



# High-performance and anti-stain coating for porcelain stoneware tiles based on nanostructured zirconium compounds



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## ABSTRACT

The technological characteristics of porcelain stoneware tiles make them suitable for a wide range of applications spanning far beyond traditional uses. Due to the high density, porcelain stoneware tiles show high bending strength, wear resistance, surface hardness, and high fracture toughness. Nevertheless, despite being usually claimed as stain resistant, the surface porosity renders porcelain stoneware tiles vulnerable to dirt penetration with the formation of stains that can be very difficult to remove.

In the present work, we report an innovative and versatile method to realize stain resistant porcelain stoneware tiles. The tile surface is treated by mixtures of nanosized zirconium hydroxide and nano- and micron-sized glass frits that thanks to the low particle dimension are able to penetrate inside the surface pores. The firing step leads to the formation of a glass matrix that can partially or totally close the surface porosity. As a result, the fired tiles become permanently stain resistant still preserving the original esthetic qualities of the original material. Treated tiles also show a remarkably enhanced hardness due to the inclusion of zirconium compounds in the glass coating.

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## 1. Introduction

Porcelain stoneware is a high performing, non-equilibrium, and glass-bonded material manufactured through a fast firing cycle with peak temperatures of about 1200–1300 °C [1–3]. Its peculiar technological characteristics, such as high density (Water Absorption WA < 0.5% ISO13006, WA < 0.2% in current production [4]), frost and chemical resistance, surface hardness, and resistance to abrasion led to an outstanding increase in production and sales of porcelain stoneware tiles. Nevertheless, despite the compact structure, the presence of surface pores with dimension in the nano- and micrometer scale makes tiles susceptible to staining and dirt penetration. The latter feature limits the use of porcelain stoneware tiles both for indoor and outdoor applications. Although mainly polished porcelain tiles suffer staining, this problem also concerns unpolished substrates. Beyond penetration of agents into the surface pores, stains can arise from material transfer from a softer medium (rubber, metals, leather, polymers, etc.) to the harder tile. The latter type of staining is much more evident for unpolished, rough, and harder tiles than for polished surfaces [5]. Due to the low porosity, as-fired porcelain tiles cannot be treated

with the specific products normally used for polished specimens [6].

Several studies have been carried out to establish a relationship between the surface microstructure and stain resistance. The roughness and the total amount, size, and morphology of surface pores have been proved to be the most influential variables [7–9]. Porosity results from a number of complex phenomena simultaneously occurring during sintering. A liquid phase forms at about 1100–1150 °C and it diffuses through the interconnected pores filling them [10]. Nevertheless, due to mullite crystallization and quartz dissolution in the liquid phase, the viscosity of the latter grows upon firing. As a consequence, the suppression of open porosity is delayed [11]. Indeed, closed porosity starts to increase before the open porosity has totally disappeared. Open porosity could be strongly reduced by increasing firing temperature. Though, above a certain temperature (i.e. the optimum firing temperature), the gas pressure inside the pores rises opposing the progressive densification of the material. This leads to the so called “body-bloating” with drastic deterioration of the mechanical properties [12]. Therefore, an optimum firing temperature must be established for each porcelain stoneware mixture. The optimum temperature is usually reached through slight over-firing conditions [13].

Beyond open porosity, pore size and morphology have been shown to play a crucial role. However, their correlation to stain

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resistance does not represent a simple task and non-univocal conclusions can be found in the literature. According to Dondi and co-workers [9], stain resistance decreases with increasing the percentage of coarse pores with an irregular internal microstructure. On the other hand, Esposito et al. [8,14] argue that stain resistance is strongly decreased by the presence of large amounts of small pores from 1 to 10–15  $\mu\text{m}$  [7,13]. In this regard, small pores are initially less easily filled with staining agents. Nevertheless, it is important to stress that once these pores are loaded by dirt they can be very difficult to clean.

Changing the porosity of porcelain stoneware tiles can be very demanding especially from a cost point of view. All steps of manufacture should be reviewed and possibly varied, starting from the powder composition, particle size, and size distribution until processing conditions (i.e. wet milling, spray drying, pressing, drying and firing [13]). Many studies on the influence of these variables upon porosity have been carried out. Up to now, no precise correlation has been established between powder composition and porosity of the final product [15]. Positive effects on stain resistance can be achieved by decreasing the powder size of raw materials below 45  $\mu\text{m}$  [7], by increasing the amount of fluxes [16], and, as already mentioned, by increasing the peak firing temperature below the body-bloating limit [13,17].

Although certainly helpful in improving porcelain stoneware stain resistance, all these procedures are very expensive. The current European production is already costly enough when compared to other tile-making countries. In fact, in the last few years the manufacturing sector has geographically shifted from the traditional European base to Asia, North Africa, and the Middle East. This drives the European tile industry to a continuous search for cheaper raw materials and manufacturing processes capable of reducing production costs without altering the final product characteristics [18].

Thus, the aim of the present study was to find a versatile and cost-effective procedure to address the stain resistance issue without affecting the tile original properties. The basic idea was to set up a technique able to close (or at least to reduce) the open porosity. In principle, tiles could be treated by nanoparticles. Thanks to their small size, nanoparticles can penetrate the surface pores closing them. Moreover, their chemistry could be opportunely tuned to tailor specific final characteristics, such as anti-stain and enhanced mechanical properties.

## 2. Experimental

### 2.1. Synthesis of hydrated and anhydrous zirconia nanoparticles

Zirconium hydroxide nanoparticles were synthesized in a homogeneous phase by adding sodium hydroxide to an aqueous solution of zirconyl chloride. Different particle dimensions were obtained by using hydrolysis ratio  $r = [\text{OH}]_0/[\text{Zr}]_0$  above and below 1.

#### 2.1.1. Synthesis with $r > 1$

13.2 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  were dissolved in 200 mL of water to obtain a 0.2 M Zr(IV) solution. 14 mL of 5 M NaOH aqueous solution were added drop-wise under vigorous stirring at 90 °C. The obtained system was kept under stirring at 90 °C for 10 min. A white precipitate formed. The precipitate was separated from the supernatant dispersion by simple sedimentation and then peptized with water in an ultrasonic bath to obtain nanosized units. The latter were collected by centrifugation at 6000 rpm for 10 min. The washing/peptization procedure was repeated three times. Thermal treatment of these particles at 550 °C for 5 h led to a mixture of monoclinic and tetragonal zirconia. The obtained oxide possessed a bimodal size distribution centered at 90 nm and 300 nm.

Both  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Aldrich, 98%) and NaOH (Fluka, 97%) were used without further purification. Milli-Q water was used for both synthesis and washing.

The detailed description of the synthesis and of hydroxide and oxide characterization is reported elsewhere [19].

#### 2.1.2. Synthesis with $r < 1$

12.5 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  were dissolved in 100 mL of water to obtain a 0.39 M Zr(IV) solution. 7 mL of 5 M NaOH aqueous solution were added drop-wise under vigorous stirring at 90 °C. The obtained system was kept under stirring at 90 °C for 10 min. A white precipitate formed, which then slowly reorganized leading to a clear solution. Thermal treatment at 500 °C for 2 h of the freeze-dried clear solution led to pure tetragonal zirconia with crystallite dimension of 17 nm.

Both  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (Aldrich, 98%) and NaOH (Fluka, 97%) were used without further purification. Milli-Q water was used for the synthesis.

The detailed description of the synthesis and of hydroxide and oxide characterization is reported elsewhere [20].

### 2.2. Preparation of zirconium hydroxide/frit mixture and application on stoneware

Commercially available micrometric zirconium hydroxide (Sigma–Aldrich) and zirconium oxide (Aldrich) were used without further purification.

Frits used are those normally employed in the ceramic field for the production of glazes. Micronized glass frits were produced through wet milling of the commercially available materials. The obtained powders were constituted by 95% of particles with dimensions below 5  $\mu\text{m}$  and of at least 1/4 of particles with dimensions in the range of nanometers. The composition of frits used in the present study is reported in the [Supplementary data](#).

A certain amount of micronized glass frit powder was added to the zirconium hydroxide dispersion so that the  $\text{ZrO}_2$  content in the final formulation was below 15%–w/w (on a dry basis). The composition of mixtures used in the present study is reported in the [Supplementary data](#). The composition was each time adapted to the properties (i.e. color, texture, etc.) of the support under treatment. The mixture aqueous suspension had density between 1.1 and 1.3 g/L and viscosity of 3.5–4 cP. Typical working temperatures were determined by a heating microscope HSM (Expert System Solutions S.r.l.): sintering 800–810 °C, softening 900–920 °C, sphere 1000–1030 °C, half-sphere 1080–1100 °C, melting 1150–1180 °C. The linear dilatation coefficient (25–400 °C) was  $55\text{--}60 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ .

The suspension was applied onto the tile surface before firing and water was allowed to evaporate slowly at 60 °C. The so treated tiles were then fired by using a SACMI single channel roller kiln. The thermal cycle was a typical industrial porcelain stoneware cycle lasting 45 min cold-to-cold with a maximum temperature of 1215 °C.

### 2.3. Methods

The color difference (before and after the treatment),  $\Delta E^*$ , was measured by means of a ColorQUEST 45/0 spectrophotometer (HunterLab) in standard conditions with a D65 illuminant and a 10° angle of vision. According to the standard ISO10545-16, the color difference is expressed as  $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$ , where  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$  are the variations in the respective CIE Lab parameters, taking the untreated surface as reference. A color is defined by three parameters  $L^*$ ,  $a^*$  and  $b^*$ , which identify the position in the CIE Lab color space. The difference between two colors,

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