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The Effect of Nepheline Syenite Addition on Pyroplastic Deformation of Sanitarywares

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Abstract:

Nepheline syenite is used instead of feldspars as fluxing in ceramics. In this study, three ceramic bodies were prepared. Nepheline syenite was substituted by Na feldspar in the ratio of maximum 30 wt.%. The pyroplastic deformation was evaluated together with technological properties, including linear shrinkage, water absorption and strength. Phase and microstructural characteristics were also investigated. Results showed that the addition of nepheline syenite provided a decrease in viscosity. The decrease in viscosity caused an increase in the tendency for pyroplastic deformation in bodies containing nepheline syenite; however, this result shows that bodies containing nepheline syenite can be sintered at a lower temperature than the standard body. The addition of nepheline syenite also decreased water absorption and increased strength.

Keywords: *Nepheline syenite; Sanitaryware; Pyroplastic deformation; Sintering; Microstructure.*

1. Introduction

Sanitaryware produced using quartz, clay and sodium feldspar are fired at a temperature between 1200 ºC and 1300 ºC [1]. Nowadays, porcelain is produced in many countries; however, the optimization of sanitaryware porcelain production is still on-going and many studies discussing the ceramic structure or the improvement of its properties, are being published every year [1-4].

Most of the studies investigate the substitution of the raw materials with others, such as spodumene and waste materials [5]. The present study investigates the effect of the addition of nepheline syenite on the pyroclastic deformation of sanitaryware porcelain. Nepheline syenite is a light-colored, silica-deficient, and feldspathic. It contains nepheline, sodium feldspar (albite), and alkali feldspar (orthoclase, microcline); however, it does not contain quartz. Nepheline syenites are essentially syenites that are under saturated in silica. Crystallizing from magma under saturated in silica results in the formation of nepheline instead of albite feldspar [4]. In literature, nepheline syenite was largely used in the electrical porcelain and chinaware body compositions. Nepheline syenite reduces the firing temperature and increasing the alkali content in the glassy phase [6]. Nepheline syenite is composed of about 25 wt.% potassium feldspar, 55 wt.% sodium feldspar and 20 wt.% nepheline. The

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higher alkali oxides content (≥14%) and the melting temperature is generally lower than the melting point of sodium and potassium feldspars containing quartz that shifts the melting point to a higher temperature are the advantages of the using of nepheline syenite in the production of ceramic bodies [7]. The higher alkali content in nepheline syenite is important due to the mixed alkali effect. The mixed alkali effect introduces two types of alkali ion into a glassy network at the same time. The mixed alkali effect causes a decrease in the viscosity with the initial replacement of Na_2O by K_2O [8, 9]. The mixed alkali effect also extends the glass working range. The decrease in viscosity contributes to increasing in densification rate and results in an increase in the amount of mullite crystals.

The increase in densification rate and amount of mullite crystals are important in terms of technological properties of the ceramic body. The increase in densification rate and amount of mullite crystals provides a high crystalline to glass phase ratio. They also increased the bulk density and bending strength [4, 5]. Nepheline-syenite has also higher Al_2O_3 content and lowers SiO_2 compared with feldspars Alumina contributes to increasing in scratch and breaking resistance. Alumina also improves the thermal endurance and the chemical durability [10].

In the authors' previous studies, the effect of nepheline syenite on the sintering behavior of sanitaryware bodies was investigated using a non-contact optical dilatometer [1]. In this study, three ceramic sanitaryware compositions were prepared to examine high-temperature deformation properties, such as the tendency for pyroplastic deformation and pyroplastic index, using an optical fleximeter.

2. Experimental procedure

Samples were prepared under industrial conditions and contained clay, kaolin, quartz and feldspar. The chemical analyses were conducted using an X-ray fluorescence (XRF) analyzer (Rigaku, ZSX Primus). An industrial production formulation was selected as the standard body (ST) composition. The composition containing nepheline syenite is abbreviated as (NS). NS1 contains 10% wt. nepheline syenite. NS2 and NS3 contain 20 % and 30 %wt. nepheline syenite, respectively. First, the raw materials were ground using a ball mill for 7 h. The laser particle size analyzer (Malvern, Hydro 2000G) was used to analyze the particle size distribution of the mixture. The mean particle size of the ST and NC was 17.4 μm. The liter weight of ST and NC slips was measured using a pycnometer and was held at 1800 g/L. Viscosity of the slips were measured using a Ford cup. The thixotropy value was measured using a Torsion viscometer (Gallenkamp type). The samples were shaped using the slip-casting in a plaster mold for measuring pyroplastic deformation, strength, firing shrinkage and water absorption. After shaping samples were dried at 110 ºC for one hour. The pyroplastic deformation trends were investigated by using optical fleximetre (MisuraFlex, Anadolu University, Turkey). Samples were sintered at 1220 ºC with a heating rate of 5 °C min^{-1} and with a 20 minute soaking time. The microstructures of the samples being investigated were examined using SEM (Quanta FEC 450, Bulent Ecevit University, Turkey). For the SEM analysis polished and fractured surfaces were etched for 2 min in 5 % HF solution, coated with Au and Pd.

3. Results and discussion

3.1. Chemical analysis

Chemical analyses of the raw materials are shown in Tab. I.

Tab. I Chemical analysis of the raw materials.

	Lol*	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3
Albite	0.39	69.96	17.84	0.16	0.19	0.57	0.26	9.92	0.41	-
Quartz	2.02	89.94	5.6	0.62	1.02	-	-	0.24	0.16	-
Kaolin 1	9.02	64.71	24.21	0.64	0.34	0.09	0.05	0.08	0.21	0.47
Clay 1	10.3	56.40	29.59	1.85	1.13	0.26	0.48	0.21	1.59	
Clay 2	10.15	56.78	27.18	1.97	1.20	0.19	0.57	0.19	1.61	0.06
Kaolin 2	11.4	48.02	36.01	1.02	0.06	0.07	0.40	0.13	2.73	-
Neph. syenite	0.78	56.9	23.86	1.12	0.01	1.34	0.03	9.58	6.37	-

*Lol: loss of ignition

Rheological properties of slips are given in Tab. II.

Tab. II Rheological properties of slips.

	Liter weight (g/ L)	Viscosity (cp)	Thixotropy (°)	Thickness rate (mm/1 hour)
STD	1800	550	55	7.8
NS1	1800	431	50	7.7
NS2	1800	429	49	7.6
NS3	1800	426	47	7.5

3.2. XRD analysis

The X-ray diffraction patterns of compositions sintered at 1220 ºC is given in Fig. 1.

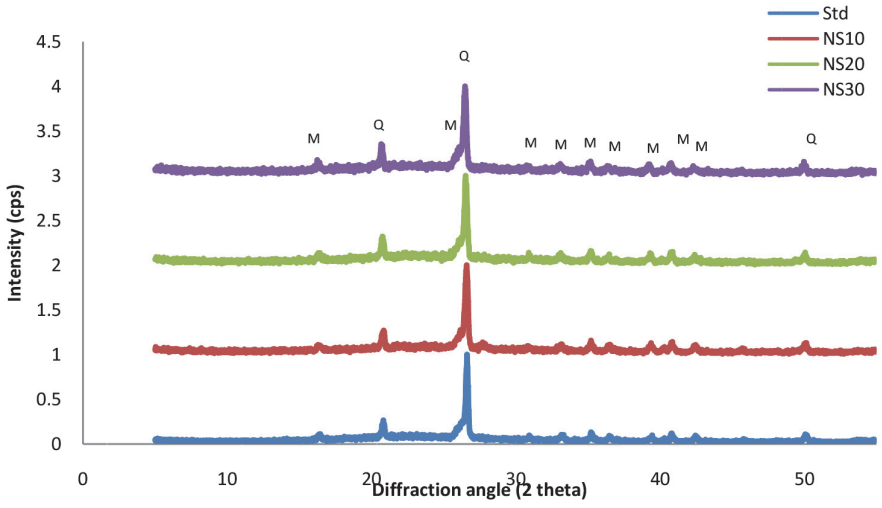

Fig. 1. X-ray diffraction patterns of fired samples.

These results show that crystalline phases are mullite and quartz in sanitaryware bodies and a glassy phase was detected. The glassy phase and amount of mullite was slightly increased with the addition of nepheline syenite. This is an important finding because nepheline syenite accelerated the densification process by decreasing the viscosity of liquid phase. As mentioned before, the mixed alkali effect resulted in a decrease in the viscosity of samples.

The decrease in viscosity and the increase in densification rate resulted in an increase in the amount of mullite crystals (secondary mullite). The increase in the amount of mullite crystals ensure an improvement in technical properties of the samples as mentioned in section 3.3.

3.3. Technical properties

Technical properties of the samples are shown in Tab. III. Variations in linear shrinkage and water absorption of sanitaryware bodies with nepheline syenite addition are shown in Fig. 2.

Tab. III Technical properties of samples.

Samples	Total shrinkage (%)	Water absorption (%)	Bulk density (g/cm^3)	Open Porosity (%)	Closed Porosity (%)	Total Porosity (%)	Firing strength (kg/cm^2)
STD	11.5	0.38	2.394	0.89	2.78	3.67	340
NS1	11.9	0.35	2.408	0.87	2.27	3.14	343
NS2	12	0.34	2.410	0.82	2.27	3.08	345
NS3	12.9	0.30	2.412	0.73	2.25	2.98	348

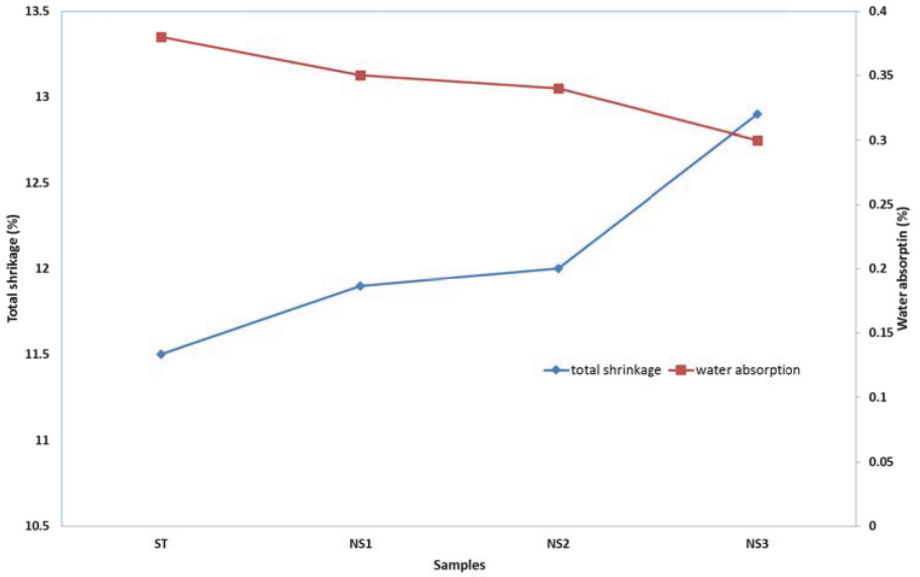

Fig. 2. Variations in linear shrinkage and water absorption of sanitaryware bodies with nepheline syenite addition.

As seen in Tab. III, there was a decrease in water absorption with the addition of nepheline syenite. There were also increases in total shrinkage and strength. Furthermore, there was a well-established correlation between bending the strength and the total porosity of the investigated bodies. As the total porosity decreases, bending strength increases. Nepheline syenite accelerated the densification process by decreasing the viscosity liquid phase [1]. The decrease in viscosity and the increase in densification rate resulted in a decrease in total porosity and an increase in bulk density. They also ensure an increase in the amount of secondary mullite crystals. To increase bending strength, a high crystalline to glass phase ratio is essential [5]. Second phase formation ensures an increase bending strength. In this

study, the increase in amount of secondary mullite provided a high crystalline to glass phase ratio and this increased the bulk density and bending strength [4, 5].

3.4. Pyroplastic deformation tendency

The term for the deformation of a ceramic material resulting from gravity during firing process is pyroplastic deformation [11]. The bending of ceramic material deteriorates the product shape during firing. Pyroplasticity is related to the amount of liquid phase and liquid phase viscosity. For sanitaryware ceramics fired in kilns, the products are transferred into the kiln using rollers. It is likely that products may be distorted on the roller due to vertical forces forcing them downwards, as a result of their weight. As a result the final products can be affected by curvatures [11]. Pyroplastic deformation occurs more frequently in highly vitrified bodies like that used in sanitaryware. The pyroplastic deformation magnitude is determined by the pyroplastic index (PI), indicating at tendency for deformation of a specimen with fixed dimensions submitted to gravity during its firing under specific conditions. The procedure for determining the pyroplasticity index consists of measuring the curvature of a specimen during its firing over two refractory.

$$PI = \frac{s.b^2}{l^4} \tag{1}$$

Where s is the maximum deformation (cm), b is the bar thickness (cm) and l is the distance between supports (cm) [12].

Pyroplastic deformation develops in the function of the vitrification of the ceramic body during firing. As temperature increases in the kiln there is a gradual rise in the amount of liquid phase formed in ceramic body. Due to the partial dissolution of the most soluble contents in the body, the liquid phase develops. As the temperature rises, the most refractory contents are gradually dissolved by the liquid phases, considerably increasing the volume of the liquid phase.

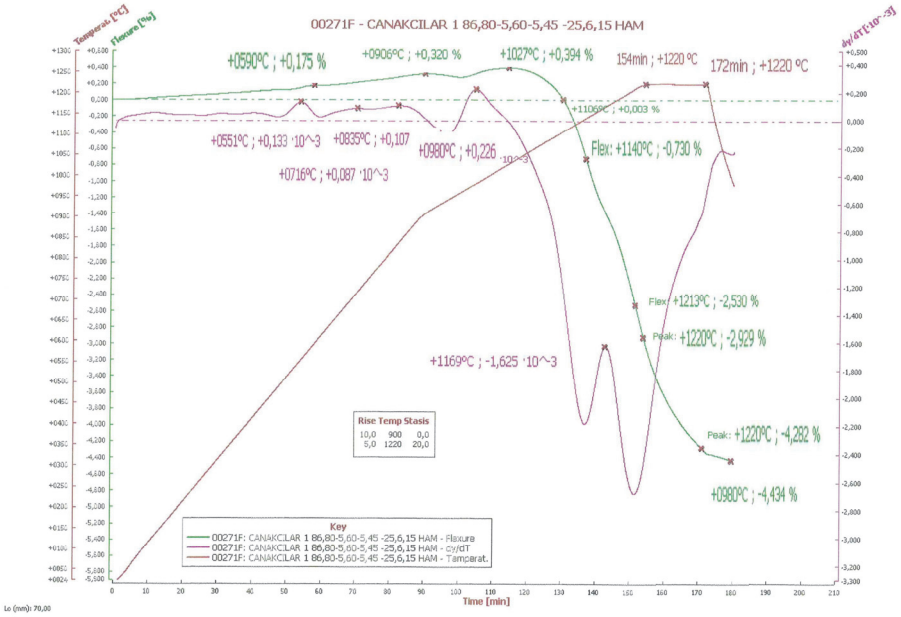

Fig. 3. Pyroplastic deformation curves of NS1 body.

Pyroplastic deformation curves of the samples are given in Fig. 3-6. As seen in Fig. 3, NS1 shows an expansion up to 1027°C. After this temperature, has been reached, deformation starts in the body. The flex point indicates the temperature where the deformation is the fastest. For the NS1 body the flex temperature was 1213 °C. Compared with its initial condition, during firing NS1 underwent deformation of 4.3 %. Fig. 4 shows the pyroplastic deformation behavior of NS2. NS2 showed an expansion of up to 1017 °C. Deformation begins after this temperature is reached. The flex temperature of NS2 was 1207 °C. For NS2, the deformation ratio was 5.14 %. The pyroplastic deformation curves of NS3 body are given in Fig. 5. As can be seen in Fig. 5, deformation commences at 1019 ºC. The temperature where the deformation is the fastest was determined as 1205 ºC. For NS3 the deformation rate was 5.24 % for NS3. In Fig. 6, the pyroplastic deformation curves of the standard body (ST) are given. Deformation of the ST body commences at 1033 ºC. The flex temperature of an STD body is much higher than that of the formulations with nepheline syenite. The flex temperature of the ST body was 1218 ºC. During firing, the ST body underwent deformation of 3.5 % compared with its initial condition.

The incorporation of nepheline syenite into the Standard composition led to a considerable decrease in the maximum deformation temperatures and increase in deformation ratio. The flex temperature for NC3 is nearly 13 °C lower than that of the standard body. It appears that the magnitude of this effect is dependent on the amount of nepheline syenite added.

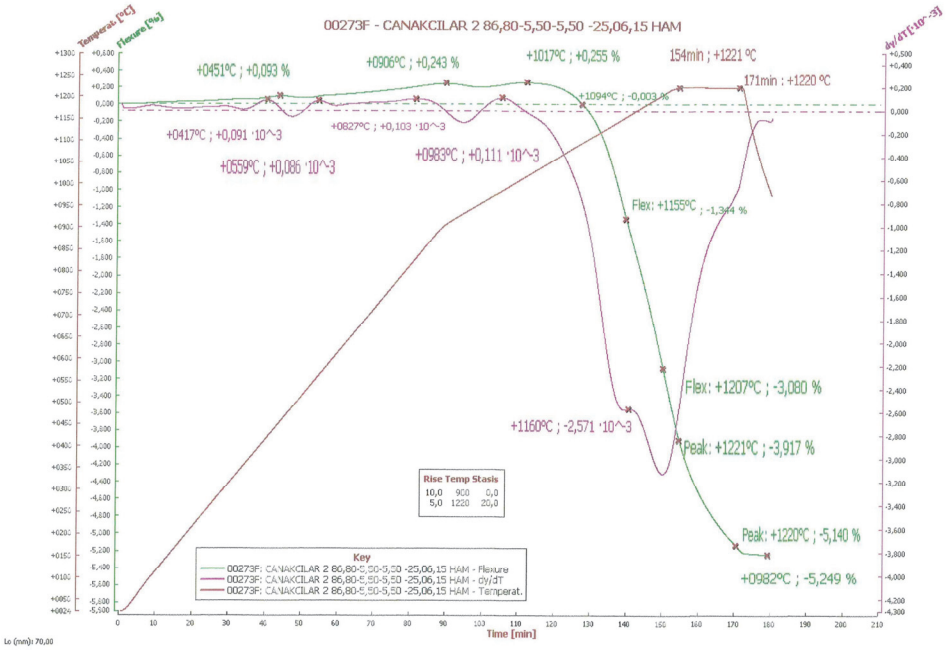

Fig. 4. Pyroplastic deformation curves of NS2 body.

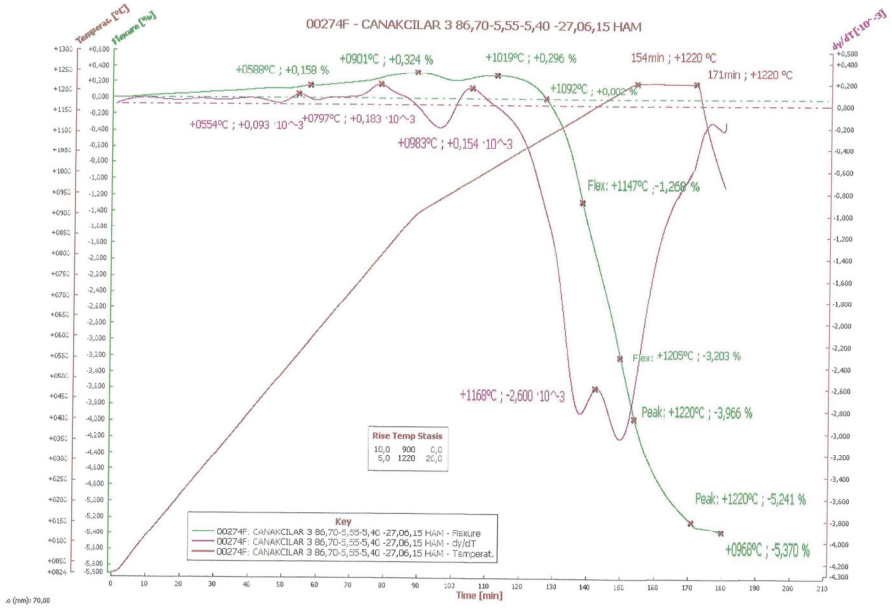

Fig. 5. Pyroplastic deformation curves of NS3 body.

Both the reduced eutectic temperatures and the liquid phase viscosity explain the increases in deformation behavior. Viscosity is calculated using Eq. 2. [12]:

$$\eta = \frac{5\rho g L^4}{32\delta_{max} h^2} \tag{2}$$

Where is ρ - density (g/cm^3), g - acceleration of gravity (cm/s^2), L - distances between supports (cm), δ_{max} - maximum deformation (cm/s) and h - thickness (cm).

The calculated pyroplastic index and viscosity values of the samples are shown in Tab. IV. As the amount of nepheline syenite in the body increases, viscosity decreases. Decrease in viscosity caused increase in tendency of pyroplastic deformation.

Tab. IV Calculated pyroplastic index and viscosity values of the samples.

Sample	PI(1/cm)	Viscosity (GPa.s)
STD	$3.16.10^{-5}$	2.39
NS1	$3.94.\ 10^{-5}$	2.20
NS2	$4.57.10^{-5}$	2.14
NS3	$4.72.10^{-5}$	1.53

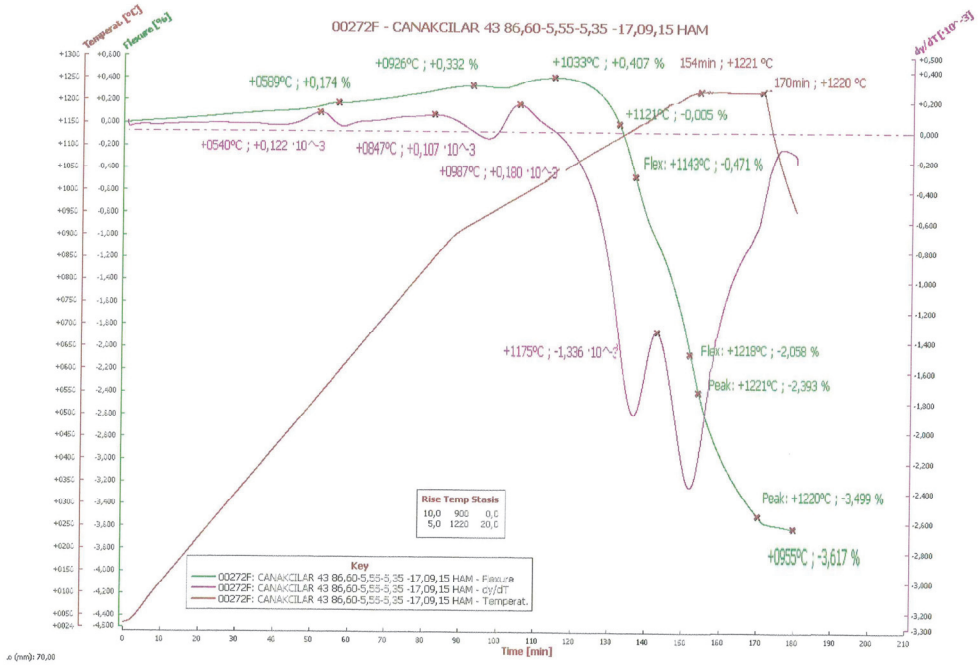

Fig. 6. Pyroplastic deformation curves of STD body.

3.5. SEM analysis

SEM micrographs of ST and NS1 are given in Fig. 7 and Fig. 8. As can be seen in micrographs, the mullite and quartz crystal phases are embedded in a glassy matrix. Needle-like secondary mullite crystals and primary mullite crystals are also detected. Needle-shaped mullite crystals (secondary mullite, Type 2) were observed in NS1 [13]. Mullite needles formed in areas containing fine clays, feldspars and quartz [14]. Feldspar particles, kaolinitic clay, or clay agglomeration formed elongated needle-shaped crystals known as secondary mullite [15]. The addition of nepheline syenite resulted in more fluid liquid phase enriched in alkalis. The fluid liquid enriched in alkalis surrounds mullite crystals. This situation enhances the fast growth of mullite crystals [15, 16]. Needle-shaped mullite crystals provide a high crystalline to glass phase ratio and enhance the mechanical properties of samples containing nepheline syenite [4, 5, 17].

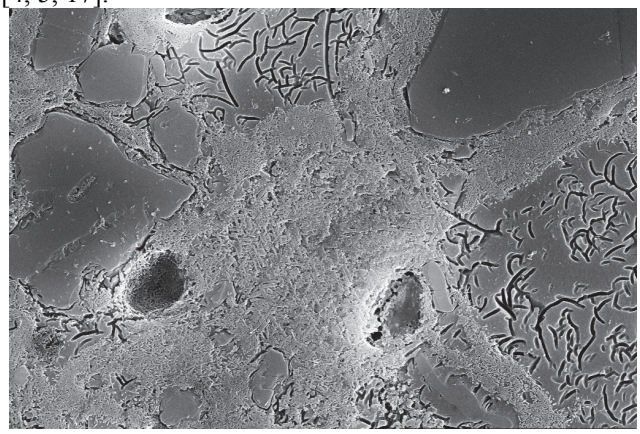

Fig. 7. Microstructure of the sanitary ware (STD) body Q: Quartz, M: Mullite and G: Glassy phase.

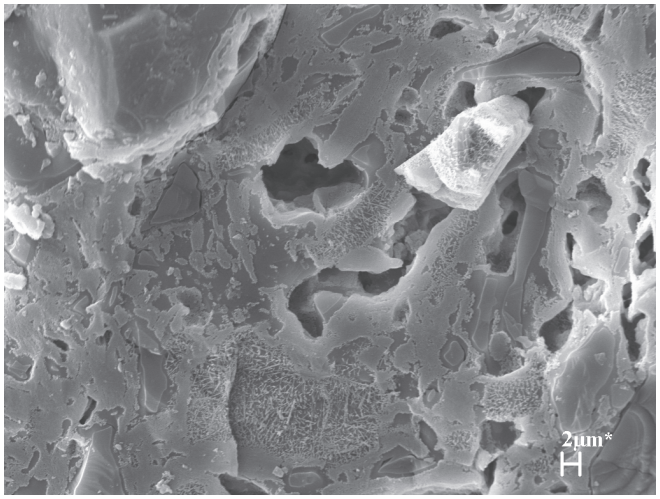

Fig. 8. Microstructure of NS1 body Q: Quartz, PM: Primary mullite, SM: Secondary mullite and G: Glassy phase.

4. Conclusions

In this work, several sanitaryware compositions containing nepheline syenite were prepared and characterized. Samples were fired at 1220 °C with a 5 °C/min heating rate and with a 20 minute soaking time. Samples were characterized by water absorption, shrinkage, XRD, flexural strength and microstructure. This study showed that by using nepheline syenite instead of Na feldspar decrease in the viscosity and acceleration in densification process is ensured. The decrease in viscosity resulted in an increase in the tendency towards pyroplastic deformation. This result showed that bodies containing nepheline syenite can be sintered at a lower temperature than the standard body. Firing at lower temperature decreases the tendency for pyroplastic deformation. The increase in the amount of secondary mullite ensures a high crystalline to glass phase ratio and the increase in secondary mullite and the decrease in total porosity increases bending strength.

Acknowledgments

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Садржај: *Уместо фелдспара, за изливање керамике коришћен је нефелин сијенит. У овом раду су припремљене три врсте керамика. Нефелин сијенит са максимум 30 тежинских % супституише натријум-фелдспар. Изучавана је пропластична деформација, заједно са технолошким својствима, укључујући скупљање, абсорпцију воде и чврстоћу. Фазни састав и микроструктура су такође проучавани. Резултати указују да додатак нефелин сијенита смањује вискозност. Смањење вискозности утиче на повећану тенденцију пропластичне деформације у узорцима који садрже нефелин сијенит. Ипак, ти узорци захтевају ниже температуре синтеровања од других узорака без додатка сијенита. Додатак сијенита такође смањује абсорпцију воде и повећава чврстоћу.*

Кључне речи: *Нефелин сијенит, пропластична деформација, синтеровање, микроструктура.*