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The use of nepheline-syenite in a body mix for porcelain stoneware tiles

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Abstract

In the study, the possibility to use nepheline-syenite, as fluxing agent, in a body mix used for porcelain stoneware tile, was determined. Starting from the reference mix composition, different amounts, 5.0, 10.0 and 15.6 wt.%, of sodium feldspar were replaced with the same amounts of nepheline-syenite. Different sintering cycles were used to understand the role of the nepheline-syenite in the development of the final microstructure. The presence of nepheline-syenite strongly favours the sintering behaviour, by reducing the sintering time necessary to reach the water absorption values, requested by the International Standard. Furthermore, the microstructure results more homogeneous and the mechanical characteristics are increased. The better mechanical performances can also be attributed to the different mineralogical compositions, in particular with lower amount of glassy phase, higher flexural strength values are obtained.

Keywords: B. Microstructure; C. Mechanical properties; Nepheline-syenite; Porcelain stoneware tiles; Mineralogical phases

1. Introduction

Porcelain stoneware tile is a high sintered product, successfully used in rather severe building applications, both outdoors and indoors, where high service performances are required. The relevant physical–mechanical characteristics, such as flexural strength, surface hardness and wear resistance [1,2] make it also possible to polish the working surface. This widespread industrial procedure, that enhances their appearance of surface, causes a general degradation in terms of physical–mechanical surface properties. This undesired effect can be attributed to a lack of homogeneity along the cross section of tile [3] and the surface flaws system, directly induced to polishing [4]. While the latter depend by the industrial procedures, the former are directly linked to the microstructure of the materials. This product is sintered by using rather fast firing cycles, that originates a surface compact layer surrounding a more porous bulk body. The removal, by machining, of the surface layer reveals the bulk porosity, that does not favour either the stains resistance or the cleanability. Staining substances and dirt can, in fact, penetrate into the uncovered porosity and induced damages and their removal can be often very difficult. One of the most annoying consequences for the polished working surfaces, concerns the aesthetic degradation due to the presence of halos and stains. So the possibility to reduce the bulk porosity of porcelain stoneware tile with the aim to have polished surfaces more compact, with few pores with controlled size, is desirable.

The densification of this class of products proceeds throughout a viscous phase sintering, with the developing of a liquid phase [5] that flows, by capillary pressure, in the interconnected voids among the particles, causing the development of a ceramic bonding, constituted by a glassy matrix embedding new-crystalline phases and part of the residual crystals. This bonding yields mechanical resistance to the product [6]. The viscosity of the liquid phase, influenced by

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the kind of the fluxing agent used and the sintering cycle, is able to drastic affect the microstructure of fired products, in particular to change the amount, morphology and size of the bulk porosity.

Feldspars, minerals with high alkali content, are generally used as fluxing agent in the production of tile [7,8]. Nepheline, even if it enters in the formulation of different ceramic products, such as sanitary ware, electrical porcelain and china ware bodies, due to reducing the firing temperature and increasing the alkali level in the glass phase [9] has not been used for the production of ceramic tiles, and not detailed studies of its effects on the microstructure of the product, tile, exist. Nepheline is a major component of several igneous rocks called nepheline-syenite, nepheline-monzonite and nephelinite. The basic difference among these rock types is the amount and type of feldspars present. In nepheline-syenite, feldspars are the most important phase. In the nepheline-monzonite rocks both K-feldspars and plagioclase are present in nearly equal proportions. In nephelinites there is little feldspar present and the rock is mostly nepheline. Even if the ideal formula of nepheline is $NaAlSiO_4$, in the natural samples, potassium is invariably present, so that the chemical analysis of nepheline is more like $Na_3K(AlSiO_4)_4$. The cation distribution is different for sodium and potassium within the cavities of the nepheline structure. Nepheline is a member of the feldspathoid group of silicates, minerals whose chemistry is close to that of the alkali feldspars, but they are poorer in silica [10].

About the use of nepheline and nepheline-syenite for the production of high temperature ceramic products, such as glasses, glass-ceramics or ceramics, it is important to make some distinctions. Nepheline should not be confused with nepheline-syenite, which is actually a mixture of about 55 wt.% albite, 25 wt.% potassium-feldspar and only about 20 wt.% nepheline. The chemical and physical properties are consequently very different. The melting point of pure nepheline is very high, 1520 °C [11], compared to that of the other feldspars: 1118 °C for sodium-feldspar, 1150 °C for potassium-feldspar and, 1223 °C for nepheline-syenite [12].

Compared to pure feldspars, the advantages coming from the use of nepheline-syenite are: (i) the content of potassium and sodium is higher, $K_2O + Na_2O$ is about 9–12% in feldspars, whereas it is larger than 14%, in nepheline-syenite, and (ii) the melting temperature is generally lower than that of potassium-feldspar, which always contains other phases, such as quartz, which shift the melting point to higher temperatures.

In the glass production, the use of nepheline-syenite provides the necessary additives of alumina and alkali for the glass formulation, and it is low in silica and does not contain free quartz. Furthermore, due to the lower melting point of nepheline-syenite, in comparison with potassium-feldspar, the glass batches obtained have lower viscosity and easier workability. The content of Al_2O_3 is high and the content of SiO_2 is lower in nepheline-syenite with respect to feldspars (considering that in feldspar Al_2O_3/SiO_2 is about 0.2, whereas in nepheline Al_2O_3/SiO_2 is 0.5). Alumina gives increased resistance to scratch and breaking, improving also the thermal endurance and the chemical durability [13].

In this paper, the use of nepheline-syenite, as fluxing agent in a body mix for porcelain stoneware tiles, was assessed. Its influence on the microstructure of the sintered samples, in terms of porosity and mineralogical changes, and on the mechanical properties was assessed.

2. Materials and experimental procedures

A formulation used for the industrial production of porcelain stoneware tiles was selected as a reference body mix, containing 10.0 wt.% of clay 1, 38.6 wt.% of clay 2, 15.6 wt.% of potassium feldspathic sand and 35.5 wt.% of sodium feldspathic sand. Starting from the reference body mix, different amounts, 5, 10 and 15.6 wt.%, of potassium feldspathic sand were replaced with the same percentages of nepheline-syenite. The new formulations were denoted C-1, C-2 and C-3, respectively. The average chemical compositions of the raw materials used are reported in Table 1.

The samples of both the reference body mix and the modified mix compositions were prepared by dispersing the raw materials in an aqueous slip, 70 wt.% solid with 1 wt.% of dispersant, and finally milled for 8 and 12 h in a ceramic jar mill, until a residue of about 0.2% on a 45 μm screen was obtained. The particle size distribution of the slips was determined by laser light diffraction (Malvern Mastersiser 2000).

After drying, at 110 °C, the samples were crushed and then sieved to pass through a 125 μm screen, in order to obtain suitable powders for pressing. The test specimens, in form of discs for the firing tests and bars for the mechanical tests, were prepared pressing the sieved powders added with 6 wt.% of water, at a pressure of 52 MPa.

Several firing tests were carried out with a laboratory electrical furnace, at the temperature of 1260 °C for different soaking times, to determine the sintering conditions, allowing the samples to reach the water absorption <0.5 wt.%, value for which a tile can be considered to belong to the porcelain stoneware tiles class [14].

Table 1
Average chemical composition, in wt.%, of the raw materials

Oxide	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline-syenite
SiO_2	78.38	66.75	79.85	70.48	60.14
Al_2O_3	15.41	21.93	10.60	18.27	23.50
K_2O	0.31	1.33	4.38	0.57	5.00
Na_2O	0.16	0.22	3.64	9.07	10.40
CaO	0.06	0.33	0.41	0.74	0.40
MgO	0.05	0.52	0.14	0.10	0.03
TiO_2	0.23	1.24	0.03	0.24	0.00
Fe_2O_3	0.12	0.99	0.45	0.13	0.09
L.O.I	5.41	6.62	0.50	0.38	0.55

To characterise the fired specimens were measured: (i) the water absorption [15], and (ii) the total porosity [16].

The mineralogical compositions of the fired samples were determined by the Rietveld method that allows both the crystalline and the amorphous fractions to be determined in a polyphase mixture. In fact, the scattering contribution of any amorphous component eventually existing in the sample is a part of the background and allows its quantification using an internal standard, suitably chosen, which is added in a known amount to the investigated mixture and treated as a mixture component itself. At the end of the Rietveld process, the refined phase fractions are converted into weight fractions and rescaled to the values of the original mixture by the ratio between the refined ($X_{s,c}$) and the known (X_s) amount of added standard. Whenever, an amorphous phase exists in the system, the values of the weight fractions are overestimated to satisfy the normalization condition. The percentage of the amorphous phase X_a in the original mixture can be calculated directly from the weight of the internal standard according to the equation [17]

$$X_a = \frac{100}{(100 - Xs)}\left(1 - \frac{X_s}{X_{s,c}}\right)$$

For all the samples, the powder diluted with 10 wt.% corundum NIST 676 as internal standard, was side loaded to minimize preferred orientation. The data collection was performed using a Philips PW 1710 instrument with a conventional Bragg-Brentano (BB) parafocusing geometry equipped with a copper tube and a secondary beam pyrolitic graphite crystal monochromator. Data were collected in the angular range 3–100° 2ϑ with steps of 0.02° and 10 s/step, a divergence slit of 1° and a receiving slit of 0.2 mm. The Rietveld refinements were performed using GSAS [18]. All the agreement indices ($Rwp < 14\%$ and $Rp < 12\%$) and the additional statistical indicators supplied by GSAS ($\chi^2 < 5$ and $R(F^2) < 15\%$) are indicative of the very good quality of the refinements and testify the accuracy of the estimated weights.

The microstructure of the fired samples was studied with a scanning electron microscope, SEM, (Jeol, T330, Japan) equipped with an energy dispersion X-ray attachment, EDS, (Noran, USA). Fresh fracture surfaces were analyzed, in some case also polished and chemically etched surface were studied, to allowing the identification of the presence and morphology of the mullite crystals.

The surface hardness of the as fired specimens was measured by a hardness tester (Zwick, 3212, Germany), equipped with a Vickers indenter, at the indentation load of 9.81 N, considering at least 10 valid impressions.

The flexural strength was determined on specimens in form of bars, 70 mm × 10 mm × 6 mm. At least twenty specimens were tested using a universal testing machine (MTS, 10/M, USA), in 3-point bending fixture, 60 mm support span and with a crosshead speed of 5 mm/min. Weibull's statistical analysis was carried out on each set of data. Weibull's modulus m, was determined by the least squares method, adopting as probability estimator of failure $P_n = (i - 0.5)/N$, where N is the number of strength measurements and i the ranking number, with $i = 1$ for the weakest specimen and $i = N$ for the strongest [19].

The modulus of elasticity, Young's modulus, E, was evaluated, using an extensometer fixed to the bending apparatus and applied in correspondence to the middle of the surface of the specimens, subjected to tensile stress.

3. Results

In Fig. 1a is reported the water absorption of the samples fired at 1260 °C for different soaking times. The STD sample reaches a water absorption <0.5% after 100 min of soaking time, while for the modified composition, the sintering speed is enhanced, only 25–30 min of soaking time are enough to obtain well sintered samples. Increasing amounts of nepheline, from C-1 to C-3, favour the sintering.

In Fig. 1b, the linear shrinkage values of the samples fired at 1260 °C for the different soaking times are shown. The maximum value of shrinkage, reached by the samples containing nepheline, C-1, C-2 and C-3, is higher than the maximum value of STD, and furthermore, it is reached in

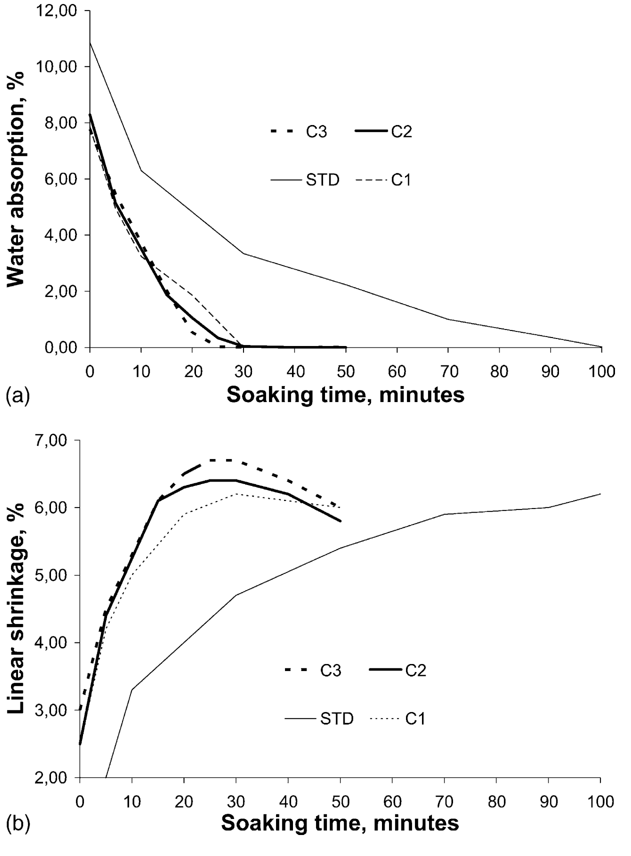

Fig. 1. Water absorption (a) and linear shrinkage (b) vs. soaking time at 1260 °C.

Table 2
Total porosity, TP, and closed porosity, CP, measured at 1260 °C for different soaking times

Soaking time (min)	STD		C-1		C-2		C-3	
	TP (%)	CP (%)	TP (%)	CP (%)	TP (%)	CP (%)	TP (%)	CP (%)
0	22.49	0.34	17.05	0.16	17.60	0.00	16.60	0.00
5	–	–	11.55	0.32	12.05	0.38	12.58	0.26
10	14.25	0.33	7.97	0.38	5.68	1.18	5.13	0.28
20	–	–	4.96	0.47	3.82	1.28	3.33	2.03
25	–	–			2.94	2.11	2.52[a]	2.44[a]
30	8.73	0.95	2.71[a]	2.55[a]	2.52[a]	2.41[a]	2.35	2.31
40	–	–	2.56	2.56	3.04	3.04	2.89	2.88
50	6.10	0.81	2.82	2.79	4.42	4.42	4.20	4.19
70	4.75	2.34	–	–	–	–	–	–
90	3.84	2.97	–	–	–	–	–	–
100	3.55[a]	3.55[a]	–	–	–	–	–	–

[a] Samples used for the mechanical tests.

rather shorter times. The range of dimensional stability is very high for STD and acceptable for C-1, sample containing the 5% of nepheline-syenite. When higher amounts of nepheline-syenite are added, the range of stability drastically reduces, and a negative shrinkage is observed (expansion) for the higher soaking times.

Table 2 reports the total and closed porosity of the samples fired at 1260 °C at the different firing conditions. With the increasing of the soaking time, the total porosity of STD decreases, reaching the same value of the closed porosity, when the open porosity is almost zero, for 100 min of soaking time. A similar trend is observed also for C-1. For C-2 and C-3 the total porosity firstly decreases till to reach a minimum value, then it increases again, while the closed porosity always increases.

Only the samples, for which the results of water absorption satisfied the request of the standard [14] to classify a product as porcelain stoneware tile, were subsequently analysed from a mechanical point of view. Table 3 reports their formulations and the different processing conditions used.

The fracture surface of STD, Fig. 2, is characterised by the presence of round pores, essentially closed porosity, whose sizes are significantly larger than the ones present in the nepheline-syenite modified samples (Fig. 3). Spherical pores indicate a mature microstructure, where a sort of equilibrium was reached, from the equilibrium between the vapour pressure of gas and the viscosity of the liquid phase, spherical pore results. The microstructures of C-1, C-2 and C 3 (Fig. 3a and b) do not present substantial differences among them, while C2–12 (Fig. 3c) shows a compact microstructure, with very few and narrows pores. The increase of the milling time, from 8 to 12 h, in C2–12, allowed to obtain a finer powder, Table 4. As a consequence, more reactive particles are produced, that allowed to produce a very compact and homogeneous material.

Table 5 shows the physical–mechanical characteristics of the samples, fired at 1260 °C adopting different firing conditions. For all the compositions modified with nepheline-syenite, a higher value of the average flexural strength, σ, is observed, even if shorter soaking times are used, comparing with STD. The different amounts of replaced nepheline-syenite do not significantly affect these values, only with

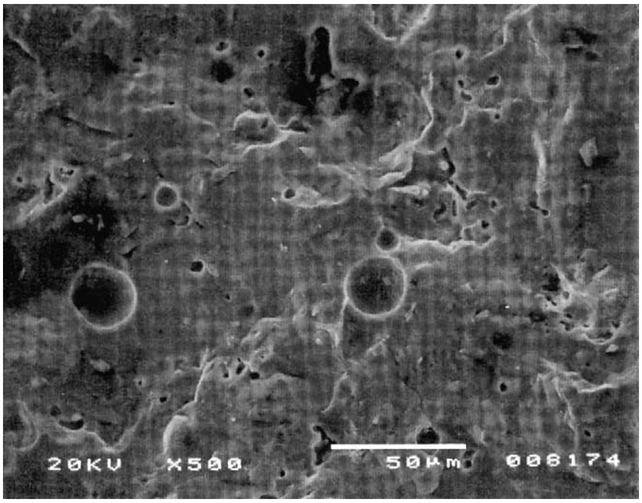

Fig. 2. SEM micrograph of the fracture surface of the sample STD, fired at 1260 °C, soaking time 100 min.

Table 3
Formulation and processing condition of the samples fired at 1260 °C, used for the mechanical tests

Sample	Nepheline (wt.%)	Milling time (h)	Water absorption (wt.%)	Soaking time (min)
STD	–	8	0.02	100
C-1	5.0	8	0.05	30
C-2	10.0	8	0.04	30
C2–12	10.0	12	0.03	20
C-3	15.6	8	0.03	25

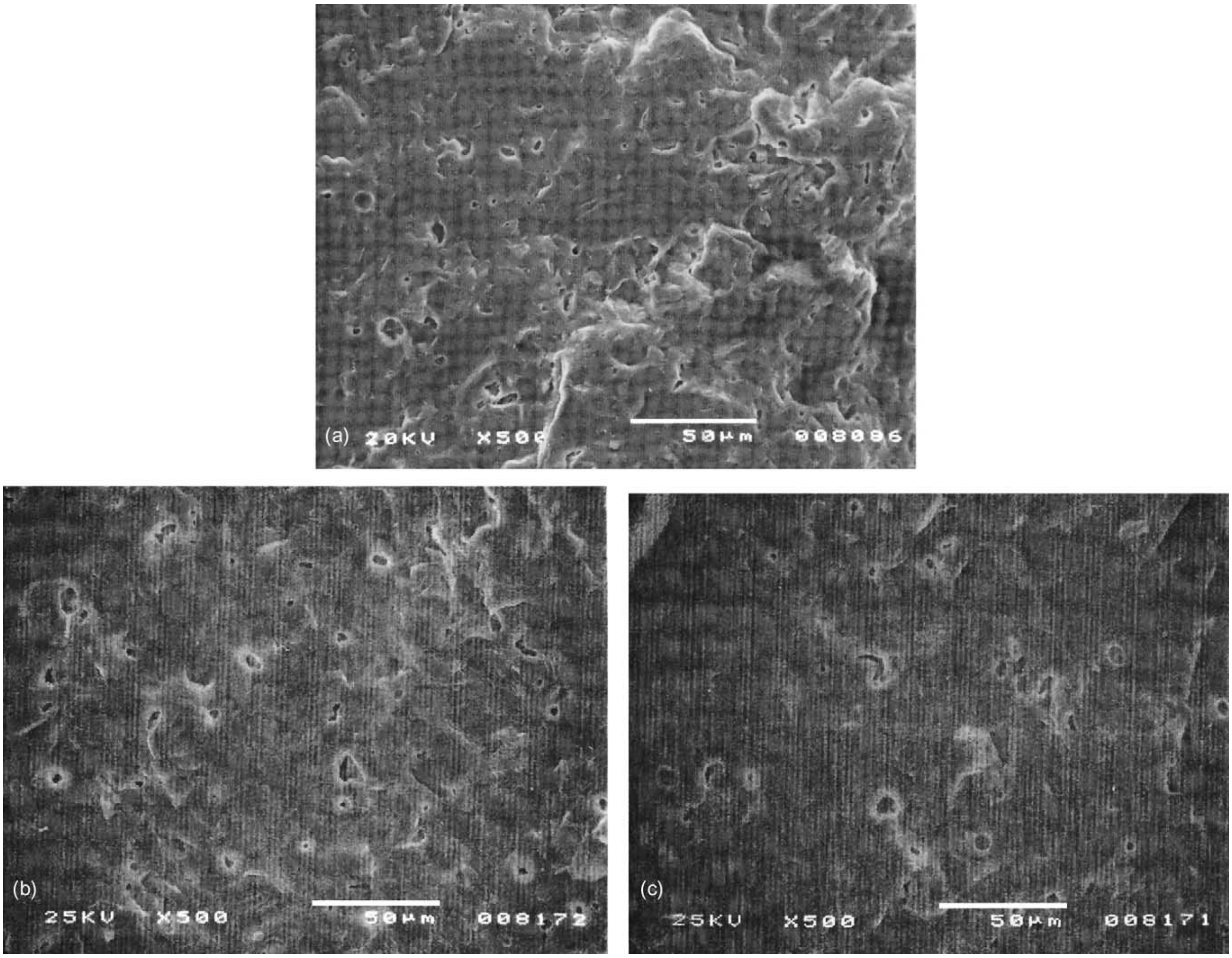

Fig. 3. SEM micrograph of the fracture surface of the sample fired at 1260 °C (a) C-1, soaking time 30 min, (b) C-3, soaking time 25 min and (c) C-2–12, soaking time 20 min.

Table 4
Particle size distribution (μm) of the tested slips

Sample	Milling time (h)	d_{10}	d_{50}	d_{90}
STD	8	1.9	11.9	48.1
C-1	8	2.2	12.5	44.8
C-2	8	1.8	11.0	44.5
C2–12	8	1.9	11.5	46.4
C-3	12	1.7	9.6	37.0

Table 5
Physical–mechanical characteristics of the fired samples

Sample	Total porosity (%)	$HV_{9.81}$ (GPa)	σ (MPa)	E (GPa)	m
STD	3.55	5.95	73.2 ± 4.1	61.4 ± 5.3	21.3
C-1	2.71	7.10	85.0 ± 3.2	66.6 ± 4.3	30.9
C-2	2.52	6.41	87.3 ± 4.9	65.3 ± 4.7	21.6
C2–12	2.53	6.85	94.6 ± 2.9	66.9 ± 2.9	40.2
C-3	2.52	6.70	86.5 ± 3.8	66.2 ± 4.2	27.4

C2–12, prepared using a longer milling time and fired for a lower soaking time, 20 min, a further and meaningful increase of σ is observed. Also the Weibull's modulus is positively influenced by the presence of the nepheline-syenite.

The modified formulations, C-1, C-2 and C-3, show also an increase of the Young's modulus and a slightly increases of hardness, even if these characteristics are not affected by the percentage of the substitution of nepheline-syenite.

In Table 6, the refined weights of the crystalline phases and relative estimated amorphous fraction of each of the samples used for the mechanical test, are reported. For comparison, also the results of the STD and C-3, both fired with a soaking time of 30 min are included. The presence of nepheline-syenite results in fired bodies with a larger degree of vitrification. Even 5 wt.% of nepheline-syenite produces nearly 10 wt.% more glass than the corresponding standard mixture, fired at the same soaking time, 30 min. The glass fraction detected in the fired bodies at 30 min of soaking time (Fig. 4), linearly increases with the amount of nephe-

Table 6
Quantitative phase composition of the fired samples

Sample	Soaking time at 1260 °C (min)	Mullite (wt.%)	Quartz (wt.%)	Albite (wt.%)	K-feldspar (wt.%)	Glass (wt.%)
STD	30	8.8 ± 0.5	25.5 ± 0.2	11.1 ± 0.3	1.0 ± 0.3	53.6 ± 1.5
STD[a]	100	9.0 ± 0.5	19.2 ± 0.2	0.0 ± 0.0	0.8 ± 0.4	71.0 ± 1.0
C-1[a]	30	9.3 ± 0.5	24.1 ± 0.2	3.7 ± 0.2	0.0 ± 0.0	62.9 ± 1.0
C-2[a]	30	7.5 ± 0.5	20.0 ± 0.2	7.2 ± 0.3	0.0 ± 0.0	65.3 ± 1.0
C2–12[a]	20	8.6 ± 0.5	23.6 ± 0.2	11.6 ± 0.3	0.0 ± 0.0	56.2 ± 1.0
C-3[a]	25	7.4 ± 0.5	18.8 ± 0.2	8.4 ± 0.3	0.0 ± 0.0	65.4 ± 1.0
C-3	30	6.2 ± 0.3	14.7 ± 0.2	7.7 ± 0.3	0.0 ± 0.0	71.3 ± 0.7

[a] Samples used for the mechanical tests.

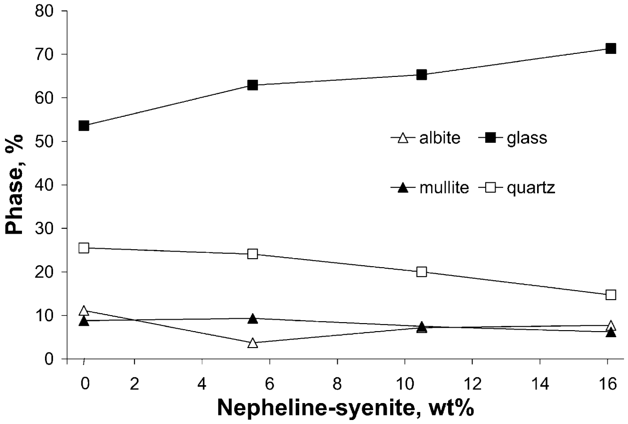

Fig. 4. Plot of the Rietveld refined weight fraction of the crystalline and amorphous phases vs. the weight fraction of nepheline-syenite, substituted in the samples, fired at 1260 °C for30 min of soaking time.

line-syenite. According to this result, the other crystalline phases, such as quartz and mullite, which are unstable in the alkali oversaturated glass matrix, decompose more easily. The fraction of albite, present in the fired samples, linearly increases with the addition of nepheline-syenite. That points as albite, in such an alkali oversaturated glass, tends to melt with a more sluggish reaction kinetic. The fraction of albite in the STD, at the same soaking time, is about 11 wt.%, the highest value found. For this composition, the melting reaction of the body mixture is not yet fully accomplished.

Only when STD is fired for a much longer soaking time, 100 min, it is able to reach a high level of sintering, but that causes the developing of a larger glass fraction, 71 wt.%. By the comparison of sample C-2 and C2–12, it is evident as increasing milling time, 12 min with respect to 8 min, and decreasing the soaking time down to 20 min, yields a much lower vitrification degree, only 56.2% of glassy phase is detected, while the amount of mullite is not very different from the value detected in STD, both fired for 30 and 100 min.

4. Discussion

The results obtained clearly point out as the replacement of the potassium feldspathic sand with nepheline-syenite strongly favours the sintering behaviour of the tested material. Even only a replacement of 5 wt.% of nepheline-syenite, C-1, causes a drastic decrease of the soaking time necessary to reach a water absorption value <0.5%. The direct correlation between the amount of nepheline-syenite present in the samples, C-1, C-2 and C-3, and the decrease of the soaking time, necessary to obtain the same water absorption of the STD (Fig. 1a), is explained by the strong action, as fluxing agent, of nepheline-syenite.

However, higher amount of nepheline-syenite is able to shorten the range of dimensional stability (Fig. 1b). The lower viscosity of the liquid phase, that decreases with the increase of nepheline-syenite, favours the shrinkage, but also the growing of rather large closed pores, that, trapped in the glassy matrix during cooling, cause the observed expansion, for the longer soaking times. All that is in agreement also with the results of porosity, Table 2. After reached the minimum value of total porosity, corresponding at the optimised sintering condition, the samples containing nepheline-syenite show, for longer soaking times, an increase of total porosity, coincident with the value of the closed porosity. This increase of closed porosity, particularly evident for C-2 and C-3, is connected with the phenomenon of negative shrinkage (expansion).

The mechanical behaviour of the tested samples can be explained taking into account the different microstructures, developed during firing. Flexural strength depends on the material composition and dimension and morphology of the flaws [20]. In the present case, bulk porosity, in term of flaws, and mineralogical phase composition have to be considered. The presence of nepheline-syenite, favouring the developing of a more compact microstructure, with lower porosity than STD, causes the observed increase of σ, for C-1, C-2 and C-3. The flexural strength reaches the maximum value for C2–12, characterised by the presence of pores with narrower sizes (Fig. 3d). A more homogeneous microstructures, is also able to justify the value of the Weibull's modulus obtained.

Furthermore, the lower the glassy amount, observed in the fired samples, the higher is the flexural strength. In a ceramic material an increase of the crystalline fraction can generally be considered responsible of the detected increased mechanical properties [21,22], if cracks due to mismatches among the glassy and crystalline phases, are not too severe. Furthermore, not only the amount, but also the morphology of the crystalline phases could have influenced

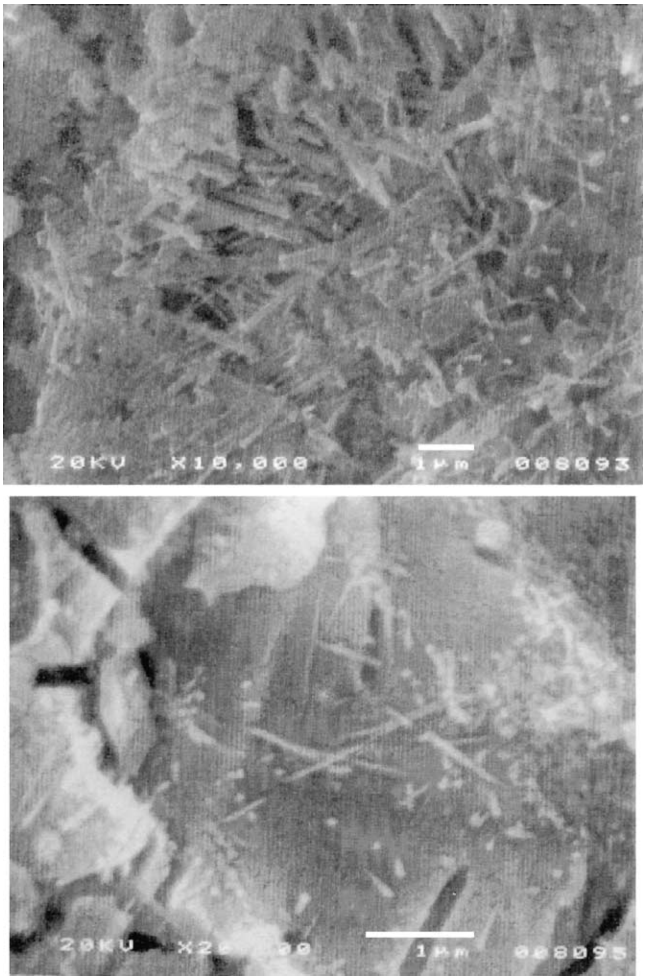

Fig. 5. SEM micrograph of polished and etched surface of the sample fired at 1260 °C (a) STD, soaking time 100 min, (b) C-2, soaking time 30 min.

the mechanical characteristics. The observation of polished and chemically etched surfaces points out as in the samples containing nepheline-syenite (Fig. 5a), the amount of secondary elongated mullite is larger than in the STD (Fig. 5b). That is essentially due to the lower viscosity of the liquid phase formed in presence of nepheline, that besides to favour the sintering, allows a better and easy growth of the elongated crystals [23].

As well known, the elastic modulus of a material besides on the material, depends on the shape and distribution of the porosity, which is considered as a second phase with $E = 0$, and in general, decreases as the total porosity increases [20]. The very low values of the total porosity of materials C-1, C-2 and C-3, lower than that of STD material, confirm the specified dependence.

5. Conclusions

In the present study, the possibility of replacing different amounts of potassium feldspathic sand with the same amounts of nepheline-syenite in a standard porcelain stoneware body mix, was investigated. From the results obtained, the following conclusions can be drawn:

- The presence of the nepheline-syenite in the standard body mix strongly favours the sintering behaviour, allowing to obtain sintered materials, with a water absorption <0.5%, firing them at 1260 °C for 25–30 min of soaking time, compared with the 100 min, necessary for the STD sample.
- The fired modified compositions show homogeneous microstructures, characterised by smaller pores, with a narrow pore size distribution, compared with the STD sample.
- The mechanical characteristics as Vickers hardness, flexural strength and Weibull's modulus, increase for the modified compositions. All that is correlated with a better microstructural homogeneity and lower amount of glassy phase.
- Further increases in the mechanical characteristics can be reached, by increasing the milling time of the starting powders, as in sample C2–12.
- The use of a 5% of nepheline-syenite, sample C-1, allows to reach the best results. Higher percentages reduce, in an unacceptable way, the range of dimensional stability.

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