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Effect of nepheline syenite on the colorant behavior of porcelain stoneware body

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The effects of nepheline syenite on the colorant behavior of porcelain stoneware tiles were assessed with special reference to the body composition. Potassium feldspar was replaced by nepheline syenite in a typical porcelain stoneware body by up to 15.6 wt.%. Technological parameters such as shrinkage, water absorption and porosity were measured. Phase composition and microstructural characteristics were determined to understand the role of nepheline syenite in the whiteness of a ceramic body. The results show that nepheline syenite had a significant effect on the sintering rate and influences remarkably the sintering behavior, increasing the shrinkage and decreasing total porosity. On the other hand there is a decrease in the amounts of mullite and quartz with addition of nepheline syenite. The bodies richer in nepheline syenite show larger amounts of albite and glassy phase. These bodies also present a higher whiteness with the same sintering conditions. The colorant characteristics appear to be directly related to the free albite crystals content. In conclusion nepheline syenite can be used in small amounts, 5 wt.%, to obtain an effective color development.

Key words: Porcelain stoneware body, Nepheline syenite, Whiteness, Crystalline and glassy phase.

Introduction

Porcelain stoneware tiles can be considered as a material in which the synergy between production technology and physical-chemical characteristics lead to excellent levels of service life [1]. Indeed the properties of porcelain stoneware tiles put them at top of their class of commercially available ceramic products [2]. Porcelain stoneware tiles are a dense material that is characterized by excellent properties such as lower water absorption less than 0.5%, high bending strength, abrasion and stain resistance, etc. These characteristics allow its use in severe applications, both indoors and outdoors, in which a high level of reliability is required [2].

Porcelain tiles are primarily composed of clay, feldspar and quartz [3]. During the heat treatment a mixture of glass and crystalline phases are formed. The composition of this type of ceramics can be presented graphically as a portion of the $(Na_2O + K_2O)$-Al_2O_3-SiO_2 phase diagram [2]. Most reactions occur during a short industrial firing cycle, therefore they do not reach thermodynamic equilibrium. Hence the finished product contains quartz and feldspar crystals that have not been completely transformed [4]. On the other hand, this type of composition allows thermal treatment at moderate temperature, around 1220 °C, to produce an abundant glassy phase, quartz without dissolution and the crystallization of small proportions of mullite [5].

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Thus the porcelain stoneware tile compositions generally are formulated based on ratios approaching 1 : 1 of plastic materials (kaolinite-illitic clay and kaolin) and non plastic materials (mainly sodium and potassium feldspars and quartz). Non plastics raw materials used in the compositions of porcelain tiles are higher quality, containing lower impurities, in order to achieve minimum final porosity, a high degree of whiteness and good color development [6].

Human color memory is quite poor and verbal color communication is not much more precise. Add to these problems, the relatively high frequency of color vision deficiency and the case for a numerical color specification is clear [7]. For the purpose of quantifying a color, the Commission International de l'Eclairage (CIE) has defined a Cartesian space of colorimetric coordination as shown in Fig. 1, where the reflected energy can be decomposed into three principal components x, y and z. Therefore, a color can be unequivocally defined by coordinates in the color space by describing whiteness, L^*, as well as the values a^* and b^*, the amount of red (positive) and green (negative) and amount of yellow (positive) and blue (negative), respectively. When a^* and b^* are near zero, the resulting color is gray [8]. The difference between two colors (ΔE) is defined as the geometrical distance between two points in the so-defined space [8]:

$$\Delta E = [(a_1^* - a_2^*)^2 + (b_1^* - b_2^*)^2 + (L_1^* - L_2^*)^2]^{1/2} \quad (1)$$

The whiteness of a porcelain stoneware body depends on the composition of the starting raw materials [3]. Investigators have shown that reducing the quantity of Fe_2O_3 and TiO_2 in a standard porcelain tile composition

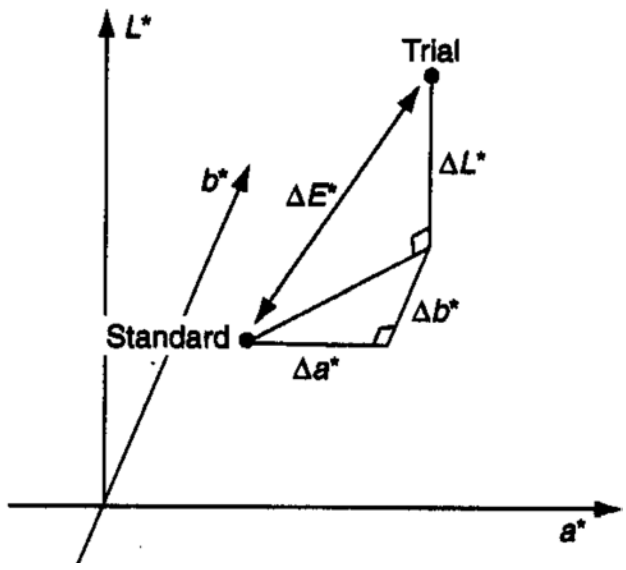


Fig. 1. Cartesian space of colorimetric coordination [7].

raises the degree of whiteness in the fired product, according to increasing L^* and reducing b^* values respectively. It has been shown that the porcelain tile working temperature of 1180-1230 °C practically coincides with a minimum whiteness as a result of the color effect of FeO with its introduction into the glassy phase. The incorporation of iron in the glassy phase is the main cause of loss of whiteness in porcelain stoneware bodies [6].

At the same the content of chromosphere impurities in the raw materials affect the color and the final whiteness of the product that depend on the nature and proportion of phases that develop during firing cycle. The presence of quartz and mullite crystals in the glassy phase is the main reason for whiteness of body [4]. Color development in the colored products depends on the content of chromosphere impurities in the raw materials. A decrease in the proportion of this type of impurities generally means a better color development. Some authors indicate that kaolin by favoring mullite formation and quartz given its scarce solubility in the melt, reduces the intensity of the color which arises L^* values. In contrast on increasing the feldspar content the colorant yield is raised strikingly and L^* decreases [6].

Nepheline syenite has been used in the formulation of different materials such as electrical porcelain, chinaware bodies and sanitaryware, due to its reducing the firing temperature and increasing the alkali level in the glassy phase [9]. Nepheline syenite is actually a mixture of about 55 wt.% albite, 25 wt.% potassium feldspar with only 20 wt.% nepheline. The advantages of nepheline syenite use in the production of ceramic bodies are: the level of alkali oxides which is higher than 14%, the melting temperature is generally lower than the melting point of feldspar which always contains other phases such as quartz that shifts the melting point to a higher temperature [10].

The purpose of the present study was to evaluate the effect of nepheline syenite on the colorant behavior of porcelain stoneware bodies. The differential changes in physical properties and mineralogical composition of porcelain stoneware using various amounts of nepheline syenite were investigated.

Experimental Procedure

An industrial composition used for the production of porcelain stoneware tiles was considered as a reference body mix consisting of a blend of illitic-kaolinitic clays, sodium and potassium feldspars and quartz. Starting from the reference body mix 5, 10 and 15.6 wt.% of potassium feldspar were replaced with the same percentages of nepheline syenite. The chemical and mineralogical analysis of reference and modified compositions are presented in Table 1. The compositions were wet milled by a laboratory ceramic jar mill containing 70 wt.% solid and 0.96 wt.% deflocculant, for 8 hours. The particle size distributions of slips were determined by laser light diffraction (Malvern Mastersiser 2000). Slips were dried at 110 °C and the samples were crushed and milled in a laboratory milling machine to obtain a particle size less than 125 μm. The

Table 1. Chemical and mineralogical analysis of porcelain stoneware compositions (wt. %)

chemical analysis					mineralogical analysis				
oxides	STD	F_1	F_2	F_3	minerals	STD	F_1	F_2	F_3
SiO_2	70.07	69.47	68.87	68.13	quartz	25.3	27.4	29.4	31.3
Al_2O_3	18.39	18.89	19.37	19.96	kaolinite	19.4	19.4	19.4	19.4
K_2O	1.78	1.71	1.63	1.54	illite	5.0	5.4	5.7	6.0
Na_2O	3.34	3.85	4.36	4.93	smectite	0.8	0.8	0.8	0.8
CaO	1.00	0.89	0.79	0.67	albite	36.7	33.6	30.9	28.2
MgO	0.30	0.29	0.29	0.28	orthoclase	4.9	5.8	6.7	7.5
ZrO_2	0.03	0.03	0.03	0.03	anorthite	2.9	3.6	4.2	4.8
TiO_2	0.52	0.52	0.52	0.52	nepheline	3.4	2.2	1.1	0.0
Fe_2O_3	0.66	0.61	0.57	0.52	impurity	1.6	1.8	1.9	2.1
SO_3	0.00	0.00	0.00	0.00					
L.O.I	3.89	3.74	3.59	3.41					

prepared powders were wetted (about 0.064 kg/kg dried powder) and sieved to 800 μm to avoid agglomerates.

A series of test pieces in the shape of disks were formed by pressing the wet powders at a pressure of 52 MPa. The test pieces were sintered with a laboratory electrical kiln (Ceramic Instrument Model 86 V) at 1260 °C for 30 minutes soaking time. To characterize the fired pieces the linear shrinkage, water absorption and open, total and closed porosities were measured by standard methods [11-13].

Furthermore, the phase compositions of porcelain stoneware bodies were quantitatively determined by an X-ray diffractmeter (Philips pw 1710 instrument). The chemical composition of the vitreous phase was calculated on the basis of bulk chemical analysis and phase composition.

The color measurements were conducted using reflectance spectrophotometry (Model Spectra Flash plus 600 CT, Data Color Lawrenceville, N.J.) equipped with a xenon lamp (Model 6050-6350k) and a suitable ultraviolet filter, illuminating D65 and a solid visual angle of 10^{o}.

To obtain a better understanding of the microstructural diffusion mechanisms, the cross section of pieces were carefully analyzed using a scanning electron microscope (SEM, Jeol, T330, Japan).

Results and Discussion

The particle size distributions of porcelain stoneware slips are presented in Fig. 2. It was observed that the characteristics of slips are very close together, confirming that the presence of nepheline syenite does not affect significantly the grindability of porcelain stoneware compositions.

Nepheline syenite has different effects on the firing behavior depending on its substantiating content. In general, linear shrinkage of a body increases with the amount of nepheline syenite which tends to make sintering faster in compared to a composition without nepheline syenite but using more than 5 wt.% of it has negligible role on the sintering rate of pieces as shown in Fig. 3. The water absorption of pieces containing nepheline syenite become

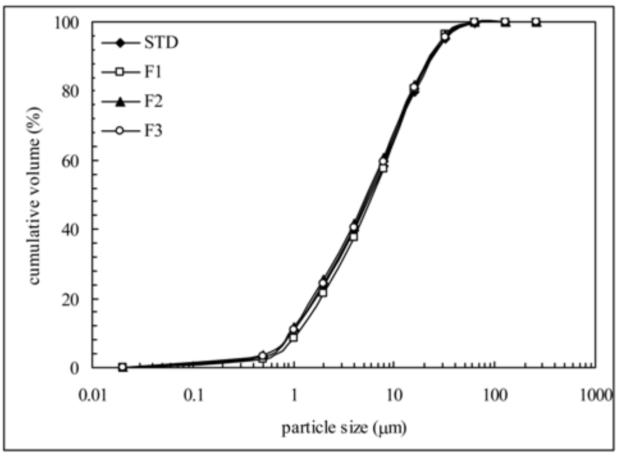


Fig. 2. The particle size distributions of reference and modified porcelain stoneware compositions.

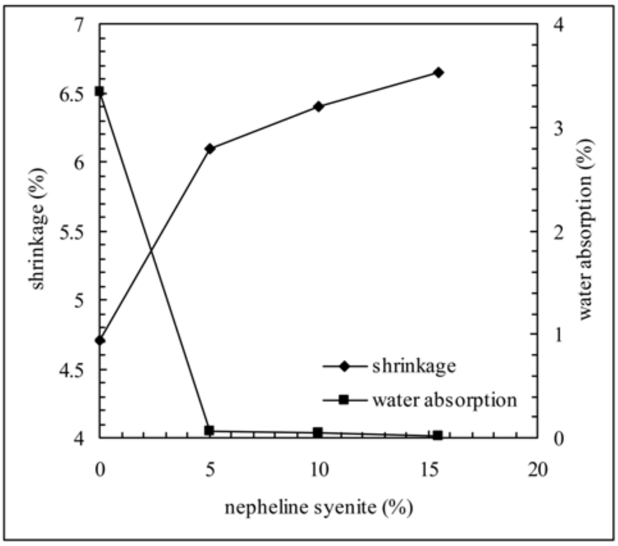


Fig. 3. The variations of linear shrinkage and water absorption of porcelain stoneware bodies with nepheline syenite content.

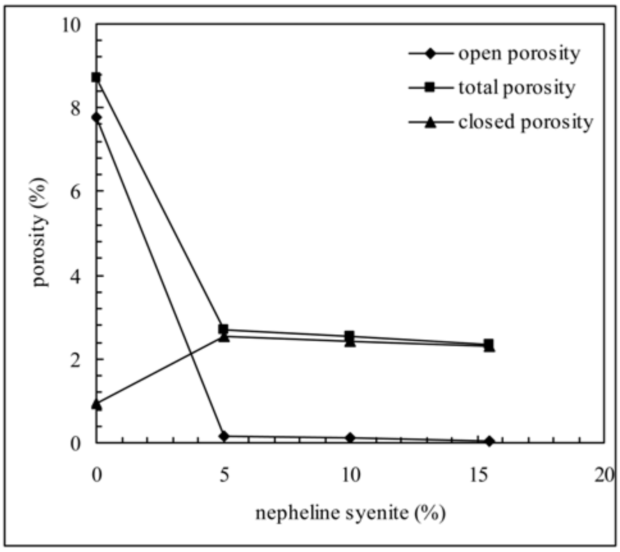


Fig. 4. The variations open, total and closed porosities of porcelain stoneware bodies with nepheline syenite content.

zero after 30 minutes while for the F_1 composition a longer soaking time is needed to obtain suitable water absorption.

The plots of Fig. 4 show the variation of open, total and closed porosities versus the percentage of nepheline syenite. The presence of 5 wt.% nepheline syenite substantially changes the values of open porosity which does not decrease much more when more than 5% nepheline is added. On the other hand nepheline syenite seems to hasten the removal of total porosity. This tendency is particularly conspicuous in bodies containing nepheline syenite. With an increase in the amount of nepheline, the closed porosity of porcelain stoneware bodies increase, reaching the same values as the total porosity, when the open porosity is almost zero. This trend is due to the melting temperature of nepheline syenite which is generally lower than that of potassium feldspar. The sintering rate is enhanced by nepheline syenite for modified compositions.

In summery nepheline syenite seem basically to accelerate the densification process, increasing the firing shrinkage and decreasing the open porosity by comparison with the standard composition, especially when the nepheline syenite addition is as high as 5 wt.%. At all events, this accelerated effect brings about the formation of a small amount of total porosity compared to the F_1 composition to reach to a satisfactory water absorption that is a requirement of the standard to classify a product as a porcelain stoneware tile [2].

The mineralogical analysis shows that porcelain stoneware tiles contain quartz, mullite, albite and an abundant glassy phase. The quantitative interpretation of X-ray patterns allows an understanding of the effect of the amount of nepheline syenite on the sintering process and physical-chemical properties. The relationship between the quantitative analysis of the phases present in the fired pieces and the amount of nepheline syenite in the porcelain stoneware composition can be explained as follows: the percentage of melted quartz ((initial quartz - remaining quartz/initial quartz) × 100) is inversely proportion to the addition of nepheline syenite as presented in Fig. 5. Also, the glassy phase fraction increases with the amount of nepheline syenite. The value of quartz decreases slowly by increasing nepheline syenite.

It is possible to calculate a mullite formation index, MFI, given by the ratio between the experimental determined quantity, M_{exp}, and the potential mullite content, M_{pot}. We assume that all the alumina in body can be converted into mullite during the firing, therefore we can calculate the MFI from the following equation:

$$MFI = \frac{M_{exp}}{M_{pot}} = 0.7183\frac{M_{exp}}{Al_2O_3} \quad (2)$$

The values thus obtained for the mullite formation index are as presented in Fig. 6. As can be observed, the value of the MFI varies with the addition of nepheline syenite and the mullite crystals which are unstable in the alkali over the saturated glass phase decompose more easily. The percentage of mullite in F_3 and F_4 compositions is less than the mullite content in the F_1 and F_2 compositions. As a matter of fact, nepheline syenite seems to modify the equilibrium between the co-existing glassy and crystalline phases in porcelain stoneware bodies. The relevant contribution of $Na_2O + K_2O$ promotes on one side a more effective melting of quartz and on the other side, probably a lower crystallization and a partial dissolution of the mullite, leading the liquid phase to be saturated in SiO_2, Al_2O_3, Na_2O and K_2O which fosters the stability of albite even at 1260 °C. According to Fig. 6 the fraction of albite decreases with the nepheline syenite content, reaching a minimum point and then rises to a constant value.

According to Orts et al. [14], sintering in the presence of a liquid phase gives a removal rate of the porosity that can be expressed by the following equation:

$$-\frac{d\varepsilon}{dt} = \frac{3\gamma}{2r\eta}\varepsilon \quad (3)$$

is not needed

where ε is total porosity of the ceramic body, t is soaking time, γ and η are surface tension and effective viscosity of the system and r is the pore radius. The removal rate of porosity, −dε/dt, is proportional to the surface tension/viscosity ratio and relevant porosity This ratio changes continuously with the chemical composition of the glassy phase. The chemical composition of the glassy phases calculated on the basis of bulk chemistry and mineralogical phases are presented in Table 2. The surface tension and viscosity at 1260 °C were estimated on the basis of their chemical compositions as presented in Table 3. Fig. 7 shows the variation of the surface tension/viscosity ratio and melting point of the glassy phases formed in porcelain

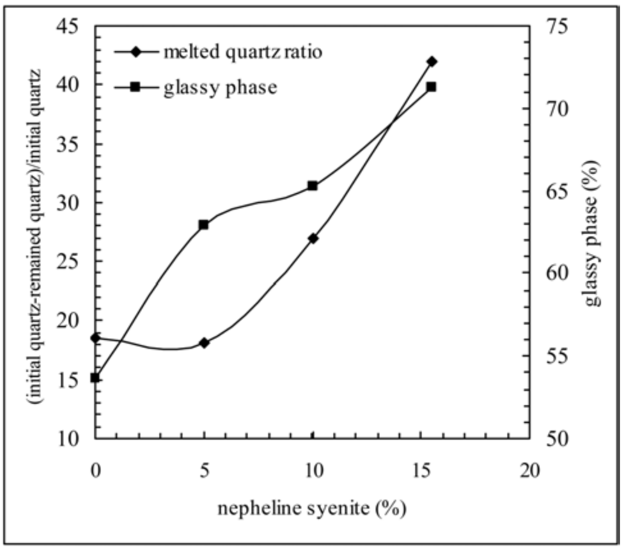


Fig. 5. The melted quartz percentage and amount of glassy phase versus nepheline syenite content.

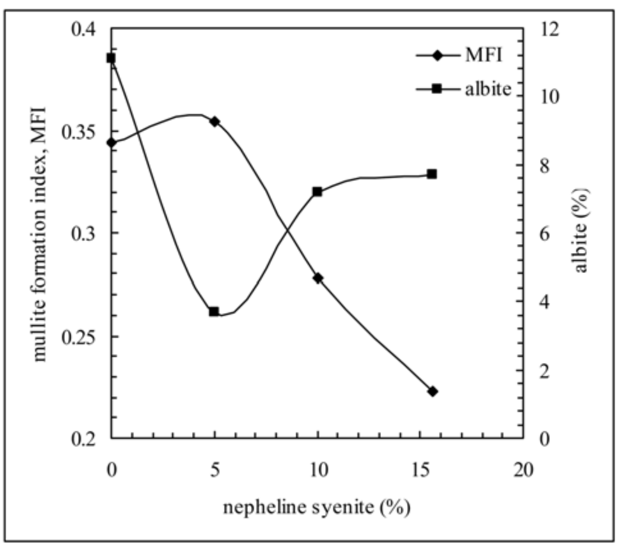


Fig. 6. The values of mullite formation index and amount of albite versus nepheline syenite content.

Table 2. The chemical analysis of glassy phase formed in porcelain stoneware bodies (wt. %)

oxides	STD	F_1	F_2	F_3
SiO_2	68.30	68.21	67.96	68.44
Al_2O_3	19.53	19.50	20.40	20.63
K_2O	3.14	2.82	2.59	2.24
Na_2O	4.03	5.66	5.62	5.88
CaO	1.94	1.45	1.25	0.97
MgO	0.58	0.48	0.46	0.41
TiO_2	1.01	0.86	0.83	0.76
Fe_2O_3	1.28	1.01	0.91	0.76

Table 3. Surface tension and viscosity of liquid phases formed at 1260 °C in porcelain stoneware bodies

composition	STD	F_1	F_2	F_3
surface tension (N/m)	0.367	0.363	0.364	0.364
viscosity (Pa.s)	23.2	18.7	22.6	23.5

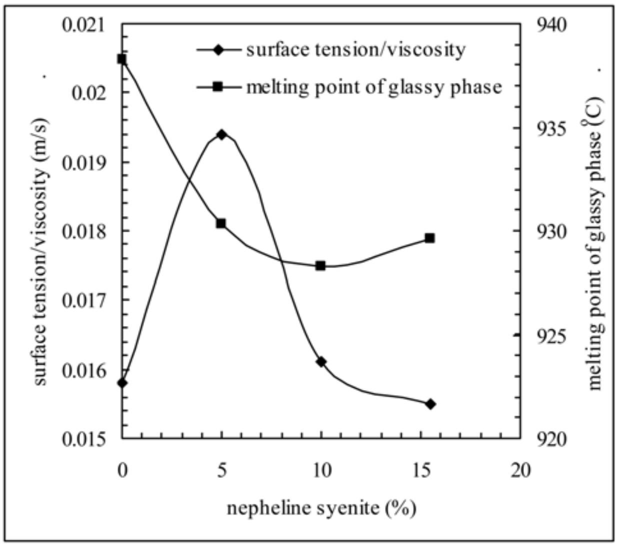


Fig. 7. The variations of surface tension/ viscosity ratio of liquid phases and melting point of glassy phases of porcelain stoneware bodies with nepheline syenite content.

stoneware bodies with the content of nepheline syenite. It is obvious that the value of the mentioned ratio decreases with a rise in nepheline syenite in the body composition and reaches a maximum value, when 5 wt.% the potassium feldspar was substituted by nepheline syenite. As expected, the presence more than 5 wt.% nepheline syenite accelerates the dissolution of quartz and mullite, appreciably increasing the viscosity of the liquid phase and the melting point of the glassy phase. On the other hand surface tension has just a modest effect on densification since its values are close to that of the reference body at 1260 °C (Table 3). It is interesting to note that the melting point of the glassy phase decreases in the presence of 5 wt.% nepheline syenite and reaches a constant value but, obviously, the variation of the melting point with the content of nepheline syenite in the composition is not considerable.

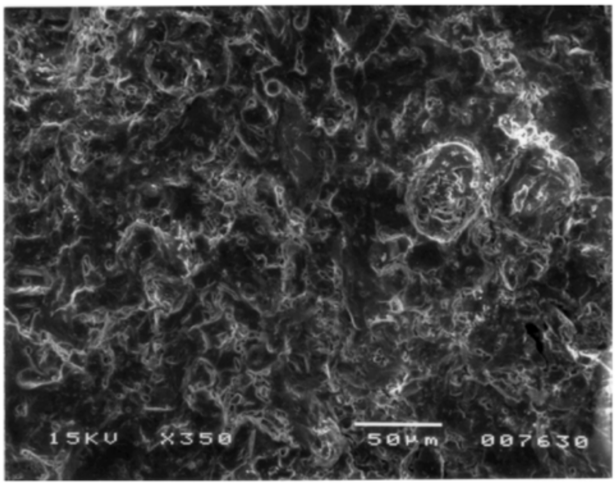
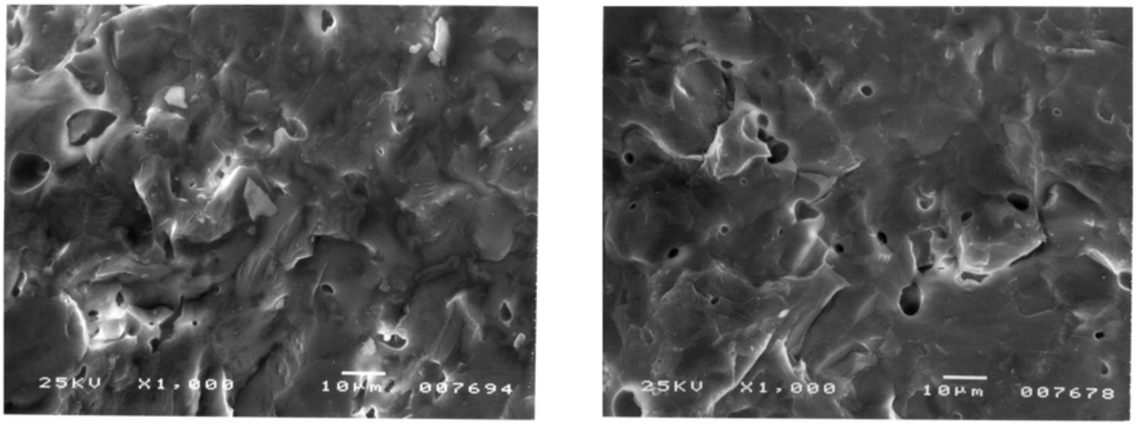


Fig. 8. SEM micrograph of the fracture surface of the reference porcelain stoneware body sintered at 1260 °C for 30 minutes soaking time.

The SEM observations of fracture surfaces of the test pieces obtained with the different contents of nepheline syenite provided a better understanding of the results obtained, allowing correlations between the surface tension/ viscosity ratio and microstructures. The microstructure of standard composition at a soaking time of 30 minutes (Fig. 8) is not particularly compact. The closed pores are present in a spherical shape. In this composition, areas of material are found where it is still possible to distinguish the individual grains of the starting mix for which fusion is not yet complete. The discontinuities are an indication of incomplete compaction due to the insufficient glassy phase development to obtain compact pieces. Addition of nepheline syenite leads to a more consistent development of glassy phase and increasing sintering rate as shown in Fig. 9. The material becomes more compact, in agreement with the lower porosity. The pores were elongated and interconnections tend to disappear. The remaining pores are closed which are spherical in shape for the most part. It is also interesting to note that the use more than 5 wt.% of nepheline syenite does not present substantial differences in the microstructures.

Moreover, nepheline syenite causes a darkening of the color. This variation consists mainly in a decrease of lightness, L^* as shown in Table 4, reaching a minimum value when 5% nepheline syenite was added to the body composition. According Sanchez et al. [3], although the difference in refractive index between mullite (~1.67) and quartz (~1.54) and the glassy phase (~1.62) are small, the presence of crystals of both compounds in glassy phase is the main opacification mechanism [3]. The bodies richer in nepheline syenite that is contains more than 5 wt.%, show a different color behavior as presented in Fig. 10. The total porosities of the bodies containing different amounts of nepheline syenite are approximately the same but the bodies richer in nepheline syenite have higher whiteness and lower amounts of mullite plus quartz. There was a



(a) (b)

Fig. 9. SEM micrographs of the fracture surfaces of modified porcelain stoneware bodies sintered at 1260 °C for 30 min soaking time (a) F_1 and (b) F_2.

Table 4. The colorant behavior of porcelain stoneware bodies with different contents of nepheline syenite

composition	ΔE[1]	quartz + mullite	albite	$Fe_2O_3 + TiO_2$
STD		34.3	11.1	2.29
F_1	8.4	33.4	3.7	1.87
F_2	5.4	27.5	7.2	1.74
F_3	4.7	20.9	7.7	1.52

[1] in comparing to reference composition

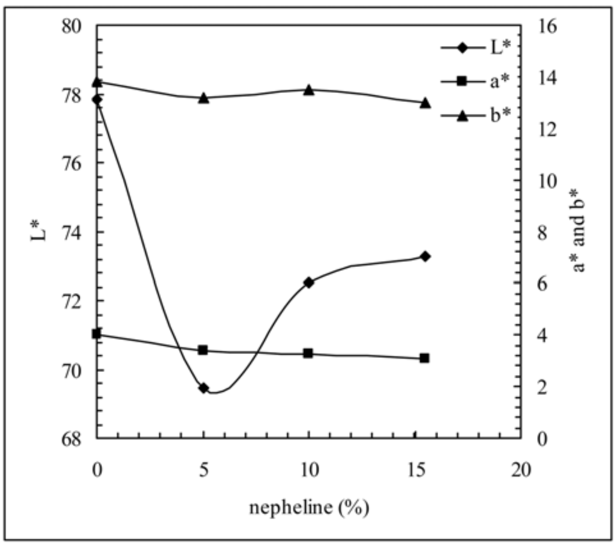


Fig. 10. The variation of colorant parameters of porcelain stoneware bodies with nepheline syenite content.

relation between the whiteness of sintered bodies and free albite content in bodies, which confirmed the opacifing effect of crystalline phase. The relation was dependent of nepheline syenite content used in the starting composition. A minimum opacification further heightens body whiteness i.e. L^* increases and $a^*$and b^* decrease because of a low content of chromosphere elements, $Fe_2O_3 + TiO_2$. Mullite has greater opacifing effect than quartz because the mullite particle size is much smaller [3, 6]. According to a study by Zhou and Weissman [15] the incorporation of iron into the glassy phase is the main cause of the loss of whiteness in a porcelain body. Finally the presence of pores in the glassy matrix also contributes to opacification thus, enhancing the whitening effect. Therefore, the whiteness of porcelain stoneware body decreases when 5 wt.% nepheline syenite was added to the composition.

It can be observed that nepheline syenite reduces the intensity of the color arising, as a result of the opacifing effect. The fraction of albite, present in sintered body, increases with the addition of nepheline syenite. The fraction of albite in the F_2 and F_3 bodies, at the same soaking time, is about 7.2 and 7.7 wt.% respectively. These are higher than the value of albite in F_1. For these compositions the melting reaction of the body mixture was not yet fully accomplished. According to this result, the amount of crystalline phase increases in the porcelain stoneware bodies. Thus in general, increasing the proportion of crystalline phase encourages whiteness since it improves the opacifying effect.

Conclusions

This study demonstrates that by using nepheline syenite, containing proper amounts of $Na_2O + K_2O$ as fluxes agents, it is possible to obtain porcelain stoneware tiles with a low porosity. 5 wt.% of nepheline syenite is sufficient to accelerate the densification process with some other positive effects such as lower open and closed porosities combined with increased shrinkage.

Nepheline syenite seems to modify the equilibrium between the co-existing glassy and crystalline phases. Minor amounts of quartz and mullite as well as an abundant vitreous phase were found with an increase in the nepheline syenite content in porcelain stoneware compositions. Moreover, the presence of nepheline syenite improves sintering kinetics.

The minimum whiteness of a porcelain stoneware body was obtained when 5 wt.% nepheline syenite was added to the body composition. The yellow color component was inversely proportional to the nepheline syenite content. The combined effect of crystalline phases, mullite + quartz + albite, and reducing the quantity of Fe_2O_3 + TiO_2 in a composition, containing more than 10 wt.% nepheline syenite, caused a positive variation in whiteness. A decrease in the chromosphere impurities content and an increase in the amount of glassy phase in body containing 5 wt.% nepheline syenite means better color development.

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