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Technological Behavior of Porcelain Stoneware Bodies with Egyptian Syenites

Chiara Zanelli[1], Roberto Soldati[1], Sonia Conte[1], Guia Guarini[1], Ali I.M. Ismail[2], M.S. El-Maghraby[3], Alberto Cazzaniga[4], Michele Dondi[1]

[1]CNR-ISTEC, Faenza, Italy.
[2]Department of Geological Sciences, National Research Centre, Cairo, Egypt.
[3]Ceramic, Refractories and Building Materials Department, National Research Centre, Cairo, Egypt.
[4]R&D Department, Minerali Industriali srl, Cacciano, Italy.

Abstract

The progressive depletion of the main feldspathic flux deposits in the World is forcing the ceramic industry to search for suitable substitutes. The aim of this study is to assess the potential of some feldspar sources in the Egyptian Eastern Desert, particularly syenites from Abu Khruq, in the manufacture of ceramic tiles. Beneficiated samples obtained by lab-scale mineral processing were tested into porcelain stoneware batches (from 10% to 30% wt in replacement of feldspars) and compared with a reference body through a laboratory reproduction of the industrial processing. The technological behavior of unfired tiles does not suffer any significant alteration due to the use of syenites. On the other hand, syenite-bearing bodies exhibit some changes in the phase composition and the chemistry of the melt, that turns richer in alkali, especially K_2O. The consequently increased sintering rate depends mainly on the viscosity of the liquid phase formed during firing. In conclusion, syenites can be used without technological hindrances to manufacture porcelain stoneware tiles. The firing behavior of syenite-bearing batches can be reasonably adjusted by setting key parameters (e.g., the feldspar amount and the Na/K ratio), but the darker color of fired bodies requires to furtherly lower the iron oxide.

Key-words: porcelain stoneware, syenite, sintering, technological behavior, vitreous phase.

1. Introduction

The ceramic tile industry is the major end-user of feldspathic fluxes that are mainly recovered from albitites, granites and acid differentiates (pegmatites, aplites) as well as feldspathic sands [1]. The importance of fluxes has been gradually enhancing due to tendencies coming with technological innovation (increasing production of porcelain stoneware, development of special batches for large slabs) and environmental sustainability (lowering of firing temperatures and reducing the CO_2 emissions). These trends converge towards a growing demand of fluxes with high fusibility, namely albitites and nepheline syenites [1-4]. At the same time, the recourse to alternative fluxes – like waste glasses – is already entered in the industrial practice [5-8]. However, technological reasons damp their use to a few percent in ceramic tile bodies, whilst feldspathic fluxes constitute more than 50% of a porcelain stoneware batch [1, 9].

The manufacture of porcelain stoneware bodies usually requires mixtures of ball clay, kaolin, quartz and feldspars, that overall bring about different amounts of Na_2O and K_2O. Variants in the ratios of these classical components (or their substitutes) were already explored in the literature. The main goals have been using raw materials locally available, fulfilling process specifications or even adjusting technological properties according to different applications and market demand [9, 10]. Concerning the feldspathic component, it was observed that high Na/K ratios tend to lower the temperature of vitrification, therefore shortening the firing schedules. However, a too high Na/K ratio may be detrimental for pyroplastic deformation, that reflects the faster sintering kinetics. Substituting Na and Na-K fluxes in favor of a higher quartz content turned into a lower firing deformation, due to the viscosity increase following the quartz dissolution in the liquid phase, depending on the initial particle size of quartz [11].

Summarizing, the liquid phase formed during firing wets the mineral particles and partially dissolves quartz and mullite, thus controlling the viscous flow sintering and the final

microstructure in porcelain stoneware bodies. In addition, the tile deformation is related to the amount of liquid phase and its viscosity [12]. For these reasons, it is recommended to properly design the vitreous phase composition by selecting the feldspathic raw materials [13-14].

Nevertheless, the progressive depletion of the main deposits in the World of highly fusible feldspathic materials – that occur at a rate of several million tons per year – is forcing the ceramic industry to search for suitable substitutes [1]. From this standpoint, intermediate igneous rocks, especially nepheline syenites and further syenites, are good prospects because of their high amount of feldspars (and possibly feldspathoids) and low amount of refractory minerals, like quartz. Alkalisyenites and quartz-syenites, in particular, are a source practically not yet exploited as ceramic flux, since their use is limited to a few proposals [15].

The utilization of nepheline syenite in ceramic tiles is not common, even if it is utilized in several countries [16, 17]. Nevertheless, it was observed that 5% wt of nepheline syenite is sufficient to accelerate the densification process with some other positive effects, such as lowering closed porosity [18]. In addition, nepheline syenite can modify the equilibrium between the co-existing vitreous and crystalline phases in porcelain stoneware bodies: the amounts of quartz and mullite are generally reduced [19]. Further, the use of 10% wt of nepheline syenite was found to decrease the viscosity of the glassy phase. This circumstance lead to an enhanced shrinkage rate; however, higher percentages seem to have a negligible effect on densification kinetics [19, 20].

The goal of this study is to assess the effect of syenite on the technological behavior of porcelain stoneware tiles. The scope is to evaluate the potential of different types of syenite exploited from the Abu Khruq ring complex in the Egyptian Eastern Desert [21]. This deposit was selected taking into account geological, petrographic and logistical issues, including the occurrence of nepheline syenite [22].

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2. Experimental

Three samples of syenites, ranging in composition from quartz-syenite to alkalisyenite and nepheline syenite, were collected from the Abu Khruq ring complex in the Egyptian Eastern Desert. Their chemical, mineralogical, petrographic and fusibility characteristics are discussed in a previous paper [22] together with lab-scale mineral processing (comminution and magnetic separation). Here, three beneficiated samples – representing the non-magnetic fractions of alkalisyenite (AS), nepheline syenite (NS) and quartz-syenite (QS) – are taken into account.

These beneficiated fluxes were tested into porcelain stoneware batches (10% or 30% wt in replacement of sodic and sodic-potassic feldspars) and compared with the reference body EG0 (Table 1). The chemical composition of raw materials is summarized in Table 2.

Simulation of the industrial processing was carried out at the laboratory scale by wet milling (15 min in planetary mill with porcelain jar and alumina grinding media). The slip so obtained (~60% solid load, 0.3% Na-tripolyphosphate) was oven dried and disagglomerated (hammer mill with grid of 500 µm) prior manual granulation (sieve 2 mm, powder moisture ~7% wt). Powders were shaped into 110x55x5 mm tiles by hydraulic pressing (40 MPa) then dried in oven (105°C overnight) and fast fired in electric roller kiln (max temperature from 1160 to 1220°C; 60 min cold-to-cold).

The technological behavior of unfired samples was appraised to get insights on the grindability and compressibility of syenite-bearing bodies. The following characteristics were determined: particle size distribution (ASTM C958 and C325); powder moisture (ASTM C324); green and dry bulk density (weight-to-volume ratio); real density by Helium pycnometry (ASTM D5550); starting porosity (by the ratio of dry bulk density and real density); springback after pressing; drying shrinkage (ASTM C326).

The following technological properties were determined on fired tiles: linear shrinkage (ASTM C326), water absorption, open porosity and bulk density (ASTM C373), bending

strength (ASTM C648). A sintering curve was drawn for each body, from which the following parameters were elaborated (Fig. 1A):

- temperature of maximum densification (T_{md}) taken in correspondence of the maximum shrinkage;

- optimal firing range (T_{of}) at which the maximum shrinkage is retained within a variation of 0.1 cm·m^{-1};

- Temperature matching the standard requirement of water absorption <0.5% (T_{Bla}).

CIE-Lab (1976) colorimetry (ISO 10545-16, Hunterlab MSXP-4000) of sintered tiles was also performed; the chromatic difference between the reference and the syenite-bearing bodies was expressed as: $\Delta E^* = [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{-1/2}$, where ΔL^*, Δa^*, and Δb^* are the difference of the L*, a* and b* values between the sample and the reference EG0.

The sintering behavior was also investigated by hot-stage microscopy (Misura 3, TA, Italy) on cylindric specimens (3 x 1 mm, height x diameter) which underwent an industrial-like firing schedule (43°C·min^{-1} to T_{md}, then 17 min soaking). Data of firing shrinkage in function of time were plotted to get the isothermal sintering rate and a bloating index (as defined in Fig. 1B). The Bloating Index (BI) is intended to highlight an inversion of the sintering curve; a suitable behavior should have BI≤0 for bodies that keep densifying, while BI>0 indicates an expansion. For this purpose, five points were pointed out: 0) start of densification (L_0, below T_{md}), 1) start of isothermal sintering at T_{md} (L_1), 2) end of the initial sintering stage (linear trend, L_2), 3) end of densification (L_3), 4) end of test (L_4).

The phase composition was quantitatively assessed by X-ray powder diffraction (XRPD, D8 Advance, Bruker, Germany) in the 10-100°2θ range, scan rate of 0.02°, equivalent time 16 s per step (LynxEye detector, Bruker, Germany). A full profile interpretation by Rietveld refinement was carried out with the GSAS-EXPGUI software package [23, 24]. The samples were admixed with 20% wt of Al_2O_3 as internal standard to determine the vitreous phase by difference, *i.e.*, 100% minus the sum of crystalline phases [25, 26]. The chemical

composition of the vitreous phase was calculated by subtracting the contribution of each crystalline phase from the body composition [26, 27]. Properties of the liquid phase at T_{md} were inferred from its chemical composition, using models developed for glasses and silicate melts: in particular, that proposed by Giordano and co-workers [28] to calculate the viscosity and the Dietzel's [29] and Appen's models [30] to determine the surface tension.

3. Results and Discussion

3.1. Chemical composition of porcelain stoneware bodies

The replacement of conventional sodic feldspar (in bodies with 10% syenite) and both sodic and sodic-potassic fluxes (in batches with 30% syenite) implies changes in the overall chemical composition. In general, the addition of syenite brings about, on one side, a slight decrease of SiO_2, Na_2O and CaO (as a tiny drop of TiO_2 and MgO) and, on the other side, a slight increase in Al_2O_3, Fe_2O_3 and loss on ignition, as well as a significant gain in K_2O (Table 3). These differences are clearly larger in bodies with 30% syenite.

3.2. Technological behavior of unfired tiles

The technological behavior of unfired tiles is slightly affected by the replacement of syenites after feldspars, as the variation of relevant parameters for grinding, pressing and drying stages is often within the uncertainty of measurement (Figure 2 and Table 4).

Grindability was appraised through particle size distribution of slips, by considering both the mean particle size and the amount of coarser fraction (>20 µm). Syenite-bearing bodies exhibit the same (or even improved) grindability of the reference batch: the 3.05-3.11 µm range arose from its median particle size and standard deviation (Fig. 2A). The compaction behavior is practically the same in all cases, except for the body EQS3, likely due to its slightly lower moisture (Fig. 2B). As expected, the higher the powder moisture, the denser the green tiles (Fig. 2C). However, both EAS1 and EAS3 had the same bulk

density of the other bodies, but it was obtained with a lower moisture. This implies a better compressibility when alkalisyenite is added. Dry bulk density substantially reflects the compressibility, with negligible differences about the drying shrinkage (Fig. 2D).

3.3. Technological behavior of fired tiles

Sintering diagrams, based on linear shrinkage and water absorption versus firing temperature, are shown in Figure 3.

The replacement of sodic and sodic-potassic feldspars induces an overall change in these curves, even though always distinct for the different types of syenite. All bodies containing 30% syenite exhibit a faster sintering rate, appreciable by lower T_{Bla} temperatures, while the tiles match the standard threshold of water absorption (<0.5%). This occurs also for addition of 10% in the case of nepheline syenite (Fig. 3B), but neither for alkalisyenite that has a slower kinetics (Fig. 3A) nor for quartz-syenite, which curve is practically overlapping that of the sample EG0 (Fig. 3C).

Overall, the firing shrinkage is always larger in syenite-bearing bodies (Table 5). This is sometimes due to a higher initial porosity, expressed by a lower dry bulk density. However, in other cases, when the dry bulk density is higher (as in batches EAS), the differences are small and likely related to enhanced densification, leading to a higher bulk density of the fired product (with respect to EG0).

Such a faster densification rate of syenite-bearing batches reflects into a slightly decreasing water absorption. This makes it possible to lower the firing temperatures of around 20°C for the two ENS batches and the EQS3 one. In any case, a compromise must be found, because in the above mentioned bodies the interval of stability (T_{of}) is drastically narrowed (Fig. 3D).

Once batches with the same syenite content are compared with the reference body, an enhancement of sintering kinetics stands out in the order: EAS1 < EG0 = EQS1 < ENS1 for 10% addition (Fig. 4A). In the case of 30% addition, the order turns into: EG0 < EQS3 <

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EAS3 < ENS3 (Fig. 4B). While the relative order is respected by quartz-syenite and nepheline syenite batches, by varying the percentage of their addition, alkalisyenite shows a significant improvement in densification kinetics when its amount switches from 10% to 30%.

The sintering curves were replicated by hot-stage microscope in order to assess the stability of porcelain stoneware bodies at the soaking temperature, i.e. T_{md} (Fig. 5). The batches containing alkalisyenite exhibit the best behavior, keeping constant size over time, like the reference body (Fig. 5A). In contrast, when the nepheline syenite is added, clues of overfiring appear even more accentuated in the ENS1 body (Fig. 5B). Batches containing quartz-syenite have clearly different behaviors: EQS3 tends to bloat, while EQS1 is still densifying (Fig. 5C). Thus, *in-situ* measurements confirm that the larger the addition of syenite, the higher the shrinkage (Fig. 5D).

The mineralogical composition of fully dense bodies is characterized by a large amount of vitreous phase (61-70%) with new formed mullite (9-12%) and residual phases, i.e., 17-22% quartz and 2-6% feldspars (Table 6). The addition of syenite affects the amount of residual quartz, which is increased in the nepheline syenite batches and in the EQS1 body, but reduced in the alkalisyenite bodies. The amount of mullite increases in the bodies with 10% syenite, but is slightly less abundant in those with 30%. About feldspars, the syenite additions caused a systematic drop of plagioclase and, at the same time, an increase of K-feldspar in the EAS and ENS batches.

These fluctuations are apparently small and within the ranges usually observed in porcelain stoneware tiles [10, 26]. Howbeit, these data imply that even small changes in the bulk chemical composition can translate into significant variations of phase composition. Overall, the increasing of alkali content, achieved with the employment of syenites, promotes a faster dissolution of quartz, mullite and plagioclase, but renders more

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stable the K-feldspar. Such changes are reflected by the amount of the vitreous phase, which increases when amount of syenites passes from 10% to 30%.

Syenite-bearing bodies induced some small variations of color (Table 7). In fact, the values of ΔE^*, expressing the total chromatic change with respect to the reference body, increased with the amount of syenite added. The main changes concern the L^* parameter: all the syenite-bearing bodies turned a bit darker. At the same time, they exhibit slightly higher values of both a^* and b^*, so resulting a little redder and yellower than body EG0.

These color changes can be related, in principle, with the variation of iron content. Nevertheless, two trends may be appreciated: bodies with 30% of syenite align along a steeper slope of ΔE^* in function of Fe_2O_3 with respect to those at 10% syenite (Fig. 6A). This might be a side-effect of the higher amount of vitreous phase when the amount of syenite passed from 10% to 30% (Fig. 6B). Another factor that can influence the observed color changes is mullite stability: the ΔE^* increment concurrent with decreasing mullite percentage might legitimate that iron was hosted in the mullite crystal structure (Fig. 6C).

The estimated chemical composition and physical properties of the vitreous phase are summarized in Table 8. Adding syenites brings about a higher amount of alkalis in the vitreous phase, due to the dissolution of feldspars and nepheline, with consequent changes in melt viscosity that explain the faster sintering kinetics and the tendency to lower bulk densities at T_{md}.

Indeed, the introduction of syenites in the batches yields an enrichment in Al_2O_3 and a dilution of SiO_2, except for the body EQS1. The K_2O amount increases while the Na_2O concentration is slightly fluctuating (±0.5% of the value in EG0). Minor components (TiO_2, Fe_2O_3, MgO and CaO) exhibit just small variations, often within the uncertainty interval.

These chemical variations of liquid phase affect the viscosity at high temperature, either decreased when alkalisyenite or quartz-syenite were added or increased in the bodies containing nepheline syenite. The expected reverse relationship between the amount of

glass network modifiers ($Na_2O+K_2O+MgO+CaO$) and the melt viscosity can be observed (Fig. 7). Nevertheless, bodies plot along two alignments that account for the firing temperature: the two ENS and the EQS3 samples (T_{md} 1180°C) are distinct from the two EAS and the EQS1 samples (T_{md} 1200°C).

The surface tension of the liquid phase, which in turn accounts for its capacity of wetting solid particles, does not present any significant variation with the amount and typology of syenite added, apart EQS1, which lower value is related to the lowest amount of Al_2O_3 in the melt (Table 8).

As observed in literature for nepheline syenite [18-20], the addition of 10% to 30% of syenite improves the initial sintering rate (Table 5). This can be reconducted to an enhanced surface tension to viscosity ratio, according to the Frenkel's model that describes the first stage of the viscous flow sintering [30, 31, 32]:

$$\frac{\Delta L}{L_0} = \frac{3\,\gamma}{8\,\eta(T)\,r}\,t$$

where L_0 is the original specimen length, ΔL is the linear shrinkage after a sintering time t, $\eta(T)$ is the temperature dependent viscosity, γ is the surface tension, and r is the initial particle radius.

The isothermal sintering rate actually scales with the surface tension to viscosity ratio, even though following different alignments for the two firing temperatures (Fig. 8).

4. Conclusions

Beneficiated syenites can be used as effective fluxes, without significant technological hindrances, to manufacture porcelain stoneware tiles. Their behavior in the tile-making process, with special care to effects on grindability and powder compressibility, is fully comparable with that of commercial feldspathic fluxes.

The substitution of conventional fluxes with different types of syenite may lead to slightly higher amounts of alkalis (and particularly K_2O) in porcelain stoneware batches. This can

induce some changes in the phase composition: a faster dissolution of quartz, mullite and plagioclase was observed, mirrored by an improved stability of K-feldspar. These reactions let the amount of vitreous phase to increase, once the syenite addition passed from 10% to 30%. The melt composition was attained by these changes through an enrichment in Al_2O_3 and K_2O, but a dilution of SiO_2.

The firing behavior is affected by the variation of phase assemblage and composition of the liquid phase: these parameters change upon the type of syenite added to the bodies. Overall, the firing shrinkage increased and the densification rate was faster, leading to a slightly decreasing water absorption in syenite-bearing bodies. Such an improved behavior offers the chance, in some cases, to lower the firing temperature (1200°C → 1180°C). However, bodies with a faster sintering rate exhibit, at the same time, a narrower interval of stability (25°C → below 15°C).

The sintering rate proved to depend on the increased surface tension-to-viscosity ratio of the liquid phase, which in turn is related with the amount of glass network modifiers (and the variable Na/K ratio resulting by the addition of different types of syenite). The slightly darker color of fired bodies, due essentially to the increased Fe_2O_3 content, requires a tailored mineral processing to lower the iron oxide amount.

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Table 1. Batch formulation of porcelain stoneware tiles.

Table 2. Chemical composition of raw materials used in porcelain stoneware batches.

Table 3. Chemical composition of porcelain stoneware bodies.

Table 4. Technological properties of semi-finished products.

Table 5. Technological properties of fired tiles and sintering parameters (for definition see Figure 1).

Table 6. Phase composition of the porcelain stoneware bodies fired at the temperature of maximum densification (T_{md}) and goodness-of-fit (RF^2) of Rietveld refinement of XRD patterns.

Table 7. CIELab parameters L*, a* and b* in the porcelain stoneware bodies fired at T_{md}.

Table 8. Chemical composition and physical properties of the vitreous phase present in the porcelain stoneware bodies fired at T_{md}.

Figure 1. Interpretation of sintering curves: A) temperature of maximum densification (T_{md}), optimal firing range (T_{of}) and temperature which the body matches the standard requirement for group BIa ($T_{BIa} < 0.5\%$ water absorption); B) isothermal (T_{md}) sintering rate and bloating index from hot-stage microscopy.

Figure 2. Technological behavior of unfired bodies: grindability (A); springback versus green bulk density (B); powder moisture versus green bulk density (C); drying shrinkage versus dry bulk density (D).

Figure 3. Sintering curves comparing porcelain stoneware bodies containing syenite at 10% and 30% wt of: alkalisyenite (A); nepheline syenite (B); quartz-syenite (C). Dotted straight lines indicate thresholds for water absorption: group BIa (<0.5%) and market (<0.2%). Suitable firing behavior (D): temperature at which the bodies match the standard requirement for BIa (water absorption <0.5%) versus the optimal firing range.

Figure 4. Sintering curves comparing porcelain stoneware bodies containing different types of syenite: 10% wt (left) and 30% wt (right). Dotted straight lines indicate thresholds for water absorption: group BIa (<0.5%) and market (<0.2%).

Figure 5. Sintering curves by hot-stage microscopy comparing porcelain stoneware bodies containing syenite at 10% and 30% with reference body EG0. A): alkali syenite; B) nepheline syenite; C); quartz-syenite; D) comparison of all bodies.

Figure 6. Color change of porcelain stoneware bodies with respect to the reference body (EG0) in function of A) iron oxide content of the body; B) amount of vitreous phase; C); amount of mullite. Batches containing syenite at 10% are shown as empty symbols and those at 30% by filled symbols.

Figure 7. Viscosity at T_{md} versus chemical composition of the melt (glass network modifiers). Symbols: empty for 10% syenite; filled for 30% syenite addition.

Figure 8. Initial sintering rate of porcelain stoneware bodies versus melt viscosity.

Table 1. Batch formulation of porcelain stoneware tiles.

Ingredients (% wt)	EG0	EAS1	EAS3	ENS1	ENS3	EQS1	EQS3
Sodic feldspar	20	10	-	10	-	10	-
Sodic-potassic feldspar	10	10	-	10	-	10	-
Sodic-magnesian feldspar	10	10	10	10	10	10	10
Potassic aplite	10	10	10	10	10	10	10
Quartz-feldspathic sand	10	10	10	10	10	10	10
Alkalisyenite AS	-	10	30	-	-	-	-
Nepheline Syenite NS	-	-	-	10	30	-	-
Quartz-syenite QS	-	-	-	-	-	10	30
Ball clay 1	30	30	30	30	30	30	30
Ball clay 2	10	10	10	10	10	10	10

Table 2. Chemical composition of raw materials used in porcelain stoneware batches.

Ingredients (% wt)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LoI
Sodic feldspar	69.50	0.45	18.00	0.35	0.20	1.00	9.50	0.40	0.50
Sodic-potassic feldspar	71.50	0.20	17.00	0.30	0.20	0.45	6.80	2.80	0.40
Sodic-magnesian feldspar	66.30	0.50	17.90	0.50	3.00	1.70	8.00	0.30	1.80
Potassic aplite	71.00	0.28	16.10	0.58	0.80	1.20	1.40	7.00	1.50
Quartz-feldspathic sand	85.20	0.04	7.00	0.18	0.20	0.90	0.20	5.20	1.00
Nepheline Syenite NS	64.37	0.04	19.60	0.52	0.10	0.30	7.72	6.05	1.30
Quartz-syenite QS	61.73	0.01	20.90	0.46	0.11	0.21	8.73	6.45	1.40
Alkalisyenite AS	64.76	0.04	19.40	0.60	0.10	0.33	7.19	6.28	1.30
Ball clay 1	60.90	1.20	25.30	1.00	0.60	0.40	0.40	2.30	7.90
Ball clay 2	61.37	1.41	24.25	1.65	0.51	0.25	0.10	2.20	8.16

Table 3. Chemical composition of porcelain stoneware bodies.

Batch (% wt)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	L.o.I.
EG0	67.71	0.69	19.42	0.69	0.69	0.77	3.67	2.52	3.76
EAS1	67.23	0.65	19.56	0.72	0.68	0.70	3.44	3.11	3.84
EAS3	66.09	0.60	19.94	0.77	0.66	0.62	3.25	4.04	4.01
ENS1	67.19	0.65	19.58	0.71	0.68	0.70	3.49	3.09	3.84
ENS3	65.97	0.60	20.00	0.75	0.66	0.62	3.41	3.98	4.01
EQS1	66.93	0.65	19.71	0.70	0.68	0.69	3.59	3.13	3.85
EQS3	65.18	0.59	20.39	0.73	0.66	0.59	3.71	4.10	4.04

Table 4. Technological properties of semi-finished products.

Property	unit	EG0	EAS1	EAS3	ENS1	ENS3	EQS1	EQS3	*std.dev.*
Median particle size	µm	3.08	3.06	2.97	2.99	3.03	3.10	3.01	0.05
Particles >20µm	% wt	8.9	9.0	8.6	7.9	8.7	9.0	8.0	0.1
Powder Moisture	% wt	7.6	6.8	7.0	7.8	7.6	7.3	6.9	0.1
Green Bulk Density	$g \cdot cm^{-3}$	1.960	1.954	1.964	1.959	1.961	1.953	1.940	0.015
Springback	$cm \cdot m^{-1}$	0.61	0.62	0.61	0.64	0.63	0.60	0.61	0.01
Dry Bulk Density	$g \cdot cm^{-3}$	1.833	1.839	1.840	1.828	1.834	1.827	1.818	0.015
Drying Shrinkage	$cm \cdot m^{-1}$	0.01	-0.05	-0.05	0.02	0.01	-0.02	-0.06	0.01

Table 5. Technological properties of fired tiles and sintering parameters (for definition see Figure 1).

Property	Unit	EG0	EAS1	EAS3	ENS1	ENS3	EQS1	EQS3	*std.dev.*
T_{md}	°C	1200	1200	1200	1180	1180	1200	1180	
T_{Bla}	°C	1198	1198	1193	1178	1179	1197	1178	*1*
T_{of}	°C	25	20	22	11	14	25	8	
Sintering rate	$\Delta L/L_0 \cdot min^{-1}$	1.48	1.83	1.85	1.56	1.65	1.64	2.01	*0.05*
Bloating index	1	-3.2	0.4	2.3	7.0	2.7	-12.8	6.2	*0.1*
Firing shrinkage ($cm \cdot m^{-1}$)	1220°C	6.5	6.7	6.7	6.6	6.6	6.7	7.3	*0.2*
	1200°C	6.9	7.0	7.3	6.9	7.0	7.1	7.5	
	1180°C	6.8	6.8	7.2	7.2	7.2	7.0	7.9	
	1160°C	6.1	5.5	5.4	6.4	7.0	5.6	6.6	
Bulk density ($g \cdot cm^{-3}$)	1220°C	2.315	2.327	2.305	2.303	2.276	2.307	2.312	*0.015*
	1200°C	2.367	2.371	2.395	2.340	2.331	2.369	2.348	
	1180°C	2.362	2.349	2.376	2.387	2.325	2.361	2.390	
	1160°C	2.249	2.224	2.239	2.317	2.358	2.250	2.266	
Water absorption (% wt)	1220°C	0.14	0.18	0.10	0.14	0.12	0.11	0.11	*0.12*
	1200°C	0.38	0.34	0.15	0.31	0.09	0.32	0.08	
	1180°C	1.60	2.03	1.11	0.22	0.40	1.65	0.29	
	1160°C	4.96	5.60	4.94	3.59	2.34	4.88	3.72	
Open porosity (% vol)	1220°C	0.3	0.4	0.2	0.3	2.1	0.2	0.3	*0.3*
	1200°C	0.9	0.8	0.4	0.7	0.2	0.7	0.2	
	1180°C	3.7	4.6	2.5	2.2	2.2	3.7	0.7	
	1160°C	11.0	11.8	10.4	7.1	4.0	10.4	9.2	

Table 6. Phase composition of the porcelain stoneware bodies fired at the temperature of maximum densification (T_{md}) and goodness-of-fit (RF^2) of Rietveld refinement of XRD patterns.

Phase	Unit	EG0	EAS1	EAS3	ENS1	ENS3	EQS1	EQS3	*std.dev.*
T_{md}	°C	1200	1200	1200	1180	1180	1200	1180	-
Quartz	%wt	19.7	17.6	17.7	21.9	20.2	21.7	19.2	0.1
Mullite	%wt	10.2	11.7	9.7	11.1	9.9	11.0	9.0	0.1
Plagioclase	%wt	3.0	-	-	2.1	1.5	1.8	2.8	0.1
K-feldspar	%wt	-	3.5	2.8	3.8	3.9	-	-	0.1
Vitreous phase	%wt	67.1	67.3	69.8	61.1	64.5	65.5	68.9	0.5
RF^2	1	8.3	9.1	10.1	9.5	8.5	9.1	9.0	-

Table 7. CIELab parameters L*, a* and b* in the porcelain stoneware bodies fired at T_{md}.

Body	T_{md} (°C)	Color CIE-Lab (1976)			
		L*	a*	b*	ΔE*
EG0	1200	67.37 ± 0.01	3.40 ± 0.02	13.25 ± 0.04	Ref.
EAS1	1200	66.19 ± 0.01	3.90 ± 0.03	12.88 ± 0.04	1.33 ± 0.02
EAS3	1200	62.08 ± 0.01	5.24 ± 0.03	12.04 ± 0.04	5.73 ± 0.02
ENS1	1180	66.90 ± 0.01	4.28 ± 0.03	12.94 ± 0.03	1.04 ± 0.02
ENS3	1180	64.02 ± 0.01	5.33 ± 0.03	12.35 ± 0.03	3.97 ± 0.02
EQS1	1200	66.68 ± 0.01	3.57 ± 0.02	13.33 ± 0.03	0.72 ± 0.02
EQS3	1180	64.96 ± 0.01	4.82 ± 0.01	12.85 ± 0.03	2.82 ± 0.01

Table 8. Chemical composition and physical properties of the vitreous phase present in the porcelain stoneware bodies fired at T_{md}.

Phase	Unit	EG0	EAS1	EAS3	ENS1	ENS3	EQS1	EQS3	std.dev.
T_{md}	°C	1200	1200	1200	1180	1180	1200	1180	-
SiO_2	%wt	68.22	67.11	65.64	66.99	65.31	69.19	65.45	0.30
TiO_2	%wt	1.07	1.11	0.97	1.03	0.91	1.01	0.88	0.05
Al_2O_3	%wt	18.32	18.51	19.60	18.52	20.03	17.09	19.73	0.20
Fe_2O_3	%wt	1.07	1.23	1.24	1.13	1.13	1.08	1.09	0.05
MgO	%wt	1.07	1.16	1.07	1.08	1.00	1.05	0.99	0.05
CaO	%wt	1.19	1.19	1.00	1.11	0.94	1.07	0.88	0.05
Na_2O	%wt	5.16	5.45	4.98	5.23	4.67	5.55	5.54	0.10
K_2O	%wt	3.90	4.24	5.50	4.91	6.01	3.96	5.45	0.10
Viscosity, $\log_{10}(\eta)$	Pa·s	4.87	4.74	4.74	4.94	4.96	4.83	4.86	0.02
Surface tension	mN·m^{-1}	337.2	337.3	336.4	337.8	338.3	333.9	338.3	0.2