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PORCELAIN STONEWARE LARGE SLABS: PROCESSING AND TECHNOLOGICAL PROPERTIES

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ABSTRACT
Porcelain stoneware large slabs, up to 360 x 120 cm^2 and 3 mm in thickness, can be bent and used in several applications, from building and construction (floorings, wall coverings, ventilated façades, tunnels, insulating paneling) to indoor furnitures (e.g. table tops, doors, panels). Large slabs are manufactured through an innovative ceramic process, starting either from conventional or pre-milled raw materials and involving wet ball mixing, powder granulation by spray drying, forming by special purpose presses, a single stage of fast drying and firing, peaking at about 1200°C, and finishing (trimming, lapping, functionalization). Industrial samples were selected in order to investigate their technological performances as well as compositional and microstructural features. The following characteristics were determined: water absorption, open and closed porosity, bulk density; phase composition; mechanical properties (modulus of rupture, Young modulus, fracture toughness); resistance to deep abrasion, chemical and stain resistance; resistance to thermal shock and freeze/thaw cycles. In addition, microstructure (scanning electron microscopy on both surface and polished sections) and pore size distribution of fired and unfired body were investigated as well as the sintering behaviour. Outstanding performances for very large and thin porcelain stoneware slabs were found. Water absorption is very low (<0.1%) according to the fast sintering rate. Mechanical properties match the top quality range for porcelain stoneware tiles: modulus of rupture (60-70 MPa), Young modulus (68 GPa) and fracture toughness (1.3 MPa $m^{1/2}$), implying that the innovative process gives high strength but not stiff products, which are tough and little sensitive to relatively coarse pores (critical defect size ~200 μm). Standard technological requirements are fulfilled, being resistant to deep abrasion (160 mm^3), chemicals, thermal shock and freeze/thaw cycles. Large slabs exhibit a compact microstructure with closed pores (5-8%) presenting a maximum size of 50 μm, mostly with irregular shape. The phase composition of large slabs is analogous to porcelain stoneware tiles, consisting of an abundant glassy phase (65-80 wt%), a low content of both residual quartz or feldspars and new formed phases mullite.

INTRODUCTION
In the ceramic tile market, the growth rate of porcelain stoneware has the considerably increased in the last decade, due to its technological properties coupled with even more improved aesthetical appearance [1-10]. The latest market trends go towards large dimensions and recently even reduced thickness of tiles, but have to face strong technological constraints in the ceramic process (e.g. the tile size to press power relationship). These limits can be overcome only by innovative technological solutions involving a new approach to shaping and thermal treatments, able to produce porcelain stoneware large slabs with dimensions up to 4x1.5 square meters and three millimeters of thickness. These products are peculiar for combining excellent technological characteristics with an unrivalled degree of flexibility, resulting in outstanding potential in novel applications. The slabs, even arranged in multilayered composites with fiberglass interlayer are suitable to be used both outdoors and indoors for building and construction (floorings, wall coverings, roofing, ventilated façades, tunnel coverings, and insulating paneling, ship furniture) and indoor furnitures (e.g. doors,

table-tops, panels). Moreover, these slabs can be used as photovoltaic cell support and their surface functionalized and decorated.
This work is aimed at characterizing the main technological, mechanical, tribological and functional properties of industrial porcelain stoneware slabs obtained by the innovative manufacturing cycle "Lamina", whose performances are compared with those conventional porcelain stoneware tiles.

EXPERIMENTAL
Slabs from three manufacturers were selected and technological characteristics were measured on both unfired and fired products. Different parts of the slabs (i.e. head, middle and tail) were sampled in order to evaluate any dishomogeneity in terms of technological properties.
Particle size distribution (ASTM C958), bulk density, microstructure (SEM) and pore size distribution (Mercury Intrusion Porosimetry) were investigated on the unfired slabs.
Finished slabs were characterized by determining: water absorption, open porosity and bulk density (ISO 10545-3); closed and total porosity (ASTM C329); modulus of rupture (ISO 10545-4); Young modulus (ENV 843-2); fracture toughness (ENV 843-1); resistance to deep abrasion (ISO 10545-6); chemical (ISO 10545-13) and stain resistance (ISO 10545-14); linear thermal expansion (ISO 10545-8); resistance to thermal shock (ISO 10545-9) and to freeze/thaw cycles (ISO 10545-12). Phase composition was quantitatively determined by X-ray powder diffraction using the Rietveld-RIR method. Microstructure was investigated by electron microscopy (SEM) on both surface and polished sections.

RESULTS AND DISCUSSION

Large slabs processing
Porcelain stoneware slabs are manufactured through an innovative ceramic process starting from either conventional or pre-milled raw materials. Bodies consist of typical porcelain stoneware formulations, being a mixture of ball clays, quartz-feldspathic sands and sodic-potassic feldspars in different amounts (Fig. 1).

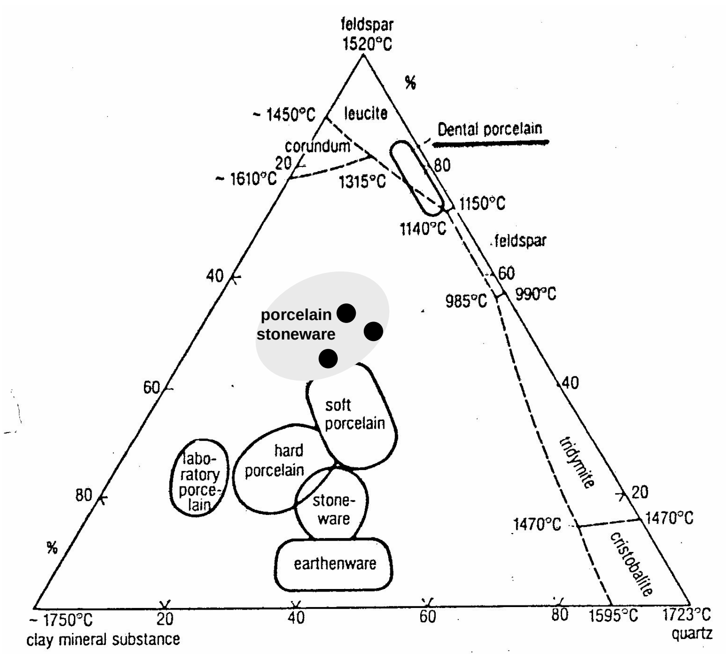

Figure 1: Body formulations for large slabs (full circles) in comparison with different ceramic products.

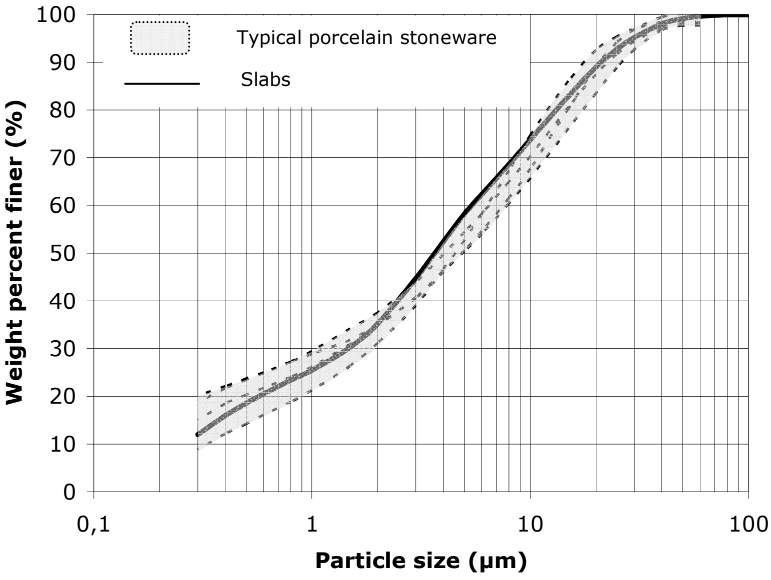

Figure 2: Particle size distribution of the bodies for large slabs and porcelain stoneware tiles.

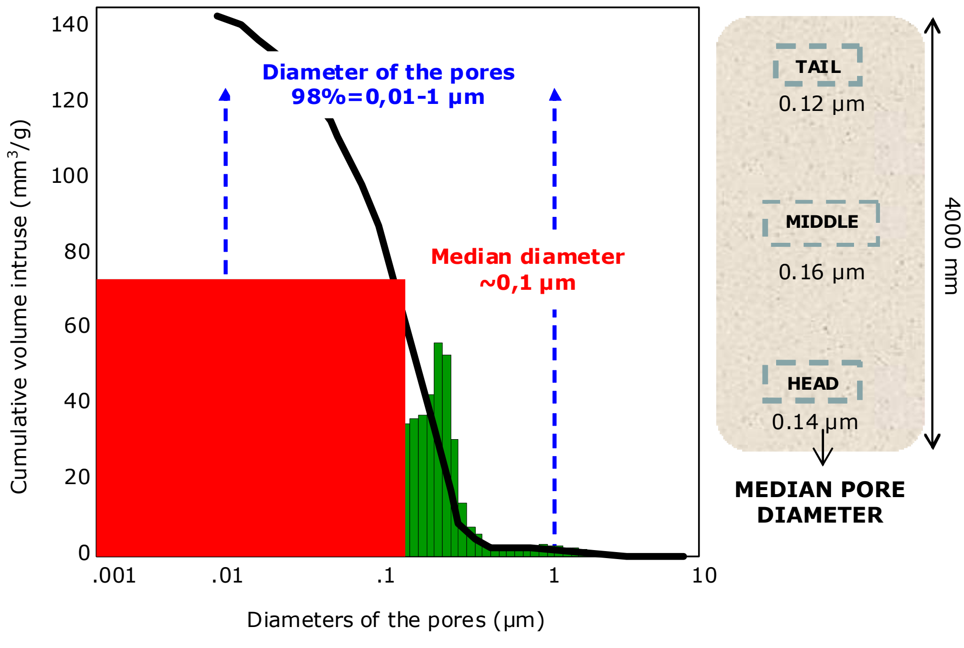

Figure 3: Pore size distribution of a unfired slab.

The particle size distribution of these products is rather fine-grained with a median diameter of about three microns and falling within the granulometric field of porcelain stoneware (Fig. 2). Processing involves wet ball mixing and powder granulation by spray drying. Special purpose press is used to obtain the green body by unconstrained forming in a dieless mould and a slow rate pressure curve instead of the hammer principle conventionally utilized in tile pressing. Once shaped, large slabs are cut and undergo a single fast stage of drying and firing carried out by a belt drier and a roller kiln (electric or hybrid, gas/electrical feed), peaking at about 1200°C accomplished in 30-45 min cold to cold.

Slabs are cut to desired size by dry trimming, and a fiberglass reinforcement can be glued to the rear of the slab, remarkably improving its flexibility and bending strength, so easing transportation and enabling applications that go beyond those classic for porcelain stoneware tiles. In addition, surface treatments can be done, i.e. lapping, decoration and functionalization (e.g. selfcleaning).

Characteristics of unfired slabs

The dieless pressing used for large slabs is able to get a remarkable densification at the dry state, going from 1.88 to 2.03 g/cm^3 depending on the specific pressure (e.g. from 30 to 35MPa) and powder characteristics (moisture, particle size distribution, mineralogical composition). Such bulk density values are comparable or even higher than those obtained by conventional pressing of porcelain stoneware (1.90-1.98 g/cm^3) emphasizing the effectiveness of the pressing technique. The uniformity of pressing is witnessed by the modest variation in the different parts of the slabs (1.92-1.88 g/cm^3 range) corresponding to 27.6-29.3% of total porosity values (Table 1). Moreover, the pore size distribution is between 0.01 and 1 μm, with a median value 0.1μm, without significant differences from head to tail (Fig. 3).

Characteristics of finished slabs

The sintering behaviour is strongly affected by the characteristics of unfired products. The uniformity of technological performances is confirmed in the fired slabs where water absorption, bulk density and closed porosity exhibit limited variations, often corresponding to the experimental uncertainty (Table 1).

Products	Properties	Range values of the different slabs	Head	Middle	Tail
Unfired slabs	Bulk density (g/cm^3)	1.88-2.03	1.921±0.002	1.915±0.003	1.884±0.001
	Total porosity (% vol.)	23-29	27.6±0.2	28.2±0.3	29.3±0.01
Fired slabs	Water absorption (%wt)	0.06-0.11	0.05 ±0.01	0.06±0.01	0.07±0.01
	Open porosity (% vol.)	0.14-0.25	0.13±0.04	0.14±0.04	0.16±0.01
	Closed porosity (% vol.)	5.0-6.5	4.5±0.2	5.4±0.3	5.0±0.3
	Total porosity (% vol.)	5.2-6.7	4.7±0.2	5.6±±0.2	5.2±±0.2
	Bulk density (g/cm^3)	2.42-2.34	2.43±0.01	2.40±0.01	2.42±0.02

Table 1: Technological properties of unfired and fired large slabs. Example of variations occurring in different parts of the slabs (head, middle, and tail).

The slabs are characterized by a compact microstructure with small and irregularly shaped pores, with maximum size of 50 μm (Fig. 4). The large slabs exhibit (Fig. 5):

- very low values of water absorption, usually below 0.1%, according to the fast sintering rate;
- closed porosity in the 5-8 % range, well fitting typical values of porcelain stoneware;
- bulk density in the 2.34-2.40 g cm^{-3} range in agreement with porcelain stoneware tiles value.

From the mechanical point of view, slabs have modulus of rupture in the 65-70 MPa range, well over the standard requirement of 35 MPa (ISO 13006), and among the highly resistant porcelain stoneware products [11].

The fracture toughness is 1.26 MPa m$^{1/2}$ and the Young modulus is 67.6 GPa, falling in the top quality range for porcelain stoneware products (Table 3).

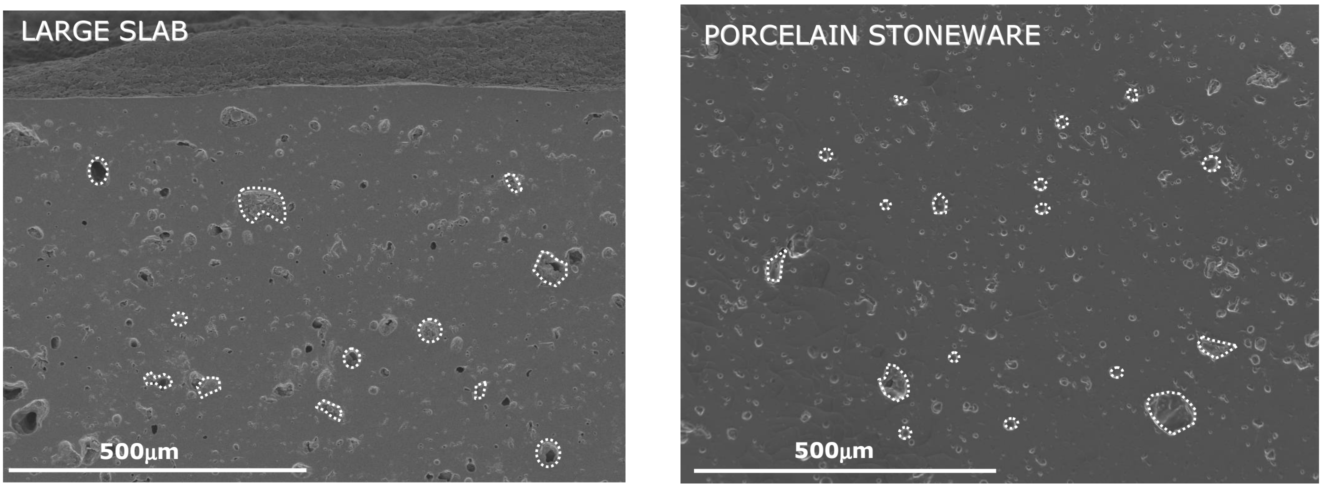

Figure 4: Microstructure of large slab in comparison with typical porcelain stoneware (SEM micrograph).

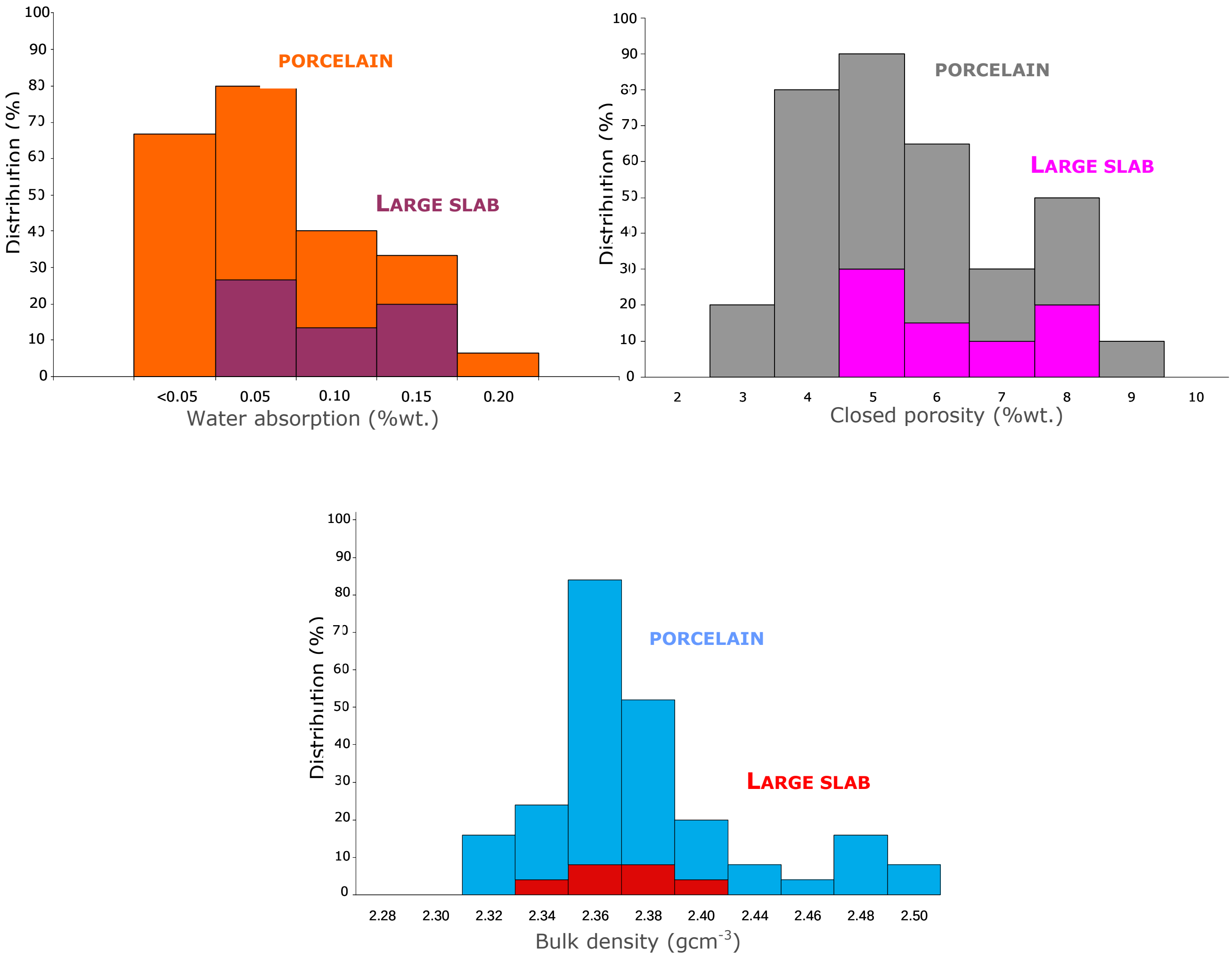

Figure 5: Main technological properties of the slabs compared to the conventional porcelain stoneware tiles.

Moreover, the critical defect size, calculated on the basis of modulus of rupture and fracture toughness, is about 200 μm, suggesting a limited sensitivity to relatively coarse pores. Large slabs are tough and high strength, but not stiff products, with mechanical performances equal or better than typical porcelain stoneware tiles.
The phase composition of slabs consists of abundant vitreous phase, residual quartz, feldspars and a small quantity of new formed mullite (Table 4). It is fully comparable to typical porcelain stoneware, even if lower amounts of quartz and higher amounts of vitreous phase may occur in pre-milled body formulations.
The main functional properties of large slabs fulfil the standard requirements for tiles of the BIa Group (Table 5). In particular, resistance to thermal shock, moisture expansion, frost resistance, chemical resistance and resistance to stains are well over the standard thresholds, falling within the field of top quality ceramic tiles. Values of resistance to deep abrasion and linear thermal expansion are fully satisfactory even though not far from the standard requirements.

Samples	Modulus of rupture (MPa)	Fracture toughness (MPa $m^{1/2}$)	Young modulus (GPa)	Critical defect size (μm)
Slabs	65-70	1.2-1.3	67-68	225-235
Typical porcelain stoneware	35-85	1.0-1.7	50-80	100-800

Table 2:Mechanical properties of slabs in comparison with typical porcelain stoneware tiles.

Phase composition (%wt)	Quartz	Mullite	Plagioclase	Vitreous phase
Slabs	11-17	7-9	2-10	65-80
Typical porcelain stoneware	15-25	5-15	0-5	55-70

Table 3: Phase composition of the slabs in comparison with the typical porcelain stoneware.

Performances	Standards value for porcelain stoneware	Market value for porcelain stoneware	Slabs
Resistance to deep abrasion	Volume removed $<175mm^3$	Volume removed $<150mm^3$	Volume removed 167 mm^3
Linear thermal expansion	No threshold	≅ 7.0 ($x10^{-6}$°C^{-1})	5.5 ($x10^{-6}$°C^{-1})
Resistance to thermal shock	No threshold	No alteration	No alteration
Moisture expansion	No threshold	<0.5	0.03 mm/m
Frost resistance	Required	No visible defects	No visible defects
Chemical resistance	Minimum class GB-UB	Minimum class GB-UB	Class GA-GLA
Resistance to stains	Minimum class 3	CLASS 3-5	Class 5

Table 4: Technological performances of the slabs

CONCLUSIONS

Large slabs manufactured by innovative process "Lamina" are peculiar for their dimensions, thickness and flexibility coupled to excellent technical performances that turn them suitable for a wide range of end use. Slabs represent a new typology of ceramic product with innovative applications, being characterized by an unrivalled versatility among ceramic building materials and by outstanding features for a ceramic ware: flexible, lightweight and aesthetically decorated.

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