Optimization of the technological properties of porcelain tile bodies containing rice straw ash using the design of experiments methodology

Álvaro Guzmán A[a], Marisol Gordillo S[a], Silvio Delvasto A[a], María Francisca Quereda V[b], Enrique Sánchez V[b]*

a: **Grupo de Materiales Compuestos, GMC. Escuela de Ingeniería de Materiales, Facultad de Ingeniería, Universidad del Valle, Cali, Colombia. Calle 13 # 100 – 00.**
b: **Instituto de Tecnología Cerámica, ITC. Universidad Jaume I, Castellón, Spain. Campus Universitario Riu Sec, Av. Vicent Sos Baynat s/n, 12006 Castellón**

e-mail: *alvaro.guzman.a@correounivalle.edu.co
mgsuarez44@yahoo.com
silvio.delvasto@correounivalle.edu.co
paqui.quereda@itc.uji.es
enrique.sanchez@itc.uji.es

ABSTRACT

This study examines the effects of replacing fluxing and filler materials with rice straw ash (RSA) in manufacturing porcelain stoneware tile, using the design of experiments (DOE) methodology. The results of the characterization were used to obtain statistically significant, valid regression equations, relating the technological properties of the dried and fired test pieces to the raw materials content in the unfired mixtures. The regression models were analysed in relation to the X-ray diffraction and scanning electron microscopy results and used to determine the most appropriate combinations of traditional raw materials and RSA to produce porcelain stoneware tiles with specific technological properties. The studied range of tile body compositions: clay (40 wt%), feldspar (20–50 wt%), feldspathic sand (5–20 wt%), and RSA (0–25 wt%) was shown to be appropriate for porcelain stoneware tile manufacture.

Keywords: rice straw ash, porcelain stoneware tile, sodium feldspar, feldspathic sand, design of experiments.

1. INTRODUCTION

Porcelain stoneware tile (name given to tiles from Group BIa, water absorption below 0.5%, in accordance with ISO standard 13006) is characterized by very low water absorption, such tiles being high performance ceramic materials [1-2]. This type of tile has been widely used as floor and wall covering and more recently in ventilated facades [3]. In recent years, the demand for porcelain stoneware tile has grown significantly compared to that of other ceramic construction materials, growth being particularly attributed to porcelain tile's enhanced performance characteristics, especially regarding water absorption, frost resistance, bending strength, and wear resistance [2-5].

Porcelain stoneware tile composition is mainly based on a triaxial mixture similar to that of porcelain, the mixture typically containing a plastic material (generally clay), an inert or filler material (usually quartz or feldspathic sand), and a fluxing material (commonly sodium feldspar (SF)) [6-8]. A typical porcelain stoneware

tile composition contains 40–50 wt% illite–kaolinite clay, 10–15 wt% quartz or feldspathic sand, and 35–45 wt% SF [9-10]. Many types of industrial and agro-industrial wastes, such as soda–lime glass, glass waste (TV/PC cathode ray tubes and screens), blast furnace slag, metallurgical slag, zeolites, rice straw ash (RSA), rice husk ash (RHA), silica fume, fly ash (FA), and coffee husk ash (CHA), have been incorporated to partially replace either the fluxing material or the filler in the porcelain stoneware tile composition. All this research has essentially been aimed at studying the effects of the incorporated waste on the material's behaviour during firing and on the technical properties of the end product [11-27]. However, the use of secondary raw materials should only be considered feasible if the industrial process remains essentially unchanged and end product quality and properties are not impaired [14–20]. The present authors have previously examined the potential use of rice straw ash (RSA) in ceramic production, based on the K_2O and SiO_2 contents in RSA, which lie within the ranges 4.59–20.13% and 52.42–88.21% respectively [28-30]. The authors' previous research on this potential use involved trial and error additions of this waste to a standard porcelain tile composition [26,30] and observation of the effect of the waste additions on composition behaviour and on end product properties. The results suggest that this agro-industrial waste could be successfully used to partially replace the composition's fluxing and filler materials. However, systematic study based on a more scientific approach such as the design of experiments (DOE) methodology is still needed to establish adequate correlations between the amount of incorporated waste and fired tile microstructure and end properties.

The DOE methodology was introduced by Correia et al. to analyse the performance of traditional ceramic compositions [7] and has been subsequently used by different authors [7,31-35]. The methodology allows the effect of each component, as well as of the possible interactions between these components, on the properties of interest (e.g. physical and mechanical properties) to be quantified. Previous work using the DOE methodology to model some of the technological properties of industrial ceramics [7,31-35] showed that only a sub-region of the original composition triangle is of interest, given the processing constraints regarding the clay, feldspar, and quartz contents in the starting mixture. Therefore, the concept of a pseudo-component must be used to create a restricted composition triangle. Key aspects of the DOE methodology include the need for replications of the experiments to enhance the confidence in the experimental results and assure their reproducibility, and how a regression polynomial is fitted to the experimental values and validated.

This study was undertaken to systematically investigate the possibility of replacing the fluxing and filler materials (sodium feldspar, SF, and feldspathic sand, FS, respectively) used in porcelain stoneware tile manufacture with different amounts of rice straw ash (RSA) with a view to maximizing the RSA addition. The DOE methodology was used to mathematically model the physical and mechanical properties as a function of the SF, FS, and RSA contents in the starting composition under constant processing conditions. The clay content was kept constant so that composition plasticity (and consequently dry mechanical strength) would remain practically constant. The triangle of compositions tested thus included two typical triaxial mixture components (feldspar, SF, and feldspathic sand, FS), in addition to the waste to be assessed (RSA). It was therefore sought to develop models that could be used to select the best combination of these three raw materials to manufacture porcelain stoneware tiles with appropriate properties.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The following raw materials typically used for manufacturing porcelain stoneware tile in Spain were used in this study: an illitic–kaolinitic clay from Ukraine (Mineria Sassolesse, Spain), sodium feldspar (SF) from Turkey (Guzmán Global, Spain), and local feldspathic sand (FS) (Imerys Tiles Minerals, Spain). Rice straw ash (RSA) was produced following process D of the Guzmán et al. methodology (i.e. calcination of the material at 800˚C to eliminate as much chlorine (Cl) and sulphur (S) as possible while a significant amount of potassium (K) and silica (SiO_2) remains in the ash) [30]. The chemical and mineralogical compositions of these raw materials, obtained by X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively, are reported in Table I.

Table I. Chemical and mineralogical compositions of the raw materials and the rice straw ash (RSA) (wt%) [36].

2.2 Mixture compositions

The mixture of raw materials was prepared taking into account the surrounding conditions or process limitations, which require the presence of a significant amount of clay (plasticity) and fluxing material (sinterability). Thus, the clay (A) content was kept constant at 40 wt% and the other raw materials contents were varied as [0 - 20] wt% FS, [0 - 60] wt% SF and [0 - 60] wt% RSA. Figure 1 shows the pseudo-components triangle (i.e. excluding the clay) within which that restricted region of experimentation was created (coloured green).

Figure 1. The raw materials pseudo-components triangle, i.e. feldspathic sand - sodium feldspar - rice straw ash (RSA), showing the restricted composition polygon (coloured green) and the studied compositions

A total of 17 mixture points, also shown in Figure 1, were defined using a simplex-centroid mixture design, of which the centroid was replicated five times to improve the confidence in the experimental results and guarantee the design replicability. From those mixture points the full mixture compositions were calculated (Table II). Mixtures M10 and M12, composed of illite-kaolinite clay, SF and FS (i.e. without RSA), were taken as primary standard mixtures.

Table II. Composition (weight proportion) of the mixtures prepared.

2.3 Composition processing

In order to obtain the typical particle size of porcelain stoneware tile body compositions, one kilogram of each of the seventeen compositions was ball-milled for the time needed to reach the typical 1.5–2.0 wt% residue on a 40 μm sieve (see Table III in Section 3.1).

In order to determine the behaviour of the ceramic bodies in the pressing and firing stages, cylindrical test pieces about 7 mm thick and 40 mm in diameter were pressed from the moistened ground powders. The same powders were used to prepare prism-shaped test pieces measuring 80 mm x 20 mm x 6 mm to determine body mechanical properties (3-point bending strength). All the pressed bodies were shaped at a moisture content of 5.5 wt% (on a dry basis) by uniaxial pressing at a pressure of 400 kg/cm^2 (39.2 MPa). The pressed test pieces were then dried at 110 ± 5 °C in an electric laboratory oven and sintered in an electric laboratory kiln with a heating ramp of 70 °C/min between 25 °C and 500 °C, and 25 °C/min from 500 °C to their respective peak firing temperatures. They were held at peak firing temperature for 6 minutes and then cooled inside the kiln in order to avoid macroscopic residual stresses [34]. The maximum firing temperatures used ranged from 1140 to 1260 °C, testing 20 °C steps, depending on each composition.

2.4 Characterization and main properties of the studied unfired and fired test pieces

The measurements of dried and fired test pieces were performed using a digital calliper. The dried bulk density (DBD) and fired bulk density (FBD) were determined using the mercury displacement method [37]. Linear firing shrinkage (LFS) and water absorption (WA) were determined in accordance with ASTM C326-09 and C373-88 (2006), respectively [38,39]. Open porosity (OP) was calculated as follows:

$$OP\ (\%) = FBD\ x\ WA\ x\ 100 \quad (1)$$

From the FBD and WA values obtained for each mixture, the corresponding vitrification curve (see Figure 2 in section 3.1) was plotted and the maximum densification temperature (TO) was determined. The maximum densification corresponds to minimum porosity (water absorption typically below 0.1%) and is representative of typical industrial firing conditions for porcelain stoneware tiles.

The modulus of rupture (MOR) of mixtures sintered at their respective maximum densification temperature was calculated analogously to ASTM C674-88 (2006) [40] using a three-point bending test assembly, the span between supports being 62.2 mm and the load application rate being 5 mm/min. Ten measurements were averaged.

Young's Modulus (E) was calculated based on the excitation pulse technique (Grindosonic J.W. Lemmens) in accordance with ASTM C1259-08 [41] for 10 prismatic test pieces (80 mm x 20 mm x 6 mm) for each mixture sintered at maximum densification temperature.

The fired test pieces were ground down to a particle size below 45 µm to determine their true density (TD) using a helium stereo-pycnometer, while the mineralogical composition was determined by XRD (PANalytical X'Pert PRO MRD).

Fired test piece total porosity (TP) was calculated as follows:

$$TP\ (\%) = \left(1 - \left(^{FBD}/_{TD}\right)\right) x\ 100 \quad (2)$$

Fired test piece closed porosity (CP) was calculated as follows:

$$CP\ (\%) = TP - OP \quad (3)$$

Test piece pyroplastic deformation during firing was determined using the pyroplastic index (PI) as follows:

$$PI\ (cm^{-1}) = \left(^{4\ h^2 s}/_{3\ L^4}\right) x\ 10^5 \quad (4)$$

where h is the thickness of the fired piece in cm; s is the deformation in cm; and L is the span between supports (6.7) in cm [42]. Sintering was carried out under the conditions described above.

The microstructural characteristics of the fired test pieces were observed using scanning electron microscopy (SEM) (Jeol JSM-6490LV). For this, the fracture surface of each sample was polished and treated with 5% hydrofluoric acid (HF) solution for 3 min and then washed with distilled water and ethyl alcohol, followed by drying, after which it was coated with carbon. The chemical composition of the phases observed in the fired pieces was determined using energy-dispersive spectroscopy (EDS) coupled with SEM.

The coefficient of thermal expansion (CTE) was calculated using the dilatometry technique (Netzsch model 402PC) with a prismatic fired test piece measuring about 30 mm x 5 mm x 5 mm, at a heating rate of 5 °C/min, from ambient temperature to a maximum temperature of 800 °C. The CIELab chromatic coordinates L*, a* and b* were measured using a spectrophotometer (CE7000, Gretag Macbeth, Switzerland) with a standard 10° CIE observer and CIE type D65 standard illumination in accordance with ASTM D2244-11 [43] on cylindrical test pieces (7 mm thickness x 50 mm diameter) sintered at maximum densification temperature.

The results obtained for the maximum densification temperatures, and those of LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, PI and PI as well as the chromatic coordinates L* and b* obtained for tiles sintered at the maximum densification temperatures were used to calculate the coefficients of the statistically relevant regression equations and the response surfaces. These properties were related to the SF, FS, and RSA contents in the starting compositions. The calculations were performed using the statistical package MINITAB 15 (ANOVA (analysis of variance), contour graphs, and optimization).

3. RESULTS AND DISCUSSION

3.1 Processing of the different mixture compositions

Table III shows the dry milling times required to prepare the formulations. In general, the higher the RSA content, the shorter was the milling time. This was due to the lower particle size of RSA with respect to that of FS, as detailed in Table I.

Table III. Milling times required to reach a residue of 1.5–2.0% on a 40 μm sieve.

The maximum densification temperature (T_O) was determined for each composition as indicated above. This characteristic temperature was derived from the composition's vitrification diagram. The vitrification diagram of a given ceramic composition represents the evolution of certain firing parameters of the ceramic piece (typically fired bulk density and water absorption) against firing temperature as widely described in the literature [3,4]. Fig. 2 shows the vitrification diagram for all compositions. The maximum densification corresponds to minimum porosity (water absorption typically below 0.1%) and was representative of typical industrial firing conditions for porcelain stoneware tile. Comparison of the compositions containing RSA with reference compositions M10 and M12 revealed a clear reduction in bulk density, whereas the vitrification curves shifted towards higher firing temperatures. Both phenomena can be at least partly explained by the reduction in dry bulk density (DBD) associated with the use of RSA as set out elsewhere [25,26]. This aspect will also be discussed in the following section.

Figure 2. Vitrification diagram in terms of fired bulk density (FBD) and water absorption (WA) of the fired test pieces as a function of firing temperature. M10 and M12 appear in all the graphs as the reference mixture compositions.

3.2 Technical properties and statistical analysis

The measured values of the technological properties T_O (deduced from the vitrification diagram), LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, and PI and the chromatic coordinates L* and b* of the 17 mixtures at maximum densification temperature are shown in Table IV.

Table IV. Technological properties (T_O, LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, and PI) and chromatic coordinates L* and b* of the mixtures at maximum densification temperature.

With these data, a regression equation was obtained for each property, subject to a significance level of 5% (see Table V). These equations were developed as a function of the amounts of FS, SF and RSA (x_1, x_2, and x_3, respectively as shown in Table II).

Table V. Regression equations of the technological properties (T_O, LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, and PI) and chromatic coordinates L* and b* of the mixtures at maximum densification temperature as a function of composition (x_1, x_2, and x_3 are the amounts of FS, SF, and RSA, respectively as shown in Table II) and ANOVA of the regressions.

Table V also shows the ANOVA results of the regressions obtained (principal statistical properties: p value, multiple correlation coefficient R^2, and adjusted multiple correlation coefficient R_A^2) for each of the technological properties T_O, LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, and PI and the chromatic coordinates L* and b*, using the nomenclature commonly found in the literature [44]. All models can be considered statistically significant to the level required (p value $\leq$ significance level) and exhibit little variability (high multiple determination coefficients). The following assumptions were made in the model: errors would be randomly distributed around a mean value of zero (i.e. they would not be correlated), suggesting a constant shared variance ($\varepsilon_i \sim N(0, \sigma^2)$); and the errors would be independent, COV (ε_i, $\varepsilon_{i'}$) = 0 $\forall i \neq i'$. Based on this analysis, the resulting regression models were used to describe the effect of the respective raw materials contents on the technological properties T_O, LFS, DBD, FBD, WA, OP, CP, TP, MOR, E, and PI and on the chromatic coordinates L* and b*. The effect of each raw material on the studied technological properties can be better observed in terms of the constant contour graphs of the surfaces of the properties, within the delimited region of the pseudo-components.

3.2.1 Composition behaviour in the pressing and firing stages

Figure 3a shows the results of the DBD. The lines represent constant properties as a function of composition, indicating the corresponding values. As previously stated, the increase in RSA content in the mixture impaired body compactness, as reflected in the reduced DBD value. This behaviour can be attributed to the fact that the introduction of a waste material disturbs the balance between the typically coarse particles contributed by the non-plastic raw materials (mainly FS) and the colloidal particles contributed by the plastic raw material (clay), as reported elsewhere [45]. However, the RSA fraction contents $\leq$ 0.40 (M2) allowed DBD values close to the minimum acceptable value for this type of ceramic product (> 1.80 g/cm^3) to be obtained [46]; Arantes et al. also found that dry bulk density values between 1.80 and 1.90 g/cm^3 yielded more favourable pore distributions, leading to essentially the same final pore volume in the test pieces [47].

Figure 3. DBD (g/cm^3) (a), LFS (%) (b), T_O (°C) (c), and FBD (g/cm^3) (d) as a function of composition.

Figure 3b shows that similarly to SF, higher RSA contents resulted in a slight increase in LFS. This was due to the reduced DBD of the compositions with a low FS content (especially those with a high RSA content) and, in the case of SF, also to the good FBD value provided by this raw material (Fig 3d). In relation to the DBD values, the compositions with a high FS content exhibited reduced LFS, replicating the results previously described by Carty and Senapati and Luz and Ribeiro [48-49]. Note that the LFS values of all mixtures were lower than the maximum allowable value $\leq$ 9% [50]. Figure 3c shows the role of albite as a fluxing agent in supplying the required viscous liquid phase that reacted with other body constituents and gradually dominated the microstructure, giving rise to densification through the well-known liquid phase sintering process [19,48,51-53]. In contrast, increasing the FS content raised mixture T_o, an expected behaviour stemming from the refractory character of this raw material due to its high quartz content. The increase in RSA content led to a slight rise in T_o, this being related to the low compactness (DBD) of the pressed pieces as well as to the high silica content in the composition: higher firing temperatures were therefore required to achieve maximum test piece densification. This behaviour coincides with the results obtained by Amorós et al. [54]. It may be noted that, in general, the T_o values lay within the range of values used in industrial practice (1180–1220 °C) [34,55], except for the mixtures without SF (M2, M6, and M13) which required higher T_o values than those used in industrial practice.

Porcelain stoneware tile densification occurs through a liquid phase sintering process [19,48,51-53]. Therefore, increasing the RSA content in some mixtures reduced the FBD because of the potassium-rich liquid phase in these mixtures, together with an increased silica content, with respect to the sodium-rich liquid phase and more reduced silica content in the mixtures containing SF, which adversely affected the densification process of the ceramic piece. This is consistent with the results described by Das and Dana and Yuruyen and Toplan [56-57]. In addition, the higher amounts of gas-generating substances (Fe_2O_3, Cl, and LOI) and higher SiO_2 content reduced the sintering capacity of the RSA-containing mixtures. However, RSA fraction contents $\leq$ 0.30 (M3, M4, M7, M8, M9, M10, M11, and M12) allowed FBD values to be obtained that matched the minimum required value (2.30 g/cm^3) for this type of ceramic product [50].

Figures 4a, b, c, and d show how the increase in SF content in the mixtures reduced fired test piece WA, OP, CP, and TP, while the increase in RSA content resulted in higher values of WA, OP, CP, and TP.

Figure 4. WA (%) (a), OP (%) (b), CP (%) (c), and TP (%) (d) as a function of composition.

The WA values of the fired test pieces of all mixtures were equal to or lower than the limit value established in ISO standard 13006 (≤ 0.5%) for the classification of Group BI_a dry-pressed ceramic tiles with low water absorption [1]. The OP values exhibited a similar trend to that displayed by the WA values, coinciding with the results reported by Márquez et al. and Pérez et al. [4,58]. The CP values of the fired test pieces lay in the range (5–12%) of CP values in a commercial porcelain stoneware tile, as indicated by Arantes et al. [47]. The increased CP values in the RSA-containing mixtures also explain why higher FBD values were not achieved, similarly to the findings reported by Braganca and Bergmann [59]. The TP values exhibited a similar trend to that shown by the CP values, in accordance with the results described by Correia et al. [7].

Figure 5 shows that the surfaces of the fired test pieces under maximum densification conditions for the RSA-containing mixtures exhibited greater porosity (M8 < M3 < M7 < M9 < M4 < M5 < M2 < M1 < M13 < M6)

than the fired test pieces of reference mixtures M10 and M12, in agreement with the density and porosity values noted above.

Figure 5. SEM micrographs in BSE (backscattered electron) mode (100x) of the polished surfaces of the fired test pieces.

The fired test pieces of the mixtures with RSA fraction contents > 0.25 (M4, M5, M2, M1, M13, and M6) exhibited a larger quantity and size of closed pores than the test pieces of reference mixtures M10 and M12. This result, which might be due to the narrow vitrification range and low compactness of these mixtures, in combination with the high content of gas-generating substances (Fe_2O_3, Cl, and LOI) in RSA, led to swelling or bloating of the body, significantly decreasing fired bulk density and increasing firing deformation.

With respect to the tendency to pyroplastic deformation, Figures 6a and b show that the increase in FS content in the mixture strongly decreased the pyroplasticity index. This result corroborates the findings reported by Carty and Senapati regarding the fact that quartz (FS in this case) forms a skeletal network during firing that keeps pyroplastic deformation low [48].

Figure 6. PI ($cm^{-1}x10^5$) as a function of composition (a) and fired test pieces after the PI test (b).

3.2.2 Fired test piece microstructure

Figure 7 shows the diffraction patterns of the fired test pieces. The mineralogical composition of the fired test pieces of the mixtures with RSA fraction contents ≤ 0.25 (M3, M7, M8, M9, M10, M11, and M12) was characterized by the typical diffraction pattern of porcelain stoneware, with the presence of phases such as α-quartz ($2\theta = 20.86°$ and $26.64°$) (ICSD 83849) and mullite ($2\theta = 16.43°$, $33.21°$, $35.26°$ and $40.87°$) (ICSD 99328). Reference mixtures M10 and M12 also displayed the albite phase ($2\theta = 21.97°$ and $27.90°$) (ICSD 87656), while the mixtures containing RSA also exhibited the presence of α-cristobalite ($2\theta = 21.76°$) (ICSD 74530), a phase essentially stemming from RSA [30]. As reported in the literature some unmelted albite grains can appear in porcelain microstructure as observed in this research for the high SF content compositions [34].

Figure 7. X-ray diffraction patterns of mixtures fired at maximum densification conditions (M= mullite, C= quartz, Cr= cristobalite, Al = albite).

The diffraction patterns of fired test pieces of mixtures with RSA fraction contents > 0.25 (M4, M5, M2, M1, M13, and M6) were characterized by the absence of mullite peaks ($2\theta = 16.43°$, $33.21°$, $35.26°$, and $40.87°$) (ICSD 99328), possibly due to the low Al_2O_3 content in these mixtures and the higher viscosity of the potassium-rich liquid phase, which prevented mass transport and crystal growth, as also reported by different authors [56,57,60]. Nevertheless we should take into account that XRD analysis has a detection limit which could be estimated in this case around 5%. It means that despite the fact that no mullite peaks were detected in some samples some mullite could exist. In general, the higher the RSA content in the mixtures, the lower the intensity of the α-quartz peaks ($2\theta = 20.86°$ and $26.64°$) (ICSD 83849) and mullite peaks ($2\theta = 16.43°$, $33.21°$, $35.26°$, and $40.87°$) (ICSD 99328), and the higher the intensity of the α-cristobalite peaks ($2\theta = 21.76°$) (ICSD 74530). There was no evidence of α-tridymite stemming from the RSA at angles $2\theta = 20.61°$ and $21.70°$ (ICSD 1109), possibly because the peaks had been overlapped by the diffraction angles of α-quartz ($2\theta = 20.86°$) and α-cristobalite ($2\theta = 21.76°$) or because the quantity of the tridymite phase was too low to be detected by XRD.

The SEM micrographs at 10000x in SEI (secondary electron imaging) mode and EDS analyses in Figure 8 demonstrate that the fired test pieces of all mixtures displayed the typical microstructure of porcelain stoneware tile as reported by De Noni Jr et al [34]. consisting of residual quartz (C), primary mullite+kaolinite glass (M+KG) and the glassy phase (GP) coming from the fluxing material (sodium feldspar and/or RSA). Regardless of the presence or not of mullite in XRD analysis, the formation of this crystalline phase in a fast firing (porcelain tile) composition is not favoured due to the rapid heating rate (phases distribution in fired specimens is very far from equilibrium conditions) as extensively reported in literature on porcelain tile firing [2, 3, 34]. Thus, when the microstructure of a standard porcelain tile is to be described it is much more convenient to include mullite phase together with the kaolin glass provided by the remaining material out of kaolinite decomposition. This is because primary mullite (produced from kaolinite reaction) and kaolinite glass share the same location in porcelain tile microstructure.

With regard to EDS analysis, bearing in mind that this type of analysis encompasses a micro-region with certain depth inside the surface three evidences can be shown. Firstly an increase of Al content refers to a M+KG zone but the chemical analysis is far from approaching to mullite chemical composition since this crystalline phase is not predominant in the zone. Mullite crystals can be observed in the border line (perimeter) of these zones (marked with arrows in Figure 8 micrographs). Secondly, an increase of Na content refers to a zone where albite glass is the main phase. Finally, an increase of K content indicates the formation of a potassium-rich glass phase when a high amount of RSA is used in the starting composition.

However, the test pieces with RSA fraction contents ≥ 0.40 (M1, M13 and M6) evidenced the almost complete disappearance of mullite. The micrographs thus confirmed the inhibiting effect of this high RSA content on the mullite crystallization noted above.

Figure 8. SEM micrographs in SEI mode (10000x) of the polished surfaces of fired test pieces. (C = quartz, M+KG= mullite + Kaolinite glass, GP= glassy phase).

3.2.3 Coefficient of thermal expansion (CTE)

The variation in the coefficient of thermal expansion (CTE) with temperature of the test pieces (see Figure 9 and Table VI) showed that increasing the RSA content in the mixtures mitigated the expansion attributed to α-quartz to β-quartz inversion (573 °C).

Figure 9. Variation of the coefficient of thermal expansion with temperature of the test pieces.

Table VI. Mean expansion coefficients ($\alpha_{50-300;\ 300-500;\ 500-650}$) and absolute coefficients (α_{100}) of the fired test pieces.

In contrast, there was an increase in CTE attributed to the tridymite stemming from RSA, which underwent α to β inversion in the temperature range 117–163 °C [45]. Tridymite inversion can be much more deleterious in ceramic processing than quartz or even cristobalite inversion. However, the fired test pieces of the mixtures with RSA fraction contents ≤ 0.25 (M3, M7, M8, and M9) exhibited a similar CTE pattern to that displayed by the fired test pieces of the reference compositions, i.e. a CTE value ≤ 9.0 x 10^{-6} °C^{-1} at temperatures < 100 °C, matching the findings of Biffi and Prado [50,61] and the results reported in ISO standard 13006 [1].

3.2.4 Mechanical properties (MOR and E)

Figure 10a shows that the MOR of the fired test pieces exhibited a similar trend to that shown by fired bulk density, coinciding with reports in the literature suggesting that mechanical strength (and also Young's modulus) are strongly affected by densification, so that the greater the fired bulk density, the higher is the MOR [59-62]. Consequently, the MOR became lower as the RSA content in the mixtures increased; however, the MOR values of all mixtures lay above the minimum value laid down in ISO standard 13006 ($\geq$ 35 MPa) for the classification of Group BI$_a$ dry-pressed ceramic tiles with low water absorption [1].

Figure 10. MOR (MPa) (a) and E (GPa) (b) of the fired test pieces as a function of composition.

The variation of E in the fired test pieces indicates the general behaviour of the materials, showing that as total porosity increased, E decreased (see Figures 4d and 10b), corroborating the findings of many authors regarding different ceramic materials who have reported the zero contribution of the pore phase to the overall Young's modulus of the ceramic body considered as a multiphase material [63-66]. Although E decreased with increasing RSA contents in the mixtures, the values of E in most mixtures were within the range of values reported by other authors (50–72 GPa) [66,67].

3.2.5 Chromatic coordinates

Sánchez et al. have indicated that in porcelain stoneware tile compositions, L*, which determines the white chromaticity component, is the most important chromatic coordinate, followed by the b* coordinate, which related to the yellow component [68-69]. The fired test pieces of reference mixtures M10 and M12 exhibited higher values of the L* coordinate than those of fired test pieces of RSA-containing compositions (see Figure 11a), which were characterized by lower values of L* (poorer whiteness) and higher values of b* (higher yellowness). This was probably due to the lower quantities of Fe$_2$O$_3$ in the standard FS and SF raw materials (see Table I).

Figure 11. Values of the L* coordinate (a) and b* coordinate (b) of the fired test pieces as a function of composition.

On the other hand, different authors have shown that the surface of Fe$_2$O$_3$ (hematite) changes from coordination number 4 to coordination number 6 when coming into contact with an alkaline glass matrix, causing a dark brown coloration [35,70], a mechanism that could lead to a change in colour of the fired test pieces in the different compositions. The present study showed that coordinate b* increased with a higher RSA content (see Figure 11b). In addition, increasing the FS (quartz) content resulted in a positive effect on chromatic coordinate L* (see Figure 11a), which is consistent with the findings reported by Sánchez et al., who indicated that crystalline phases such as quartz and mullite in porcelain stoneware tiles contributed to enhancing opacification, thus raising coordinate L* and lowering coordinate b* [68-69].

When fabricating porcelain stoneware tile, the body must be as white as possible, this being a typical commercial requirement [71]. In this study, although the values of L* exhibited by the fired test pieces of RSA-containing mixtures (69-72) were lower than those of fired test pieces of reference mixtures M10 and M12 (78 and 77, respectively), the resulting values of L* were similar to those reported by Perez (68-71) [72], indicating that these compositions would also be feasible for porcelain stoneware tile manufacture from the point of view of tile colour.

3.2.6 *Applicability and product specification restrictions*

Assuming that the raw materials and processing methodology at issue in this study are intended to be used in manufacturing porcelain stoneware tile (Group BIa in accordance with ISO standard 13006 [1]), a set of restrictions on product end characteristics are detailed below. That is, the values of properties such as DBD, FBD, LFS, MOR, WA, T_O, PI, and E are limited as follows:

$$DBD \ (g/cm^3) \geq 1.8$$
$$FBD \ (g/cm^3) \geq 2.3$$
$$LFS \ (\%) \leq 9$$
$$MOR \ (MPa) \geq 35$$
$$WA \ (\%) \leq 0.5$$
$$1180 \geq T_O \ (°C) \leq 1220$$
$$3.0 \geq PI \ (cm^{-1}x10^5) \leq 5.3$$
$$50 \geq E \ (GPa) \leq 78$$

The selection of an appropriate range of mixture compositions (feasible region), which meets all the requirements, implies finding a graphical solution (i.e. an intersection) for the equations indicated in Table V (or analysing the constant contour graphs shown in Figures 3, 4, 6, and 9), in combination with the inequalities.

Figure 12 shows the feasible compositional region (in white) for the manufacture of porcelain stoneware tile with the desired properties, i.e. which meets the restrictions set.

Figure 12. Intersection of the DBD, FBD, LFS, MOR, WA, T_O, PI, and E surfaces (feasible region in white) showing the appropriate compositional range for porcelain stoneware tile manufacture (DBD $(g/cm^3) \geq$ 1.8; FBD $(g/cm^3) \geq$ 2.3; LFS (%) $\leq$ 9; MOR (MPa) $\geq$ 35; WA (%) $\leq$ 0.5; 1180 $\geq$ To (°C) $\leq$ 1220; 3.0 $\geq$ PI $(cm^{-1}x10^5) \leq$ 5.3; and 50 $\geq$ E (GPa) $\leq$ 78).

For the raw materials and processing conditions used in this study, the results obtained in Figure 12 indicate that there is a range of relative raw materials contents: clay (A) (40 wt%), SF [20–50 wt%], FS [5–20 wt%], and RSA [0–25 wt%], which would meet the set requirements. It is clear that reference mixtures M10 and M12 and those containing RSA (M3, M8, M7, and M9) lie within this composition range. These were therefore selected to verify the applicability of the mathematical models (see Table VII).

Table VII. Mixtures selected to verify the applicability of the mathematical models and their corresponding (experimental and predicted) DBD, LFS, FBD, MOR, WA, T_O, PI, and E values.

The table shows a good correlation between the experimental values and those predicted by the mathematical models, confirming the validity of the derived equations and the model used.
Note furthermore that, relative to standard porcelain stoneware tile composition M10 (20FS;40SF;0RSA;40A), the mixtures containing RSA, i.e. M3 (15FS;32.5SF;12.5RSA;40A), M7 (20FS;20SF;20RSA;40A), and M9 (10FS;25SF;25RSA;40A), allow partial replacement of non-plastic materials (SF and FS) in the following proportions: 18.75% and 25%, respectively, for M3; 50% and 0%, respectively, for M7; and 37.5% and 50%, respectively, for M9. Similarly, relative to standard porcelain stoneware tile composition M12 (10FS;50SF;0RSA;40A), the mixtures containing RSA, i.e. M8 (5FS;42.5SF;12.5RSA;40A) and M9

(10FS;25SF;25RSA;40A), allow partial replacement of the non-plastic materials (SF and FS) in the following proportions: 15% and 50%, respectively, for M8; and 50% and 0%, respectively, for M9. This can be done without any significant disturbance to the technological process and allows the typical technical properties, microstructure, and mineralogical phases of porcelain stoneware tiles to be obtained.

The above demonstrates the feasibility of using RSA as a partial replacement for SF and FS in the formulation of a particular type of ceramic tile, which would reduce its environmental impact and manufacturing costs.

4. CONCLUSIONS

The study shows that RSA, synthesized using calcination Process D (2 hours of heat treatment at 800°C), exhibits a fluxing behaviour that makes it appropriate for the partial replacement of non-plastic raw materials (sodium feldspar, SF, and feldspathic sand, FS) in porcelain stoneware tile compositions without causing any significant change in the processing, microstructure, and technological properties compared to those of commercial products.

The fired test pieces of all the RSA-containing mixtures exhibited the required characteristics for Group BIa porcelain stoneware tile (MOR $\geq$ 35 MPa and water absorption $\leq$ 0.5%), in accordance with ISO standard 13006. However, there were mixtures with high RSA contents (>25 wt%) in which the processing and properties of the fired tiles were significantly affected as a result of the higher content of gas-generating substances (Fe_2O_3, Cl, and LOI), the low bulk density of the pressed test pieces, and the increased viscosity of the liquid phase that developed when this material was used in those amounts.

The addition of RSA as a replacement for FS and/or SF in porcelain stoneware tile compositions reduced the inversion of α-quartz to β-quartz (573 °C), decreasing the coefficient of thermal expansion (CTE) between 500 and 650 °C, as well as increasing this parameter between 50 and 300 °C, possibly stemming from the presence of tridymite from the RSA, which undergoes α to β inversion in the temperature range 117–163 °C.

Although coordinate L* of the fired test pieces of RSA-containing compositions decreased when the ash content increased, the values obtained for L* (69–72) enable these mixtures to be used for porcelain stoneware tile manufacture.

For the raw materials and processing conditions used in this study, it was verified that there was a range of relative contents of the raw materials: clay (40 wt%), SF [20–50 wt%], FS [5–20 wt%], and RSA [0–25 wt%], which were suitable for the production of Group BIa porcelain stoneware tile with the required properties. This confirms the possibility of using RSA as a partial replacement for SF and FS in the formulation of a ceramic material (tile) which would lead to reducing its environmental impact and manufacturing costs.

The extreme vertices mixture design methodology proved to be a useful tool for the design, planning, and analysis of experiments that relate the influence of raw materials to the technological properties of porcelain stoneware tile. In addition, the regression models obtained for each property in the dried and fired states were shown to be statistically significant at the required level and exhibited little variability. These models further

allowed the best combination of these raw materials to be formulated to produce a ceramic product with specific, pre-determined properties.

5. ACKNOWLEDGEMENTS

6. REFERENCES

[1] ISO 13006:1998. Ceramic tiles - Definitions, classification, characteristics and marking. International Organization for Standardization, 1998.

[2] E. Sánchez, M.J. Ibáñez, J. García-Ten, M.F. Quereda, I.M. Hutchings, Y.M. Xu. Porcelain tile microstructure: Implications for polished tile properties. *J Eur Ceram Soc* 2006;26:2533-2540.

[3] C. Zanelli, M. Raimondo, G. Guarini, M. Dondi. The vitreous phase of porcelain stoneware: Composition, evolution during sintering and physical properties. *J Non-Cryst Solid* 2011;357:3251–3260.

[4] J.M. Márquez, J.M. Rincón, M. Romero. Effect of firing temperature on sintering of porcelain stoneware tiles. *Ceram Int* 2008;34:1867-1873.

[5] A. De Noni Jr, D. Hotza, V. Cantavella, E. Sánchez. Analysis of the development of microscopic residual stresses on quartz particles in porcelain tile. *J Eur Ceram Soc* 2008;28:2629–2637.

[6] J.F. Motta, M. Cabral Jr, L.C. Tanno, A. Zanardo. As matérias primas cerâmicas. Parte II: Os minerais industriais e as massas da cerâmica tradicional. *Revista Cerâmica Industrial*, [pdf] 2002;7:33-40. (Available from: <http://www.ceramicaindustrial.org.br/main.php> [Accessed on 05/14/2014]).

[7] S.L. Correia, A.P. Oliveira, D. Hotza, A.M. Segadaes. Properties of triaxial porcelain bodies: Interpretation of statistical modeling. *J Am Ceram Soc* 2006;89(11):3356–3365.

[8] A. De Noni Jr, D. Hotza, V. Cantavella, E. Sánchez. Effect of quartz particle size on the mechanical behaviour of porcelain tile subjected to different cooling rates. *J Eur Ceram Soc* 2009;29(6):1039–1046.

[9] F. Andreola, L. Barbieri, A. Corradi, I. Lancellotti, T. Manfredini. Utilisation of municipal incinerator grate slag for manufacturing porcelainized stoneware tiles manufacturing. *J Eur Ceram Soc* 2002;22:1457–1462.

[10] C. Zanelli, M. Raimondo, M. Dondi, G. Guarini, P.M. Tenorio. Sintering mechanisms of porcelain stoneware tiles. In Qualicer 2004, Proceedings of the VIII World Congress on Ceramic Tile Quality, Cámara Oficial de Comercio, Industria y Navegación. Castellón, Spain 2004; papers C:247-259. (Available from: <http://aulavirtual.camaracastellon.com/qualicerCD/pdf/0413191e.pdf> [Accessed on 07/20/2014]).

[11] K. Dana, S.K. Das. Partial substitution of feldspar by B.F. slag in triaxial porcelain: Phase and microstructural evolution. *J Eur Ceram Soc* 2004a;24:3833–3839.

[12] C.S. Prasad, K.N. Maiti, R. Venugopal. Effect of rice husk ash in whiteware compositions. *Ceram Int* 2001;27:629-635.

[13] C.S. Prasad, K.N. Maiti, R. Venugopal. Effect of silica fume addition on the properties of whiteware compositions. *Ceram Int* 2002;28:9-15.

[14] F. Matteucci, M. Dondi, G. Guarini. Effect of soda-lime glass on sintering and technological properties of porcelain stoneware tiles. *Ceram Int* 2002;28:873-880.

[15] R. De Gennaro, P. Cappelletti, G. Cerri, M. De Gennaro, M. Dondi, G. Guarini, A. Langella, D. Naimo. Influence of zeolites on the sintering and technological properties of porcelain stoneware tiles. *J Eur Ceram Soc* 2003;23:2237–2245.

[16] K. Dana, S.K. Das. High strength ceramic floor tile compositions containing Indian metallurgical slags. *J Mater Sci Lett* 2003;22:387–389.

[17] K. Dana, S.K. Das. Evolution of microstructure in fly ash-containing porcelain body on heating at different temperatures. *Bull Mater Sci* 2004b;27:183-188.

[18] K. Dana, S.K. Das. Enhanced resistance to thermal cycling of slag-containing vitrified porcelain tiles. *Industrial Ceramics* 2008;28:121-124.

[19] K. Dana, S. Das, S.K. Das. Effect of substitution of fly ash for quartz in triaxial kaolin–quartz–feldspar system. *J Eur Ceram Soc* 2004;24:3169–3175.

[20] A. Tucci, L. Esposito, E. Rastelli, C. Palmonari, E. Rambaldi. Use of soda-lime scrap-glass as a fluxing agent in a porcelain stoneware tile mix. *J Eur Ceram Soc* 2004;24:83-92.

[21] K. Dana, J. Dey, S.K. Das. Synergistic effect of fly ash and blast furnace slag on the mechanical strength of traditional porcelain tiles. *Ceram Int* 2005;31:147-152.

[22] R. De Gennaro, M. Dondi, P. Cappelletti, G. Cerri, M. De Gennaro, G. Guarini, A. Langella, L. Parlato, C. Zanelli. Zeolite–feldspar epiclastic rocks as flux in ceramic tile manufacturing, Microporous. *Mesoporous Materials* 2007;105:273–278.

[23] M. Raimondo, C. Zanelli, F. Matteucci, G. Guarini, M. Dondi, J.A. Labrincha. Effect of waste glass (TV/PC cathodic tube and screen) on technological properties and sintering behaviour of porcelain stoneware tiles. *Ceram Int* 2007;33:615–623.

[24] A.S. Demirkiran, E. Artir, E. Avci. Effect of natural zeolite addition on sintering kinetics of porcelain bodies. *J Mater Process Technol* 2008;203:465-470.

[25] A. Guzmán, S. Delvasto, E. Sánchez, V. Amigó. Cenizas del tamo de arroz como substituto del feldespato en la fabricación de cerámica blanca. *Boletín de la Sociedad Española de Cerámica y Vidrio* 2013;52:25-30.

[26] A. Guzmán, J. Torres, M. Cedeño, S. Delvasto, V. Amigó, E. Sánchez. Fabricación de gres porcelánico empleando ceniza de tamo de arroz en sustitución del feldespato. *Boletín de la Sociedad Española de Cerámica y Vidrio* 2013;52:283-290.

[27] W. Acchar, E.J.V. Dultra, A.M. Segadaes. Untreated coffee husk ashes used as flux in ceramic tiles. *Appl Clay Sci* 2013;75-76: 141-147.

[28] B.M. Jenkins, L.L. Baxter, T.R. Miles Jr, T.R. Miles. Combustion properties of biomass. *Fuel Process Technol* 1998;54:17-46.

[29] P. Thy, B.M. Jenkins, S. Grundvig, R. Shiraki, C.E. Lesher. High temperature elemental losses and mineralogical changes in common biomass ashes. *Fuel* 2006;85:783-795.

[30] A. Guzmán, S. Delvasto, E. Sánchez. Valorization of rice straw waste: an alternative ceramic raw material. *Revista Cerâmica* 2015;61:126–136.

[31] S.L. Correia, D. Hotza, A.M. Segadaes. Simultaneous optimization of linear firing shrinkage and water absorption of triaxial ceramic bodies using experiments design. *Ceram Int* 2004;30 (6):917–922.

[32] A.M. Bernardin, D. Souza de Medeiros, R.H. Gracher. Pyroplasticity in porcelain tiles. *J Mater Sci Eng* 2006;427(1-2):316-319.

[33] S.L. Correia, D. Hotza, A.M. Segadaes. Predicting porosity content in triaxial porcelain bodies as a function of raw materials contents. *J Mater Sci* 2008;43(2):696–701.

[34] A. De Noni Jr, D. Hotza, V. Cantavella, E. Sánchez. Influence of composition on mechanical behaviour of porcelain tile. Part I: Microstructural characterization and developed phases after firing. *Mater Sci Eng: A* 2010a;527(7-8):1730–1735.

[35] M.L. Gualtieri, M. Romagnoli, A.F. Gualtieri. Influence of body composition on the technological properties and mineralogy of stoneware: A DOE and mineralogical–microstructural study. *J Eur Ceram Soc* 2011;31(5): 673-685.

[36] A. Guzmán, S. Delvasto, M.F. Quereda, E. Sánchez. Valorization of rice straw waste: production of porcelain tiles. *Revista Cerâmica* 2015;61:442–449.

[37] J. García-Ten. Descomposición durante la cocción del carbonato cálcico contenido en el soporte crudo de los azulejos. Ph.D Thesis, Universidad Jaume I, Castellón, Valencia, España; 2005.

[38] ASTM C326 – 09. Standard Test Method for Drying and Firing Shrinkages of Ceramic Whiteware Clays. American Society for Testing and Materials, West Conshohocken, PA: ASTM, 2009.

[39] ASTM C373 – 88 (2006). Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity, and Apparent Specific Gravity of Fired Whiteware Products. American Society for Testing and Materials, West Conshohocken, PA: ASTM, 2006.

[40] ASTM C674 – 88 (2006). Standard Test Methods for Flexural Properties of Ceramic Whiteware Materials. American Society for Testing and Materials, West Conshohocken, PA: ASTM, 2006.

[41] ASTM C1259 – 08. Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio for Advanced Ceramics by Impulse Excitation of Vibration. American Society for Testing and Materials, West Conshohocken, PA: ASTM, 2008.

[42] Instituto de Tecnología Cerámica (ITC). Manual de Laboratorio de Materias Primas Cerámicas. 2013. Castellón.

[43] ASTM D2244 – 11. Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates. American Society for Testing and Materials, West Conshohocken, PA: ASTM, 2011.

[44] D.C. Montgomery. Design and Analysis of Experiments. 5th Edition. 2001. New York: John Wiley & Sons, Inc, p. 472-484.

[45] A. Barba, V. Beltrán, C. Felíu, J. García, F. Ginés, E. Sánchez, V. Sanz. Materias primas para la fabricación de soportes de baldosas cerámicas. 2da Edición. 2002. Castellón: Instituto de Tecnología Cerámica (ITC), p. 1-291; 272-286.

[46] S.L. Correia, G. Dienstmann, M.V. Folgueras, A.M. Segadães. Effect of quartz sand replacement by agate rejects in triaxial porcelain. *J Hazard Mater* 2009;163(1):315-322.

[47] F.J.S. Arantes, D.F. Galesi, E. Quinteiro, A.O. Boschi. O Manchamento e a porosidade fechada de gres porcelanato. *Revista Cerâmica Industrial*, [pdf] 2001;6(3):18-25. Available from: <http://www.ceramicaindustrial.org.br/main.php> [Accessed on 01/21/2011].

[48] W.M. Carty, U. Senapati. Porcelain—Raw materials, processing, phase evolution and mechanical behaviour. *J Am Ceram Soc* 1998;81(1):3–20.

[49] A.P. Luz, S. Ribeiro. Uso de pó de vidro como fundente para produção de grês porcelanato. *Revista Matéria*, [pdf] 2008;13(1):96-103. Available from: <http://www.materia.coppe.ufrj.br/sarra/artigos/artigo10760> [Accessed on 01/21/2013].

[50] G.O. Biffi. Gres porcelanato: manual de fabricação e técnicas de emprego, 3.ed. 2002. São Paulo, Brasil: Faenza Editrice do Brasil Ltda.

[51] Y. Iqbal, W.E. Lee. Fired porcelain microstructures revisited. *J Am Ceram Soc* 1999;82(12):3584–3590.

[52] Y. Iqbal, W.E. Lee. Microstructural evolution in triaxial porcelain. *J Am Ceram Soc* 2000;83(12): 3121–3127.

[53] F. Andreola, L. Barbieri, E. Karamanova, I. Lancellotti, M. Pelino. Recycling of CRT panel glass as fluxing agent in the porcelain stoneware tile production. *Ceram Int* 2008;34(5):1289–1295.

[54] J.L. Amorós, M.J. Orts, J. García-Ten, A. Gozalbo, E. Sánchez. Effect of the green porous texture on porcelain tile properties. *J Eur Ceram Soc* 2007;27(5):2295-2301.

[55] M. Raimondo, C. Zanelli, G. Guarini, M. Dondi, R. Fabbroni, T. Cortesi. Process of pyroplastic shaping for special-purpose porcelain stoneware tiles. *Ceram Int* 2009;35(5):1975–1984.

[56] S.K. Das, K. Dana. Differences in densification behaviour of K, Na feldspar containing porcelain bodies. *Thermochim Acta* 2003;406(1-2):199-206.

[57] S. Yuruyen, H.O. Toplan. The sintering kinetics of porcelain bodies made from waste glass and fly ash. *Ceram Int* 2009;35(6):2427-2433.

[58] J.M. Pérez, J.M. Rincón, M. Romero. Effect of moulding pressure on microstructure and technological properties of porcelain stoneware. *Ceram Int* 2012;38(1):317-325.

[59] S.R. Braganca, C.P. Bergmann. Traditional and glass powder porcelain: technical and microstructure analysis. *J Eur Ceram Soc* 2004;24(8):2383–2388.

[60] J.A. Baucia Jr, L. Koshimizu, G. Gibertoni, M.R. Morelli. Estudo de fundentes alternativos para uso em formulações de porcelanato. *Cerâmica*, [pdf] 2010;56(339):262-272. (Available from: <http://www.scielo.br/pdf/ce/v56n339/a0956339.pdf> [Accessed on 07/02/2013]).

[61] D.A.C. Prado. Argilas da formação corumbataí como base para obtenção de grés porcelanato por via seca. M.Sc Thesis, Universidad Estadual Paulista, 2003; pp. 36-38.

[62] J.M. Pérez, M. Romero. Microstructure and technological properties of porcelain stoneware tiles moulded at different pressures and thicknesses. *Ceram Int* 2014;40(1):1365-1377.

[63] A.R. Boccaccini, Z. Fan. A new approach for the Young's modulus-porosity correlation of ceramic materials. *Ceram Int* 1997;23(3):239-245.

[64] W.D. Callister Jr. Fundamentals of Materials Science and Engineering, 5th edition. 2001. New York, USA: John Wiley & Sons, Inc.

[65] J.M. Márquez, J.M. Rincón, M. Romero. Effect of microstructure on mechanical properties of porcelain stoneware. *J Eur Ceram Soc* 2010;30(15):3063-3069.

[66] A. De Noni Jr, D. Hotza, V. Cantavella, E. Sánchez. Influence of composition on mechanical behaviour of porcelain tile. Part II: Mechanical properties and microscopic residual stress. *Mater Sci Eng: A* 2010b;527(7-8):1736–1743.

[67] M. Dal Bó, V. Cantavella, E. Sánchez, A.P.N. Oliveira. Histéresis térmica del módulo de elasticidad en matrices vítreas con cuarzo. In Qualicer 2012, Proceedings of the XII World congress on Ceramic Tile Quality, Cámara Oficial de Comercio, Industria y Navegación. Castellón, Spain, 2012; [pdf] Posters:1-4. (Available from: <http://www.qualicer.org/recopilatorio/ponencias/pdf/2012136.pdf> [Accessed on 01/22/2013]).

[68] E. Sánchez, M.J. Orts, J. García-Ten, V. Cantavella. Porcelain tile composition: effect on phase formation and end products. *Am Ceram Soc Bull* 2001a;80(6):43-49.

[69] E. Sánchez, M.J. Orts, J. García-Ten, V. Cantavella. Efeito da composição das matérias-primas na fabricação de grês porcelanato sobre as fases formadas durante a queima e as propriedades do produto final. *Revista Cerâmica Industrial*, [pdf] 2001b;6(5):15-22. (Available from: <http://www.ceramicaindustrial.org.br/main.php> [Accessed on 01/15/2011]).

[70] A.F. Gualtieri. Development of low-firing B-fluxed stoneware tiles. *J Am Ceram Soc* 2009;92(11):2571-2577.

[71] M.J. Cabral, A.O. Boschi, J.F.M. Maricano, L.C. Tanno, A. Sintoni, J.M. Coelho, M. Caridade. Panorama e Perspectivas da Indústria de Revestimentos Cerâmicos no Brasil. *Revista Cerâmica Industrial*, [pdf] 2010;15(3):7-18. (Available from: <http://www.ceramicaindustrial.org.br/main.php> [Accessed on 01/18/2014].

[72] F. Pérez. Fundentes: Como Escolher e Como Usar. *Revista Cerâmica Industrial*, [pdf] 2008;13(4):31-35. (Available from: <http://www.ceramicaindustrial.org.br/main.php> [Accessed on 01/21/2011]).