oxides (SiO_2), modifier oxides (Al_2O_3) and fluxing oxides (CaO, MgO, Na_2O and K_2O). In respect to a standard porcelain stoneware, Mix 1 and Mix 2 contain a similar amount of silica but a significantly higher amount of flux (in particular CaO and Na_2O).

The ceramic suspensions containing 100 % of waste show a rather different rheological behaviour (Fig. 2) in respect to a standard porcelain stoneware suspension [5]: Mix 1 shows a flow curve indicating an higher viscosity and a slightly shear-thickening behaviour; Mix 2 shows an high thixotropic behaviour that may create problems during the industrial process (mill emptying phase). Therefore Mix 2 cannot be used as new receipt in the industrial process because it requires to be optimised from the rheological point of view.

The firing behaviour of Mix 1 and Mix 2 is reported in Fig. 3 in respect to a standard porcelain stoneware mix. Both mixes show an optimum firing temperature (960 °C) significantly lower in respect to the standard mix (1160 °C) which was fired in the same laboratory conditions for a previous work [5]. The stability during firing, represented by the dotted lines in Fig. 3, is rather similar for all the samples. It is due to the incipient crystallization during the sintering process, especially in the new mixes (Mix 1 and Mix 2), in which the synergy among waste promotes the formation of wollastonite and plagioclase. In Tab. 2 the quantitative mineralogical composition is reported for each samples together with the Crystalline Index (CI) that indicates the capability of the materials to develop crystals of new formation during sintering. This index was determined following eq. 1:

$$CI = \frac{new\ Crystals}{amorphous\ Phase + residual\ Crystals} \qquad (eq.\ 1)$$

Considering that in the standard composition the new crystals are only mullite, this index is very low ($CI = 0,1$) respect to the innovative mixes ($CI = 0,4$) in which new crystals are wollastonite, cristobalite and plagioclase.

The microstructure of the polished cross section of the samples fired at their optimum sintering temperature shows some differences especially in terms of porosity and pore size (Fig. 4). The closed porosity determined by image analysis is significantly higher in Mix 1 and Mix 2 in respect to the standard (Tab. 3).

The mechanical properties are reported in Tab. 3 respect to a standard porcelain stoneware. All the fired samples of Mix 1 and Mix 2 show flexural strength, σ, rather high and, considering the standard deviation, similar to the traditional porcelain stoneware fired at higher temperature. In both the samples of Mix 1 and Mix 2, the Young's modulus values, *E*, are significantly lower than the standard composition. The Weibull's modulus, *m*, that is an index of the material reliability is rather high in all the fired samples. For some commercial porcelain tile this modulus can be significantly lower, till 5.

Conclusion

Results showed that exhausted lime creates problems during the milling step and its re-use should be avoided unless of higher addition of expensive dispersant agents. At this time, that is not considered economically sustainable. By the way, it is possible the industrialization of the mix without exhausted lime (Mix 1), due to:

- rheological behaviour similar to the traditional mix
- good stability during firing
- good mechanical properties.

Even if this material is fired about 200 °C lower than a traditional porcelain stoneware following the standard requirements of EN 14411 (Ceramic Tiles – Definitions, Classification, Characteristics, Evaluation of Conformity and Marking) it belongs to the same class of products (BIa).

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