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FAST FIRING OF GLAZED TILES CONTAINING PAPER MILL SLUDGE AND GLASS CULLET

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Abstract
The present paper reports on the results of some experiments on the progress of a previous research and describes the production, in single fast firing, of tiles containing 30 wt% of a natural red clay and a mixture of 42 wt% of paper mill sludge [PS] and 28 wt% of glass cullet [GC] which were coated with a commercial "matt white" glaze. Fired materials were characterized as a function of the top temperature (1090 or 1140°C) reached during the sintering process made within an industrial roller kiln. It is observed that tiles fired at 1090 °C display the best overall performances since the matt glaze well covers the substrate concurring to maintain in line with the official standard for production the mechanical and physical properties of the tiles.

Keywords: paper mill sludge; glass cullet; fast firing; glazed tiles, shrinkage, water absorption, mechanical properties

1. Introduction
In a previous paper [1] we described production and characterisation of some sintered ceramics obtained by mixtures of GC and some PS; we demonstrated that materials containing 60 wt% of PS and 40 wt% of GC have good physico-mechanical properties independently of the type of PS used. Conversely, their shrinkage exceeds the limits established by the standards for tiles production. On the progress of that research [2], we have reported the results obtained with materials prepared by mixing the above mixture with increasing amounts of a natural red clay. It was demonstrated that the addition of 30 wt % of clay enables fast firing production of unglazed tiles.
The present paper reports on production and characterization of glazed tiles containing 42 wt% of paper mill sludge and 28 wt% of glass cullet (60/40) and 30 wt% of a natural red clay. Before firing, tiles were first coated with an engobe and then wet sprayed with a commercial "matt white" glaze. Sintering was performed, by single fast firing (cold to cold), in an industrial roller kiln at two different temperatures. Fired materials were characterized by shrinkage, water absorption, bend strength and hardness measurements, their properties being compared to those of a reference product, presently under production, which was fired at 1140 °C.
The aim of this work is to demonstrate that PS can be used in the production process of red "monoporosa" or earthenware tiles. In order to make the goal, it is necessary first to incinerate the starting sludge and then to blend this product with adequate amounts of GC and clay.

2. Materials and Methods
Description and characterization of the starting materials as well as the preparation procedure of the green supports are reported elsewhere [1, 2]. Chemical composition of engobe glaze are displayed in table 1. Green samples were first coated by a white engobe as a shelter layer and then sprayed with the glaze. The use of the engobe was established in order to minimize the substrate color effect of the final look of the tile. Sintering was performed by single fast firing (50 min-cold to cold) in air, by an electric roller kiln (Nannetti), at temperatures of 1090 and 1140 °C respectively. Shrinkage on firing was evaluated along the longest sample dimension by a caliper using the ratio $(h_0-h_1)/h_0$ (subscripts 0 and 1 referring to sample dimensions before and after the sintering). Water absorption was determined following the norm EN99. Sintered tiles were cut into specimens having a cross section of 6.5x4 mm and a span of about

50 mm for the bending rupture strength tests. Rupture strength (σ) was evaluated by 4-point bending (40/20 mm) with a crosshead speed of 0.2 mm min^{-1} using Shimadzu AG10 equipment. Vickers hardness (H_v), was measured both on substrate as on glazes by a 20 N load with a Zwick indenter on polished surfaces (1 mm diamond paste). Fracture toughness (K_{IC}) was evaluated by the Indentation Strength in Bending (ISB) method. All data reported in the present paper are averaged over 5 measurements. Strength was determined under two different conditions: the first with the glaze upwards, the second with the glaze down. Micrographics were acquired by a Nikon Eclipse L150 optical microscope on polished surfaces (1µm diamond paste).

3. Results and discussion

Table 1 reports the chemical composition of glaze and engobe in terms of oxides; it can be remarked that their similar composition, with low amount of coloring components and high fraction of barium, lead stannous and zircon oxides. **fig. 1** shows the particle size distribution of the powders before pressing. It can be seen a bimodal PSD with a first peak at 10 µm and a second with a maximum around 85 µm. This result shows that the milling process could be better optimised and powders mixtures turned into products with better sintering performances, nevertheless, the milling parameters were selected in order to replicate industrial conditions. The glaze, which makes waterproof the surface of porous tiles and determines their surface hardness, sometimes does not uniformly cover the substrate and it is necessary to introduce, between substrate and glaze, a further layer of material. This layer, called engobe, must have the required colour and has the function to optimize the surface look of the tiles. The use of the engobes is particularly important when the substrate is coloured as is in our experiments. Table 1 also shows that the glaze contains greater amounts of SiO_2, K_2O and Na_2O than the engobe with the consequence that the softening temperature of the first could speculatively expected lower than that of the second.

Component	SiO_2	Al_2O_3	CaO	MgO	SrO	BaO	Na_2O	K_2O	ZrO_2	SnO_2	PbO	Undeterm.	LOI
Engobes	43.23	14.88	2.16	2.39	3.38	6.12	1.98	1.42	13.44	5.87	1.76	2.10	3.28
Glaze	50.21	13.39	<0.01	0.87	0.21	4.92	3.89	1.95	9.20	6.37	7.01	1.47	0.93

Tab. 1: Composition (wt %) and LOI (%) of engobes and glaze

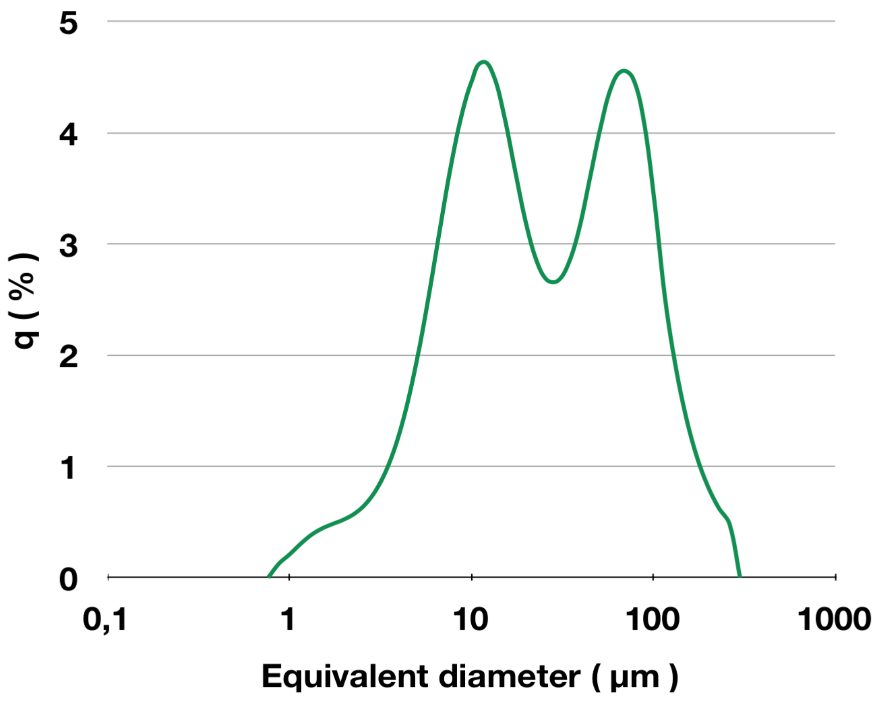

Fig. 1: Particle size distribution of the powders after milling and before pressing

Table 2 shows some properties of the fired products. It is observed that the measured values are in line with the official standard for production of "red monoporosa" or "earthenware" [3] and not greatly different from data measured on the reference tile. It can be also pointed out that shrinkage is very low thus minimizing changes of shape or dimensions on sintering. Conversely, Vickers hardness is low, being 2.6 GPa in the product fired at 1090 °C and 4.1 for that sintered at 1140 °C; the reference tile has an average value of 3.2 GPa. Hardness was measured also on the glaze. Averaged data are 5.6 GPa for materials fired at 1090 °C, 5.4 GPa for those fired at 1140 °C and 5.2 GPa for the reference tile. Such values make our products suitable also as floor tiles [3]. Bending rupture strength is in line with the official standards for each sintering cycle and for all the product tested. Table 2 displays two strength values: the first was determined keeping the glaze upwards, the second keeping it down. It is observed that the difference between the two values of each product could be reasonably be considered negligible. The presence of a sealant layer over the tensile surface (glaze) could increase fracture toughness by limiting number and dimension of flaws as well as their fast growth from the surface where tension loads reach the highest values. Due to the presence of an outer sealant layer, the results of our experiments show relatively high toughness values in all the samples tested.

	Top sintering temperature		Reference
	1090°C	1140°C	1140°C
Water absorption (%)	15.5	13.7	14.0
Shrinkage(%)	0.25	1.85	2.3
Vickers hardness (GPa)	2.6 (± 0.3)	4.1 (± 0.5)	3.2 (± 0.5)
Bending rupture strength (MPa) 1*	34 (± 5)	38 (± 4)	27 (± 5)
Bending rupture strength (MPa) 2**	35 (±2)	39 (± 2)	29 (± 4)
Fracture toughness (MPa m1/2)***	2.4 (± 0.3)	2.3 (± 0.2)	2.1
Vickers hardness of the glaze (GPa)	5.6 (± 0.5)	5.4 (± 0.4)	5.2 (± 0.4)

Tab. 2: some properties measured on the fired products

Fig. 2 shows the tiles after the sintering respectively at 1090 (left) and 1140 °C (right). It can be observed that the tile fired at 1090°C maintains the matt nature of the glaze whereas in that fired at 1140 °C the glaze turns smart thus showing that 1140 °C seems a too high temperature for the sintering of our materials. **Fig. 2** also highlight that, due to the greater shrinkage, the planarity of the product fired at 1140 °C is partially compromised being the outer edges thicker than the inner portion of the tile.

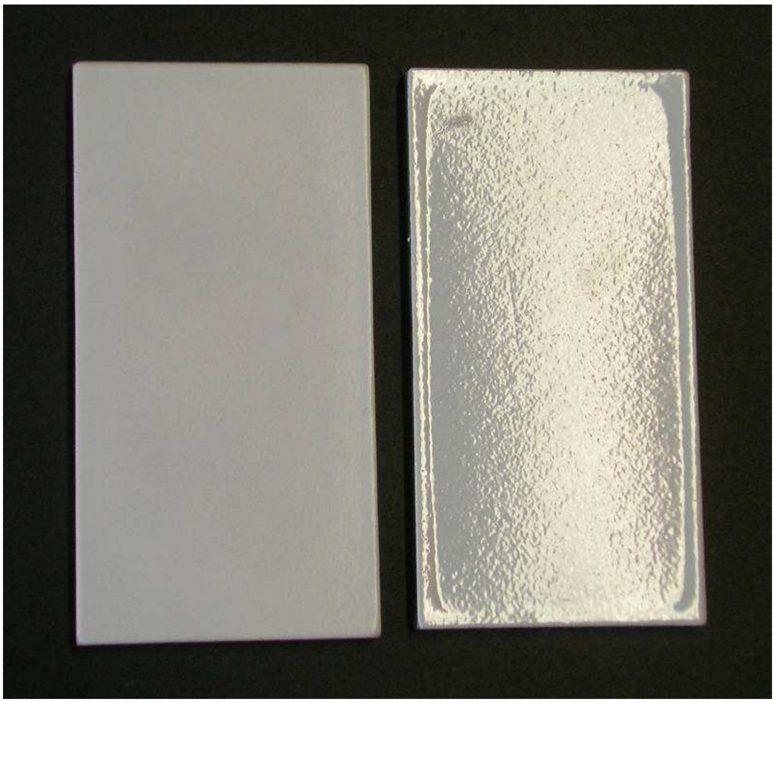

Fig. 2: tiles after the sintering respectively at 1090 (left) and 1140 °C (right)

Fig. 3 a and b shows the polished (1mm diamond paste) transverse section of the tiles fired at 1090 and 1140 °C respectively. It can be observed that engobe thickness in the tile fired at 1090 °C is approximately twice that the tile fired at 1140 °C. Conversely, the glaze thickness does not suffer great changes while changing the maximum sintering temperature. A higher thickness could be reasonably associated to a better coating effect in product fired at 1090 °C with respect to those fired at 1140 °C. It can be also observed that the glaze over the tile fired at 1090 °C contains a greater number of crystalline domains than the other has. This is a reasonable consequence of the higher sintering temperature which enable the transformation into glass phase most of the crystalline components of the glaze before sintering.

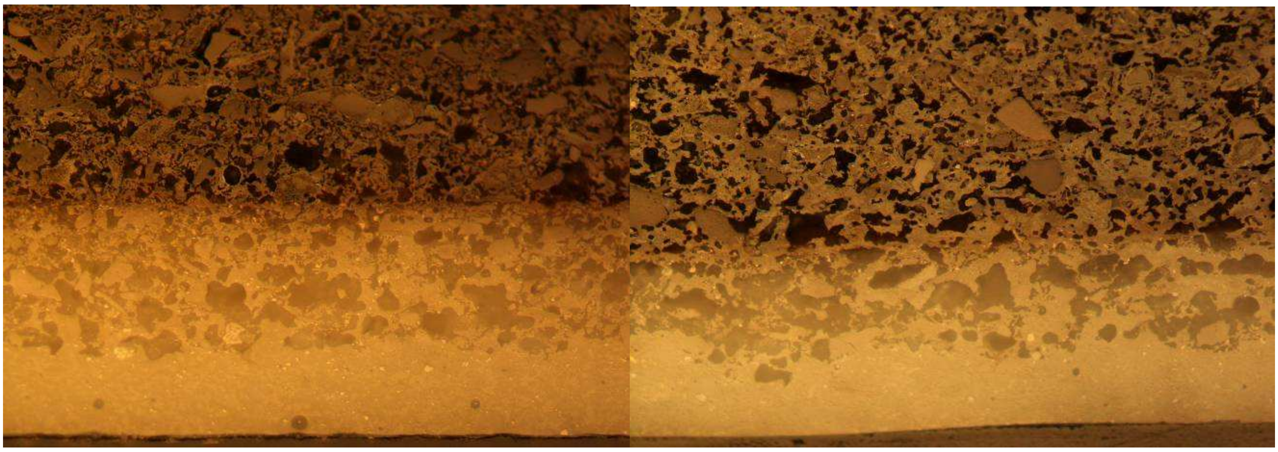

Fig. 3: shows the polished respectively at 1090 (left) and 1140 °C (right)

Concluding remarks

In the present research we demonstrated that mixtures of powders containing 42 wt% of paper mill sludge, 28 wt% glass cullet and 30 wt% of natural red clay may be used for the industrial production of glazed tiles, in fast firing. The sintering temperature, selected at 1090 °C, leads to materials that meet the Italian standards for production of red stoneware and/or " red monoporosa".

Acknowledgements

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