PHYLLITE AS FELDSPAR SUBSTITUTE IN PORCELAIN STONEWARE TILES: EFFECT ON SINTERING BEHAVIOR AND PHASE COMPOSITION

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1. ABSTRACT

The objective of this work was to report the preliminary results of substituting feldspar by phyllite in a typical Brazilian porcelain stoneware batch (i.e. sericite instead of K-feldspar as flux). Two bodies were prepared (50% K-feldspar replaced by 50% phyllite) and their behavior during firing was compared after an industrial-like schedule and in isothermal conditions (by optical dilatometry). Pyroplastic deformation and quantitative phase composition (XRD-Rietveld) were determined, along with an estimation of the chemical and physical properties of the vitreous phase at high temperature. The results show that the substitution of feldspar by phyllite has important repercussions on technological behavior, with pros and cons, dictated by a different evolution of the phase composition. The main drawback of the phyllitic batch is the higher firing temperature (+30°C) necessary to achieve water absorption below 0.5%. Clear advantages in the use of phyllite are easier grindability and lower pyroplastic deformation. The differences are not simply justified by the viscosity of the vitreous phase but are likely linked to the relatively large amount of skeleton (and an appropriate shape of the crystals dispersed in the melt).

2. INTRODUCTION

Mainly due to local scarcity, relatively high price, and logistical problems in the supply of feldspar, Brazilian glazed porcelain stoneware tile production is nowadays largely based on the use of phyllite. It is a peculiar, fine-grained metasedimentary rock, primarily composed of sericite (i.e., microcrystalline muscovite), kaolinite and quartz, with alkali content of about 3-6 %, responsible for its fluxing characteristics [1]. Due to its chemical and mineralogical composition, phyllite acts in a ceramic batch simultaneously as a flux, a plastic component and skeleton. For this reason, Brazilian phyllite is widely employed in ceramic production, especially in the São Paulo area, thanks to its relatively low cost, in comparison with feldspar, and relative abundance in the Southern regions of Brazil [2-5], representing up to 50% by weight in porcelain stoneware formulations.

Despite the facts mentioned above and the relevance of the Brazilian ceramic tile industry (third largest producer in the world), just a few papers have evaluated the effects of the substitution of phyllite after feldspar in porcelain stoneware batches. To fill this gap, two recent papers have investigated the technological behavior of batches where K-feldspar was replaced by the same content of phyllite [6-7]. As can be seen in Figure 1, such a substitution has an important effect on the behavior during firing. In general, both the slope of the vitrification curves and the target temperature (at which water absorption goes below 0.5%) are quite different. In the feldspathic body, water absorption values decrease considerably faster than in the phyllitic one. In particular, the variation of linear shrinkage as a function of temperature denotes not only a faster sintering rate of the feldspar-based batch, but also an early overfiring (>1190°C) that in the phyllite-based body was not observed in the thermal range investigated. Overall, the variation of water absorption and linear shrinkage with increasing temperature is considerably lower in the phyllitic body than in the feldspathic one [6-7].

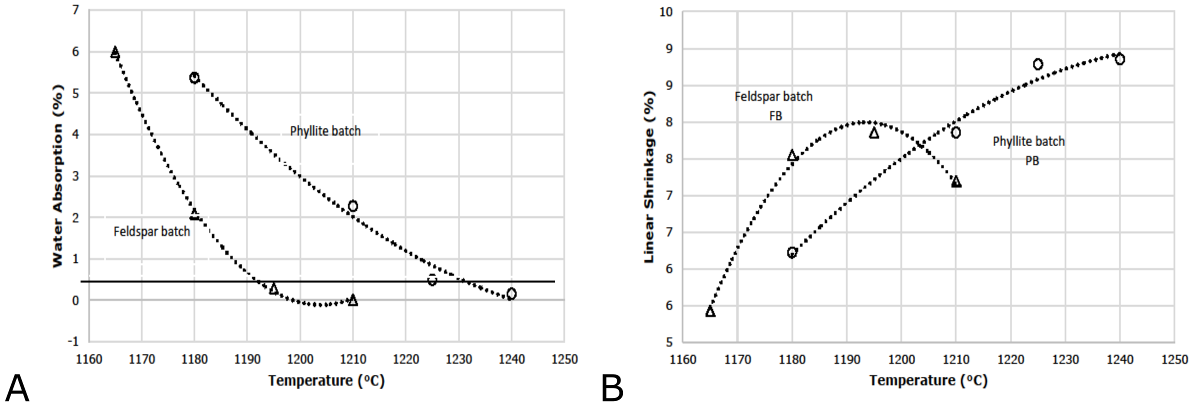

Figure 1: *Variation of water absorption (A) and linear shrinkage (B) with firing temperature of two glazed porcelain stoneware compositions containing 50% in weight of the fluxes Feldspar and Phyllite.*

The present work takes over from the previous studies [6-7] in order to comparatively study the effects on firing behavior of the use of phyllite in total substitution of K-feldspar in a typical Brazilian porcelain stoneware batch. The objective is to understand which factors are behind the differences in sintering path and kinetics between two bodies based on phyllite and feldspar, respectively.

3. EXPERIMENTAL

In this study, two different batches of Brazilian-style porcelain stoneware are considered: one phyllite-based (PB) and the other feldspar-based (FB).

The raw K-feldspar mineralogical composition is characterized mainly by quartz (≅23wt%), illite (≅6wt%), plagioclase (≅43wt%) and albite (≅28wt%). The raw phyllite mineralogical composition is characterized mainly by quartz (≅55wt%), sericite (≅29wt%), kaolinite (≅15wt%) and hematite (≅1wt%).

Batches were designed and prepared at the laboratory scale by mixing different Brazilian raw materials (ball clays, talc, calcium carbonate, potassic feldspar and phyllite) then simulating the industrial tile-making process (Table 1). The K-feldspar used is a typical raw material on the Brazilian market, while the phyllite comes from the state of Minas Gerais in Brazil.

Ingredients (wt%)	Phyllite batch PB	Feldspar batch FB
Clays	42	42
Talc	6	6
Calcium carbonate	2	2
Phyllite	50	-
Feldspar	-	50

Table 1: *Batch design of the porcelain stoneware bodies.*

Components (wt%)	Phyllite batch PB	Feldspar batch FB
SiO_2	69.74	69.79
TiO_2	0.77	0.41
Al_2O_3	15.43	15.07
Fe_2O_3	1.56	1.05
MgO	2.21	1.82
CaO	1.70	1.70
Na_2O	0.07	1.29
K_2O	2.50	4.58
P_2O_5	0.04	0.09
Loss on ignition	5.74	4.14
Total	99.76	99.94

Table 2: *Chemical composition of the porcelain stoneware bodies.*

Batches were characterized from a chemical, mineralogical and granulometric viewpoint.

Chemical compositions of the two different batches were evaluated by X-ray fluorescence (XRF, Phillips MagiX) and listed in Table 2. The particle size distribution was determined on milled bodies by X-ray monitoring of gravity sedimentation (SediGraph 5100, Micromeritics, UK) (Figure 2).

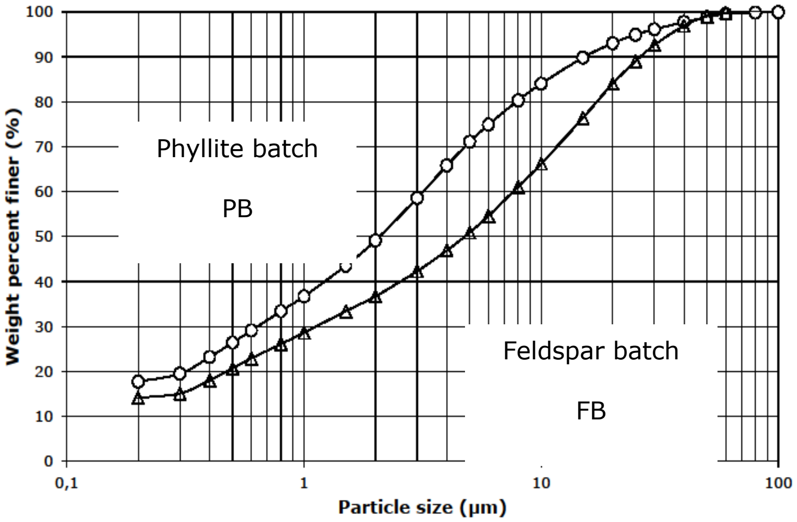

Figure 2: *Particle size distribution of the porcelain stoneware bodies.*

The experimental procedure and the main physical and technological properties of both semi-finished and finished products were discussed in previous papers [6-7]. The main technological properties are summarized in Table 3. A key indicator was defined: the maximum densification temperature, T_{md}, as the temperature at which bulk density reaches its maximum value (1225°C for PB and 1195°C for FB).

The phase composition was quantitatively assessed on samples fired at different temperatures (at max temperatures from 1180 to 1240 for Phyllite batch P1 and at max temperatures from 1165 to 1210 for Feldspar batch) by X-ray powder diffraction (XRPD, D8 Advance equipped with LynxEye detector; Bruker, Germany). A full profile interpretation by Rietveld refinement was carried out with the GSAS-EXPGUI software package [8-9]. The samples were admixed with corundum (20 wt%) as internal standard to estimate the vitreous phase by difference, that is, 100% minus the sum of crystalline phases [10].

	Physical and technological properties	Phyllite batch (PB)	Feldspar batch (FB)
Powder	Real density (g·cm^{-3})	2.636	2.588
	Median particle size (µm)	2.1	4.7
Semi-finished products	Bulk density (g·cm^{-3})	1.875	1.846
Finished products	Temperature of maximum densification - T_{md} (°C)	1225	1195
	Real density (g·cm^{-3})	2.592	2.510
	Bulk density (g·cm^{-3})	2.337	2.341
	Water absorption (%weight)	0.50	0.29
	Total porosity (% volume)	9.85	6.75
	Linear shrinkage (cm·m^{-1})	9.5	8.6

Table 3. *Technological properties of semi-finished and finished products [6-7].*

Based on the quantitative chemical and phase composition of the fired body, the chemical composition of the vitreous phase was obtained by subtracting the contribution of each mineralogical phase, considering its stoichiometric formula, from the bulk chemistry (the thus obtained values were normalized to 100%). The physical properties of the vitreous phase were estimated by its chemical composition using models developed for glasses and silicate melts [11-13].

The sintering behavior was determined in isothermal conditions by optical thermo-dilatometric analysis (TA ODP868). The isothermal tests were carried out at Tmd (maximum densification temperature) with a heating rate of 80°C/min up to Tmd and 30 min soaking time.

The pyroplastic deformation is quantified by the pyroplastic index (measurement of curvature after firing of a cubic sample body on two refractory supports), calculated from equation: DI=(4*h2*S)/(3*L4). Where, DI: represents the pyroplasticity index (cm-1); S: represents the maximum strain (cm); h: represents the thickness of body (cm) and L: the distance between the refractory supports (cm).

4. RESULTS AND DISCUSSION

The substitution of phyllite after potassium feldspar caused a distinct firing behavior of the two porcelain stoneware batches, as already reported [6-7]. This can be justified by significant differences in terms of mineralogical composition and particle size distribution. In particular, the phyllite-based batch is primarily composed of quartz, sericite and kaolinite, while the feldspathic one is mainly characterized by microcline, plagioclase, quartz and illite. On the other hand, grindability was different, as PB has a lower median particle diameter (d50=2.1 µm) than FB (d50=4.7 µm); as was to be expected, sericite and kaolinite are easier to mill than feldspars.

The porcelain stoneware under investigation consists of a large amount of vitreous phase (58-78%) together with newly formed mullite (up to 7%) and residual phases: quartz (16-32%), K-feldspar (up to 12%) and plagioclase (up to 6%). Such a phase composition evolves with increasing firing temperature (Table 4).

In detail, sample PB has relatively high amounts of quartz (decreasing in the thermal range under study) and just some remnants of feldspars (1.3% at T_{md}). Mullite is stable around 7% (this value roughly corresponds to the maximum percentage achievable starting from about 15% kaolinite in the batch). The vitreous phase is between 59 and 67%, not too high with respect to porcelain stoneware records [14]. It must be emphasized that sericite is completely decomposed, already at the lowest firing temperature.

On the other hand, sample FB exhibits lower amounts of quartz, with respect to PB, but quite stable over temperature. Residual feldspars are abundant and dissolve extensively just at the highest temperature, still being 9.4% at T_{md}. Mullite formation is scarce and always below 2%.

	Firing temperature	Quartz	Mullite	Plagioclase	K-feldspar	Vitreous phase	RF^2
Unit	(°C)	(wt%)					
Phyllite batch (PB)	1180	31.7±0.2	6.5±0.1	2.2±0.1	0.7±0.1	58.9±0.5	8.3
	1210	31.7±0.1	6.8±0.1	2.0±0.1	0.5±0.1	59.0±0.4	8.5
	1225	25.4±0.3	7.1±0.1	1.0±0.1	0.3±0.1	66.2±0.6	9.1
	1240	25.0±0.1	7.0±0.1	0.7±0.1	0.2±0.1	67.1±0.4	8.0
Feldspar batch (FB)	1165	20.3±0.2	0.5±0.1	5.8±0.1	10.5±0.3	62.9±0.7	8.0
	1180	19.3±0.1	1.8±0.1	4.4±0.1	11.5±0.2	63.0±0.5	8.1
	1195	16.4±0.3	1.2±0.1	2.9±0.1	6.5±0.1	73.0±0.6	8.4
	1210	18.8±0.1	1.0±0.1	1.3±0.1	1.0±0.1	77.9±0.4	8.9

Table 4. *Phase composition of porcelain stoneware bodies.*

Such a different phase evolution was expected, considering the ternary diagram SiO_2-Al_2O_3-K_2O: the phyllite-based batch plots in the mullite-quartz-feldspar, while the feldspar-based one falls close to the meta-aluminous line, in the quartz-feldspar-potassium silicate field. This can justify the mullite instability and feldspar persistence in sample FB and the opposite behavior in batch PB.

The estimated chemical composition and physical properties of the vitreous phase are summarized in Table 5. The composition of the vitreous phase reflects the described differences in the evolution of the phase composition.

Phase	Unit	Phyllite batch (PB)				Feldspar batch (FB)			
Firing temperature	°C	1180	1210	1225	1240	1165	1180	1195	1210
SiO_2	wt%	66.83	67.04	69.96	69.98	67.59	68.60	69.01	67.32
TiO_2		1.39	1.39	1.24	1.22	0.69	0.69	0.59	0.55
Al_2O_3		18.12	17.80	16.17	16.23	18.59	17.49	17.48	18.48
Fe_2O_3		2.82	2.82	2.51	2.48	1.74	1.74	1.50	1.41
MgO		3.98	3.97	3.54	3.49	3.01	3.01	2.59	2.43
CaO		2.32	2.38	2.43	2.49	1.68	1.96	1.94	2.07
Na_2O		0.12	0.12	0.11	0.11	1.72	1.82	1.67	1.65
K_2O		4.31	4.36	3.93	3.91	4.78	4.50	5.04	5.92
P_2O_5		0.07	0.07	0.06	0.06	0.15	0.15	0.13	0.12
Viscosity, $\log_{10}(\eta)$	Pa·s	4.84	4.58	4.79	4.66	5.05	4.97	4.96	4.73
Surface tension	N/m	0.355	0.350	0.344	0.342	0.351	0.347	0.343	0.341

Table 5. *Chemical composition and physical properties of the vitreous phase in the porcelain stoneware bodies as a function of firing temperature.*

The surface tension of the vitreous phase, which accounts for its ability to wet solid particles, fluctuates in narrow ranges, this being slightly higher in PB (Fig. 3A). The viscosity range is between 4.6 and 5.1 log Pa·s; although values should decrease regularly with temperature, the trend is uneven for both FB and PB (Fig. 3B).

The melt present in PB is less viscous than that in FB: it can be appreciated comparing data at the same temperature, i.e. 1180 or 1210°C. The difference is small, around 0.14 log Pa·s, and stems from a combination of factors: the most relevant appear to be the higher percentages of MgO, CaO, Fe2O3 and the lower content of alkalis in PB with respect to FB. SiO2 and Al2O3 amounts do not vary systematically.

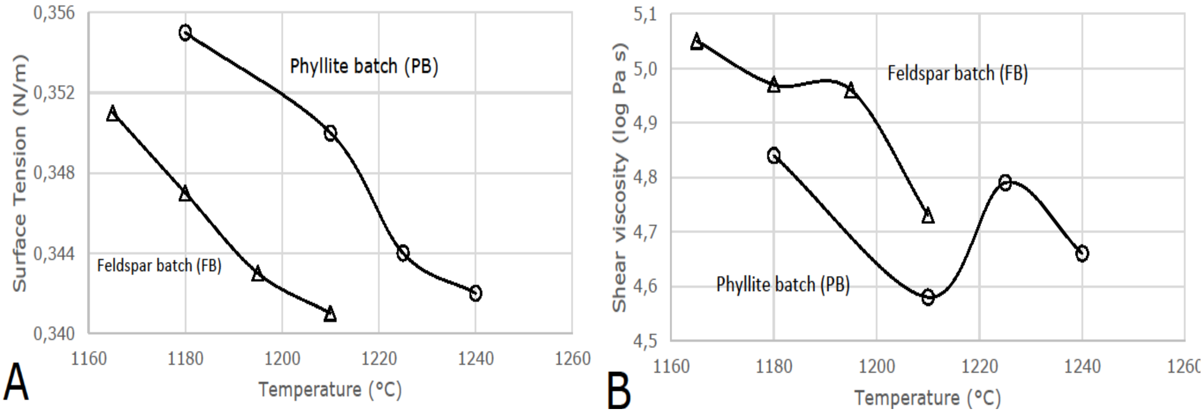

Figure 3: *Surface tension (A) and shear viscosity (B) estimated for the vitreous phase.*

Viscous flow sintering occurs in a window of melt viscosity that in these samples is 4.6-4.8 log Pa·s (PB) versus 4.7-5.1 (FB). This difference exists also at Tmd: 4.79 log Pa·s at 1225°C (phyllitic batch) versus 4.96 log Pa·s at 1195°C (feldspathic batch). The higher firing temperature of the phyllite-based batch is necessary to reach the effective flowability window for feldspar-based bodies.

Although the PB batch is undoubtedly more refractory than the FB batch, the two bodies have a similar sintering behavior, when a comparison is carried out at the temperature of maximum densification (Fig. 4). During constant rate sintering, the phyllitic batch presents a slightly faster kinetics than the feldspathic one. This behavior can be due to the convolution of various factors: lower melt viscosity, larger solid load, and smaller particle size of batch PB with respect to FB.

Moreover, as can be seen from figure 4, the isothermal sintering at Tmd confirms that the phyllitic batch has a more efficient densification: PB has a higher shrinkage, even if it takes more time to get to the maximum value. Such a slower kinetics in the final sintering stage is mirrored by a different stability during dwell time. In fact, the feldspar-based batch exhibits a slightly faster coarsening rate than that of the phyllite-based body. This is coherent with the larger solid load (skeleton) of PB.

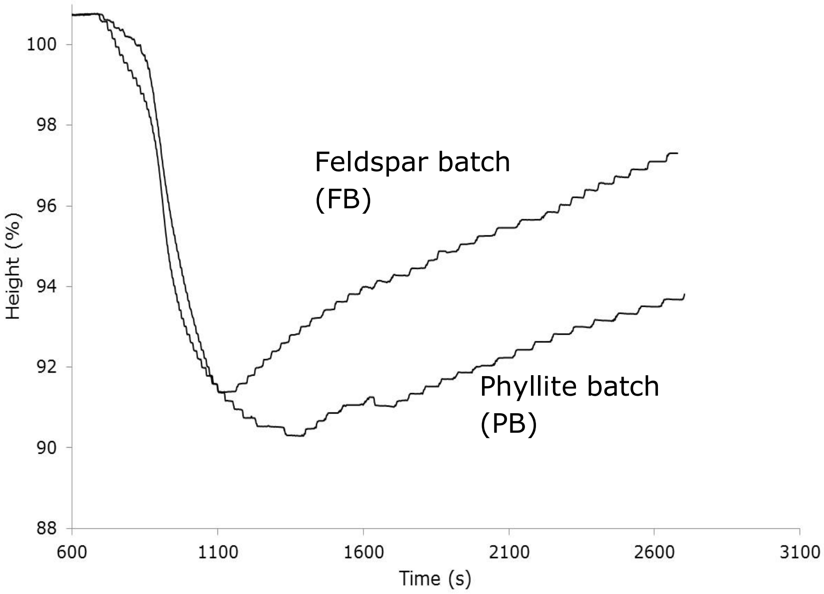

Figure 4: *Isothermal curves at Tmd of the porcelain stoneware bodies.*

The results show that the substitution of feldspar by phyllite significantly reduced tile pyroplastic deformation [6-7]: the index measured on PB is less than half that of FB (Table 6). Pyroplasticity depends not only on the amount and viscosity of the liquid phase, but also on the contribution of the crystals dispersed in the melt at the highest temperature. Such a contribution varies according to the amount, size and shape of the crystals [15]. However, the different pyroplasticity cannot be simply explained by the viscosity of the liquid phase, because FB exhibits a higher value with respect to PB (4.96 versus 4.58 log Pa·s). Nevertheless, the amount of liquid phase at T_{md} is significantly higher in the feldspar-based body (73%) with respect to that of the phyllite-bearing mixture (62%). This fact makes the effective viscosity, i.e. that accounting for the bulk (melt + crystals), almost the same in the two bodies (Table 6). Effective viscosity was estimated by the Brinkman's relation: $\eta\cdot(1-\Phi)^{-2.5}$, where η is the shear viscosity of the melt and Φ is the crystal fraction [16]. Since neither the melt viscosity nor the solid load seem to be the determinant factors, the improved pyroplasticity of PB could stem from a favorable shape of the crystals [15].

Properties	Phyllite batch (PB)	Feldspar batch (FB)
Firing temperature (°C)	1225	1195
Pyroplastic Index (x10^{-6} cm^{-1})	5.3 ± 0.1	12.2 ± 0.1
Effective viscosity (log Pa·s)	5.24	5.30

Table 6. *Pyroplastic deformation of the porcelain stoneware bodies at maximum densification temperature Tmd.*

5. CONCLUSIONS

In summary, the evaluation of the effects on sintering behavior and phase composition of substituting feldspar by Brazilian phyllite in porcelain stoneware tiles led to the following preliminary conclusions:

There are clear differences in the tile-making process, for instance in terms of grindability: the phyllite batch tends to be milled more easily than the feldspar batch, due to a favorable mineralogical composition.

As phyllite is less fusible than feldspar, a higher firing temperature is necessary to achieve the target for porcelain stoneware tiles (water absorption below 0.5%).

However, sintering behavior is similar, compared at maximum densification temperature, T_{md} (PB 1225°C – FB 1195°C); the phyllitic body presents a slightly faster kinetics and a more efficient densification with respect to the feldspathic body.

The main advantage of the phyllite-based batch is its pyroplastic deformation and coarsening rate, these being definitely smaller than those of the feldspar-based formulation. Such differences are not justified by the viscosity of the vitreous phase, but by the relatively large amount of skeleton (and likely by an appropriate shape of the crystals dispersed in the melt).

6. ACKNOWLEDGEMENTS

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7. REFERENCES

[1] F.B. Angelieri, P. Souza Santos, J.E. De Paiva Netto, A.C. Nascimento, Característicos físico-químicos e tecnológicos de materiais cerâmicos designados usualmente por filitos, *Cerâmica,* 6, 22, (1960), 2-15,

[2] J.F.M. Motta, M. Cabral Jr., L.C. Tanno, Panorama das matérias-primas utilizadas na industria de revestimentos cerâmicos: Desafios do setor produtivo, *Cerâmica Industrial,* 3, 4-6, (1998), 30-38,

[3] W. Acchar, E.J.V. Dultra, Porcelain Tile, in *Ceramic Materials from Coffee Bagasse Ash Waste*, vol, VI, OnLine, Springer Briefs in Applied Sciences and Technology, (2015), 3-15,

[4] S. Fróes Abreu, Recursos Minerais do Brasil, Volume I, vol, I, E, E, B, Ltda, Ed,, São Paulo, SP: Universidade de São Paulo, (1973), 325,

[5] M. Cabral Junior, Matérias-primas para a produção de porcelanato no Brasil: cenário atual, demandas e oportunidades, São Paulo, Expo Revestir, (2018).

[6] Hernández-Sánchez, M.Y.; Nastri, S., Melchiades, F.G., Boschi, A.O., Efeito da Substituição do Feldspato por Filito sobre a Deformação Piroplástica de Massas de Porcelanato Esmaltado. 2019, http://dx.doi.org/10.4322/cerind.2019.004 Cerâm. ind., 24(1), 15-19.

[7] Hernández-Sánchez, M.Y., Nastri, S., Melchiades, F.G., Boschi, A.O., Effects of Substituting Feldspar by Brazilian Phyllite in Glazed Porcelain Bodies. cfi/Ber. DKG 96 (2019) No. 7-8, pp 42-45.

[8] Larson, A. C., Von Dreele, R. B. (1988). GSAS, General Structure Analysis System. Los Alamos National Laboratory, Los Alamos, NM, pp. 86-748.

[9] Toby, B. H. (2001). EXPGUI, a graphical user interface for GSAS. Journal of applied crystallography, 34(2), 210-213.

[10] Gualtieri, A. F., Riva, V., Bresciani, A., Maretti, S., Tamburini, M., Viani, A. (2014). Accuracy in quantitative phase analysis of mixtures with large amorphous contents. The case of stoneware ceramics and bricks. Journal of Applied Crystallography, 47(3), 835-846.

[11] Appen, A.A. Chemistry of Glass (Russ.); Khimiya: Leningrad, Russia, 1974; Volume 351.

[12] Dietzel, A. Relation between the surface tension and the structure of molten glass. Kolloid-Z. 1942, 100, 368–380.

[13] Giordano, D., Russell, J. K., Dingwell, D. B. (2008). Viscosity of magmatic liquids: a model. Earth and Planetary Science Letters, 271, 123-134.

[14] Zanelli, C., Raimondo, M., Guarini, G., Dondi, M. (2011). The vitreous phase of porcelain stoneware: composition, evolution during sintering and physical properties. Journal of Non-Crystalline Solids, 357, 3251-3260.

[15] dos Santos Conserva, L. R., Melchiades, F. G., Nastri, S., Boschi, A. O., Dondi, M., Guarini, G., Raimondo, M., Zanelli, C. (2017). Pyroplastic deformation of porcelain stoneware tiles: Wet vs. dry processing. Journal of the European Ceramic Society, 37, 333-342.

[16] Conte, S., Zanelli, C., Ardit, M., Cruciani, G., Dondi, M. (2018). Predicting viscosity and surface tension at high temperature of porcelain stoneware bodies: a methodological approach. Materials, 11, 2475.