



## Kinetic model for isothermal sintering of porcelain stoneware body in presence of nepheline syenite

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### ABSTRACT

The effect of nepheline syenite on porosity–soaking time relationship of porcelain stoneware bodies has been studied using the experimentally measured total porosity. A new kinetic model was applied to quantify porosity as function of temperature and soaking time. In the first part of work, the effect of nepheline syenite was evaluated on the kinetic parameters and the porosity variations were found to be related to surface tension/viscosity ratio of melted phase which influences the minimum porosity of ceramic body. The kinetic analysis of data indicated that the optimum soaking time to achieve minimum porosity in ceramic body is controlled by amount of nepheline syenite and milling time. The validity of presented theory to predict the experimental results was substantiated by computing total porosity at other temperatures and soaking times. The proposed model can be used to describe the sintering process of ceramic bodies that are sintered by diffusing melted phase.

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### 1. Introduction

Porcelain stoneware bodies are of prominent importance in building applications because of special attributes namely, lower water absorption, greater chemical stability and higher strength. These materials are well-known clay-based products that successfully used at indoor and outdoor of buildings [1]. This ceramic group contains kaolin or illitic–kaolinitic clay, quartz and fluxing agents such as feldspars [2]. The amount of fluxing agents in porcelain stoneware body composition plays important role in sintering process. The common fluxing agents/non-fluxing materials ratio is 1:1. The type and content of alkali oxides are the main factors in fluxing behavior of feldspars [3]. If the content of  $K_2O$  exclusively exceeded than amount of  $Na_2O$  in structure of feldspar, the fluxing agent is known as potassium feldspar. Quartz also, is the second important mineral that can be found in feldspars [4].

The applicable range of feldspars depends on the kind and amount of fluxing oxides, other feldspatic minerals and non-fluxing crystals. The addition of feldspars in composition of clay-based ceramics is function of firing temperature and water absorption of final product [5]. Although feldspars are the main fluxing agents in manufacturing porcelain stoneware bodies but nepheline syenite was used in fabricating other ceramic products such as electrical porcelain, china ware and sanitary ware. Nepheline syenite is

the most important material among the fluxing agents because it contains high amount of  $Na_2O + K_2O$ . This material also contains about 25 wt.% nepheline. The presence of large amount of quartz in feldspars is the main reason for high melting temperature of them. The microstructure of porcelain stoneware body depends extensively on the quality of feldspars used in body composition [6].

The type of pores in ceramic materials was divided to open and closed pores. An open pore is cavity or channel that communicates with surface of ceramic body. Closed pores are located inside of the ceramic body and are completely isolated from the external surface. The summation of open and closed porosity gives the value of total porosity [7].

Sintering in presence of liquid phase is the heat treatment applied to certain type of materials to develop a dense microstructure and to achieve suitable physical-mechanical properties. The term of compacted microstructure denotes dense body that usually follows by decreasing total porosity of ceramic body [8]. Densification of porcelain stoneware body in presence of liquid phase is an important step for improving mechanical properties of ceramic body. This process is carried out in continues roller kiln at high temperatures between 1200 and 1240 °C. During the sintering process, the porosity of body decreases due to diffusing melted phase into the interconnected pores [8]. This phenomenon is the most significant mechanism in sintering of porcelain stoneware body that is carried out by capillary pressure. During the heat treatment a considerable amount of liquid phase is produced which diffuses into the open pores and reduces the total porosity of ceramic body. This

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variation in porosity significantly improves the physical, chemical and mechanical properties of ceramic body [9].

The reported models describe the sintering process in presence of liquid phase by viscous flow. In developing the semi-theoretical models, the densification rate was assumed to be controlled by surface tension, viscosity and average pore size during sintering process [10,11]. These assumptions in developing mathematical models were based on simplifications of the microstructure and pores morphology of ceramic body. Orts et al. [10] and Jazayeri et al. [12] were presented semi-theoretical simplified models for describing densification rate of stoneware bodies. Therefore, these models only predict total porosity of ceramic body by using some physical parameters such as surface tension and viscosity.

In sintering process of porcelain stoneware body the total porosity continuously changes owing to variations in viscosity and pore size distribution. Since the variations in these parameters are very complex, the use of only theoretical models proposed in the literature is not applicable to estimate the total porosity [8]. In this investigation a new kinetic model has been proposed to describe isothermal sintering of porcelain stoneware composition. The kinetic parameters of model were calculated by experimental data and effect of nepheline syenite and milling time were evaluated thereafter, the validity of model was studied to estimate the optimum soaking time for reaching minimum total porosity at each temperature.

## 2. Modeling considerations

In this part of study a mathematical model is derived for densification of porcelain stoneware body by using capillary pressure and creeping flow. According previously investigation carried out by Jazayeri et al. [12], the following equation was obtained for removal rate of total porosity based on mass and momentum balances:

$$-\frac{d\varepsilon}{dt} = \frac{9\gamma}{\eta} n^{1/3} \left(\frac{4\pi}{3}\right)^{1/3} \varepsilon^{2/3} (1-\varepsilon)^{1/3} \quad (1)$$

where  $\varepsilon$  is total porosity,  $\gamma$  is surface tension,  $\eta$  is viscosity of system and  $n$  is the number of pores per unit volume of the material. The densification process of porcelain body is usually carried out at constant temperature in experimental scale and total porosity is measured as function of soaking time. The obtained results by Orts et al. showed that the pores with small dimensions are eliminated during sintering process and the average pore size increases continuously. In this investigation, it is assumed that total number of the pores per unit of real volume of material do not change if their dimensions are equal during sintering process [9]. Also, the average volume was considered for all of the pores. If the Eq. (1) is integrated, it is possible to calculate the soaking time as function of total porosity:

$$\int_{\varepsilon_0}^{\varepsilon} -\frac{d\varepsilon}{\varepsilon^{2/3}(1-\varepsilon)^{1/3}} = a \int_0^t dt \quad (2)$$

where  $a = (9\gamma/\eta)n^{1/3}(4\pi/3)^{1/3}$ . The left part of above equation can be easily evaluated by substituting  $x^3 = \varepsilon/(1-\varepsilon)$  and the result is summarized as follows:

$$F(x) - F(x_0) = at \quad (3)$$

$$F(x) = \frac{1}{2} \ln \frac{x^3 + 1}{(x+1)^3} - \sqrt{3} \tan^{-1} \left( \frac{2x-1}{\sqrt{3}} \right) \quad (4)$$

$F(x_0)$  is the value of  $F(x)$  if the sintering process is started at  $\varepsilon = \varepsilon_0$ . The generalized form of Eq. (3), which is applicable for all the materials that are sintered in presence of liquid phase, can be expressed by following equation:

$$F(x) - F(x_0) = at^b \quad (5)$$

**Table 1**  
Chemical and mineralogical analyses of raw materials.

Chemical analysis					
Oxides (%)	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline syenite
SiO <sub>2</sub>	78.38	66.75	72.35	70.11	60.14
Al <sub>2</sub> O <sub>3</sub>	15.41	21.63	13.50	17.82	23.50
K <sub>2</sub> O	0.31	1.33	6.58	0.59	5.00
Na <sub>2</sub> O	0.16	0.22	0.21	8.97	10.40
CaO	0.06	0.33	2.53	1.32	0.40
MgO	0.05	0.52	0.17	0.19	0.03
ZrO <sub>2</sub>	0.00	0.07	0.00	0.00	0.00
TiO <sub>2</sub>	0.23	1.24	0.00	0.06	0.00
Fe <sub>2</sub> O <sub>3</sub>	0.12	0.99	1.02	0.30	0.09
SO <sub>3</sub>	0.00	0.00	0.00	0.00	0.00
L.O.I <sup>a</sup>	5.41	6.62	3.60	0.64	0.55
Mineralogical analysis					
Minerals (%)	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline syenite
Quartz	60.0	38.0	38.0	13.0	0.0
Kaolinite	39.0	40.0	0.0	0.0	0.0
Illite	0.0	13.0	6.0	0.0	0.0
Smectite	0.0	2.0	0.0	0.0	0.0
Albite	0.0	2.0	2.0	76.0	56.0
Orthoclase	0.0	0.0	39.0	4.0	22.0
Anorthite	0.0	2.0	12.0	6.0	0.0
Nepheline	0.0	0.0	0.0	0.0	22.0
Impurity	1.0	3.0	3.0	1.0	0.0

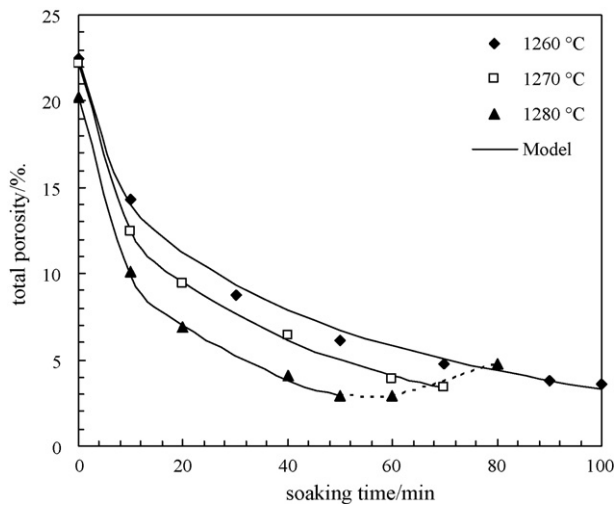
<sup>a</sup> Loss on ignition.

If the assumptions are correct, the parameters of Eq. (5) should be obtained by non-linear regression method. The constant of  $a$  must be related to surface tension/viscosity ratio of system and total number of the pores per unit volume of real material. In the next section of this work the validity of proposed model was evaluated by experimental data.

## 3. Experimental procedure

An industrial porcelain stoneware composition containing a blend of natural illitic-kaolinitic clay, potassium and sodium feldspars were used in experiments as reference body, STD. The reference body composition contains 10 wt.% of clay 1, 38.6 wt.% of clay 2, 15.5 wt.% potassium feldspar and 35.5 wt.% of sodium feldspar. In order to evaluate the effect of nepheline syenite on densification rate 5.0, 10.0 and 15.5 wt.% of potassium feldspar were replaced with the same amounts of nepheline syenite. The modified compositions were denoted as C<sub>1</sub>, C<sub>2</sub> and C<sub>3</sub> respectively. The chemical and mineralogical analyses of raw materials are reported in Table 1. Each batch of compositions was wet-milled in laboratory ceramic jar mill for 8 and 12 h. The obtained slips were dried at 110 °C in laboratory oven and the samples were crushed and sieved to pass through a 125 μm screen in order to prepare suitable powders for shaping process. A series of disc specimens, 40 mm × 4 mm, were shaped by pressing of sieved powder containing 0.06 kg water per 1 kg dry powder. A specific pressure of 52 MPa was applied according to normal industrial practice. The specimens were subjected to firing cycles with different peak temperatures in an electrical gradient kiln. These test specimens were isothermally sintered at different soaking times to obtain the correlations between the total porosity, soaking times and temperatures. To characterize the sintered specimens, the bulk and true densities were measured according the standard methods and the total porosity was calculated by following equation [13,14]:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_t} \quad (6)$$



**Fig. 1.** The variations of total porosity as function of soaking time for STD milled at 8 h and sintered at three different temperatures.

where  $\rho_b$  and  $\rho_t$  are the bulk and true densities of samples respectively.

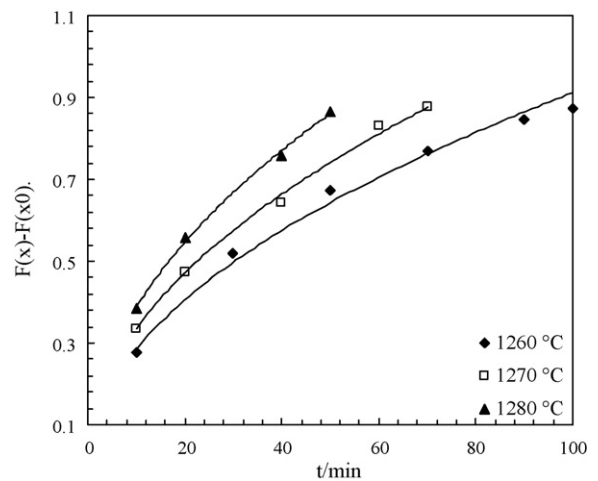
#### 4. Results and discussion

Total porosity–soaking time plots shown in Fig. 1 refer the sintering of STD composition at three firing temperatures. All curves are identical in nature and are characterized by exponential behavior. This kind of plot is generally observed in sintering of ceramic body in presence of liquid phase. In present study, the observed exponential behavior can be attributed to diffusing liquid phase formed at high temperatures.

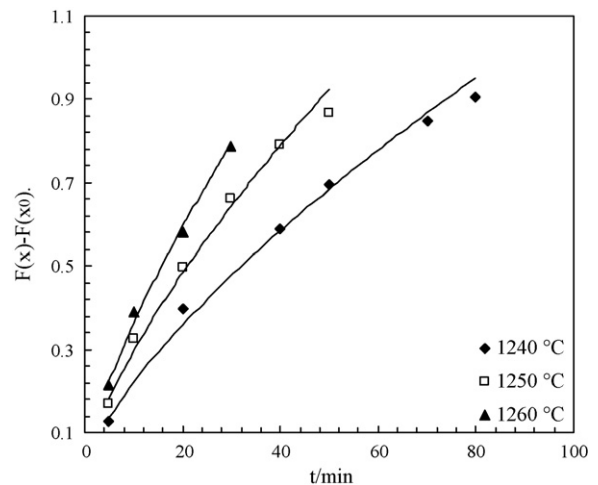
The obtained results show that total porosity decreases as soaking time rises, expect for temperature and soaking times that specimen undergoes over firing followed by expansion of air inside the occluded pores. The decrease in total porosity is result of diffusing liquid phase into the open pores due to capillary pressure. As the sintering progresses, the closed pores grow and open pores are transformed into the closed pores. Finally, the total porosity increases due to expansion of air into the closed pores, leading to an expansion in specimen dimensions. It is obvious that there is a clear increase in densification rate with increase in temperature.

To obtain the parameters of Eq. (5) and thereby to calculate the total porosity for each body composition, the modified kinetic model has been used to correlate total porosity–soaking time data. This equation is significantly complex model and depicts structural changes taking place in the pores of ceramic body during sintering process. Eq. (5) also is used for estimating exponential behavior of total porosity–soaking time data. Since the sintering of porcelain stoneware body occurs by diffusing liquid phase and takes place by capillary forces, application of this new model is justified. Model parameter,  $a$ , is related to kinetic rate constant and depends on temperature. Parameter  $b$  is related to physical changes occurring in ceramic body matrix. This parameter is very important since its value determines the total porosity characteristics. Thus for  $b = 1$ , the total porosity changes follows homogenous first order kinetic. For  $b < 1$  a exponential behavior is guaranteed.

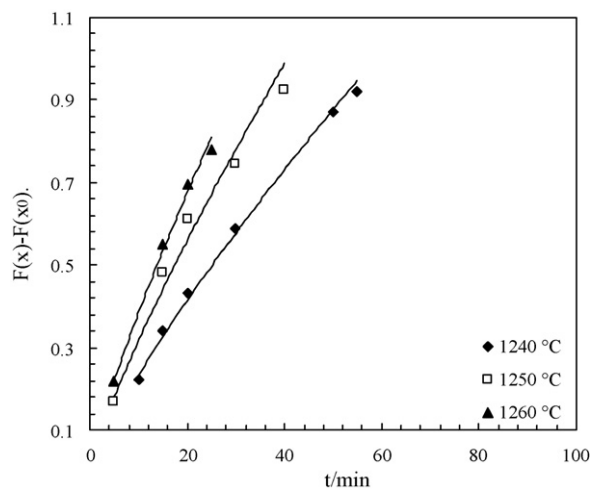
The model given by Eq. (5) is a general one and is applicable to all temperatures and compositions. A non-linear plot of  $F(x) - F(x_0)$  versus  $t$  will give the values of  $a$  and  $b$ . Figs. 2–5 show the fitting of kinetic model for sintering of porcelain stoneware bodies containing different amounts of nepheline syenite. It is interesting to note that total porosity–soaking time data of porcelain stoneware body



**Fig. 2.** The variations of  $F(x) - F(x_0)$  versus soaking time for STD milled at 8 h and sintered at three different temperatures.



**Fig. 3.** The variations of  $F(x) - F(x_0)$  versus soaking time for  $C_1$  milled at 8 h and sintered at three different temperatures.



**Fig. 4.** The variations of  $F(x) - F(x_0)$  versus soaking time for  $C_2$  milled at 8 h and sintered at three different temperatures.

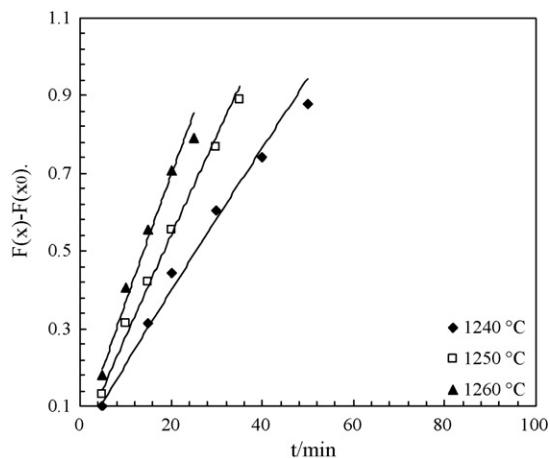


Fig. 5. The variations of  $F(x) - F(x_0)$  versus soaking time for  $C_3$  milled at 8 h and sintered at three different temperatures.

sintered at different temperatures fit the new model very nicely both for reference and modified compositions.

From the parameters of the non-linear correlations, the constants of  $a$  and  $b$  were easily calculated. By use of the constant parameters the rate constant was computed in each temperature. The values of  $a$ ,  $b$  and non-linear correlation coefficients,  $r$ , have been tabulated in Table 2. It is observed that the value of  $b$  virtually remains constant for each composition whilst the parameter  $a$  increases considerably as sintering temperature rises. The values of  $a$  have been plotted versus the inverse of temperature on semi-logarithm scale according to Eq. (7). The plots were observed to fit straight lines well, which indicate that the variation of  $a$ , with temperature may be represented by an exponential equation form as follows:

$$a = a_0 \exp\left(-\frac{Q}{T}\right) \quad (7)$$

where  $a_0$  and  $Q$  are the constant parameters of the Eq. (7). Table 3 details the values of these parameters. Since sintering process of porcelain stoneware body takes place in presence of liquid phase, the rate of densification defined in term of rate constant,  $k(\varepsilon)$ , varies continuously with soaking time due to continuous structural changes in pores of ceramic body. The densification rate can

Table 2  
The constant values and non-linear correlation coefficients of Eq. (5) for reference and modified porcelain stoneware compositions.

Composition	Temperature (°C)	$a$	$b$	$r^a$
STD	1260	0.0897	0.5035	0.996
	1270	0.1073	0.4940	0.999
	1280	0.1231	0.4973	0.999
$C_1$	1240	0.0435	0.7043	0.997
	1250	0.0578	0.7089	0.995
	1260	0.0702	0.7134	0.996
$C_2$	1240	0.0357	0.8182	0.997
	1250	0.0480	0.8196	0.993
	1260	0.0593	0.8127	0.998
$C_3$	1240	0.0235	0.9438	0.992
	1250	0.0306	0.9587	0.994
	1260	0.0442	0.9205	0.996
$C_2-12$	1240	0.0522	0.7458	0.997
	1250	0.0728	0.7453	0.999
	1260	0.0927	0.7430	0.999

<sup>a</sup> Non-linear correlation coefficient.

Table 3

The parameters of Eq. (7) for reference and modified porcelain stoneware compositions.

Composition	$a_0$	$Q$ (K)	$r$	$rms$
STD	$4.3 \times 10^9$	37689	0.997	4.67
$C_1$	$2.2 \times 10^{14}$	54719	0.998	8.77
$C_2$	$2.9 \times 10^{15}$	58871	0.996	8.31
$C_3$	$2.4 \times 10^{19}$	73235	0.995	9.80
$C_2-12$	$7.0 \times 10^{17}$	66623	0.996	5.89

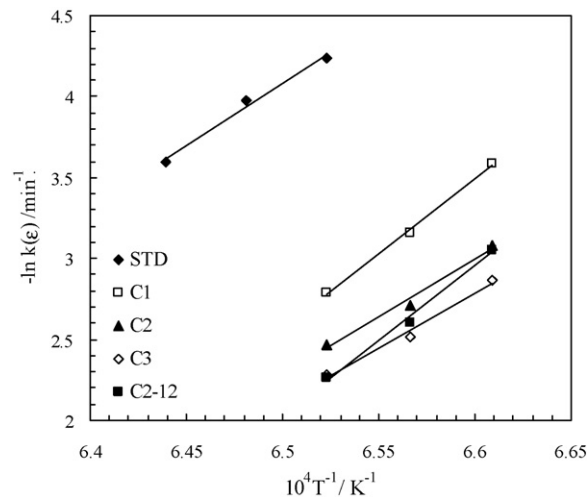


Fig. 6. Variations of rate constants with temperature for reference and modified porcelain stoneware bodies.

be expressed as following equation:

$$-\frac{d\varepsilon}{dt} = k(\varepsilon)\varepsilon \quad (8)$$

The expression for the rate constant was given by following equation:

$$k(\varepsilon) = ba^{1/b} \frac{\left[ F\left(\sqrt[3]{\varepsilon/(1-\varepsilon)}\right) - F\left(\sqrt[3]{\varepsilon_0/(1-\varepsilon_0)}\right) \right]^{(b-1)/b}}{\sqrt[3]{\varepsilon/(1-\varepsilon)}} \quad (9)$$

$k(\varepsilon)$  can be calculated at each total porosity, for example in minimum total porosity of STD body at 1280 °C,  $\varepsilon \cong 3.0\%$ . Arrhenius plots for reference and modified porcelain stoneware compositions were shown in Fig. 6 according following equation:

$$k(\varepsilon) = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

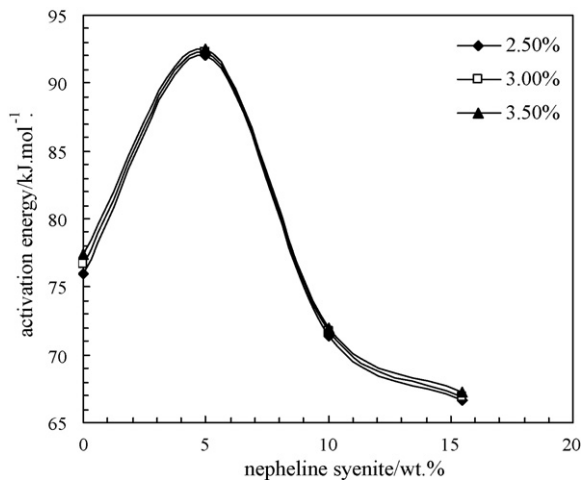
where  $E_a$  is activation energy,  $k_0$  is the frequency factor and  $R$  is the constant of ideal gas. The values of kinetic parameters were presented in Table 4. Also, the value of activation energy for reference and modified composition were shown in Fig. 7 at three values of total porosity as function of nepheline syenite content.

This range of porosity was selected because it covers all of the minimum porosity values for reference and modified compositions

Table 4

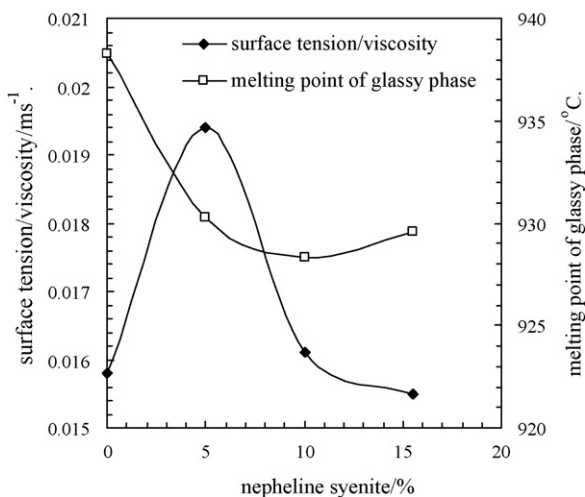
The kinetic parameters of Arrhenius equation for reference and modified porcelain stoneware compositions.

Composition	$k_0$ (min <sup>-1</sup> )	$E_a$ (kJ/mol)	$r$
STD	$7.4 \times 10^{19}$	76.7	0.995
$C_1$	$8.8 \times 10^{24}$	92.3	0.999
$C_2$	$1.8 \times 10^{19}$	71.7	0.993
$C_3$	$9.6 \times 10^{17}$	66.9	0.998
$C_2-12$	$1.2 \times 10^{25}$	91.9	0.998

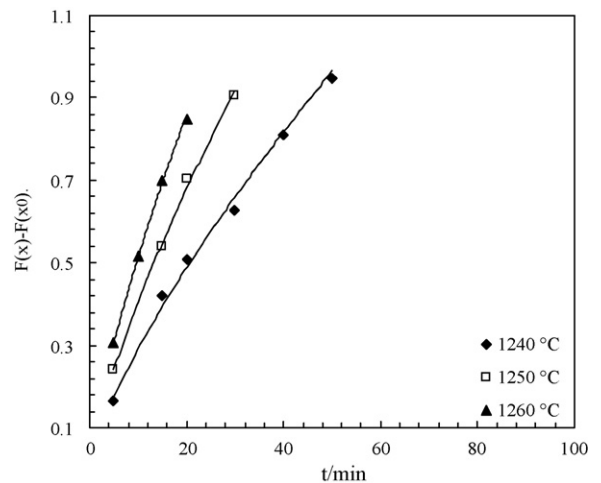


**Fig. 7.** The variation of activation energy as function of nepheline syenite content at three different total porosity.

in studied conditions. The value of activation energy approximately remains constant for each composition in the domain of porosity. It is also observed that the value of this parameter increases, reaching to maximum value in presence 5.0 wt.% of nepheline syenite. This phenomenon indicates that the mechanism of pore changes in ceramic structure is different in presence mentioned amounts of nepheline syenite. It should be note that the total porosity changes involve typically with surface tension/viscosity ratio of liquid phase that increases as nepheline content reaches to 5.0 wt.% in body composition. As the amount of nepheline syenite rises in body composition this ratio falls down because of dissolving quartz and mullite crystals in melted phase [6]. The authors showed that the surface tension/viscosity ratio of liquid phase grows and reaches maximum value in presence of 5.0 wt.% nepheline syenite, Fig. 8 [15]. The increase in surface tension/viscosity ratio accelerates the removal rate of porosity but the more increase in nepheline content cannot positively increase the surface tension/viscosity ratio. Therefore, the increment of nepheline syenite content in body composition has negligible role on densification rate of porcelain stoneware body. The trends of these changes in kinetic parameters show an overall positive effect on densification rate and as result, total porosity decreases considerably in presence 5.0 wt.% nepheline syenite. The addition of nepheline syenite in porcelain



**Fig. 8.** The variations of surface tension/viscosity ratio of liquid phase and melting point of glassy phase of porcelain stoneware body with nepheline syenite content [15].



**Fig. 9.** The variations of  $F(x) - F(x_0)$  versus soaking time for  $C_2$  milled at 12 h and sintered at three different temperatures.

stoneware composition results an increase in activation energy and frequency factor for  $C_1$  composition. Finally, the variations of kinetic parameters improve the densification rate in presence of 5.0 wt.% nepheline syenite.

The densification of a porcelain stoneware body is governed by the viscosity of the liquid glassy phase formed at high temperature which is controlled by the  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  content. The  $\text{Na}_2\text{O}/\text{K}_2\text{O}$  ratio is also a controllable factor on viscosity of liquid glassy phase. In porcelain stoneware compositions modified by nepheline syenite, the bodies contain more  $\text{Na}_2\text{O}$  with lower amount of  $\text{K}_2\text{O}$  and  $\text{SiO}_2$ . Although, potassium oxide leads to a liquid phase with less viscosity compared to sodium oxide but, increasing  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  content from 5.12, in STD, to 5.56, in  $C_1$ , and low content of silica in modified compositions were compensated this negative effect. These variations bring about a lower viscosity of liquid phase in materials containing nepheline syenite. Fluxing agent like nepheline syenite should help in enhancing the densification rate of ceramic bodies if melted phase viscosity is reduced by addition fluxing agent. It is clearly seen that the rate constant improves in presence 5.0 wt.% nepheline syenite. Also, it is observed that the addition of nepheline syenite content more than 5.0 wt.% has negligible role in densification rate. Therefore, the viscous melted phase is not able to diffuse into the pores by capillary pressure since viscosity of liquid phase is not effectively influenced by nepheline syenite content especially at low sintering temperature.

Fig. 9 shows the variation of  $F(x) - F(x_0)$  versus soaking time for  $C_2$  composition milled for 12 h. The constant values of Eq. (5) were presented in Table 2 for this condition. Also, the kinetic parameters of Eqs. (7) and (10) are summarized in Tables 3 and 4 respectively.

**Table 5**

Experimental total porosity of reference composition sintered at different soaking time and temperatures.

Soaking time (min)	1230 °C		1240 °C		1250 °C	
	$\epsilon_{\text{exp.}}$ (%)	$\epsilon_{\text{cal.}}$ (%)	$\epsilon_{\text{exp.}}$ (%)	$\epsilon_{\text{cal.}}$ (%)	$\epsilon_{\text{exp.}}$ (%)	$\epsilon_{\text{cal.}}$ (%)
20					12.72	11.87
40			9.16	10.03	8.74	8.88
50	11.42	11.59	8.53	9.15	6.98	7.83
60	10.23	10.77			6.50	6.95
120			5.08	5.63	3.51 <sup>a</sup>	3.64
180			3.22 <sup>a</sup>	3.55		
200	4.31	4.76				
260	3.51 <sup>a</sup>	3.88				

<sup>a</sup> Corresponded to minimum total porosity.

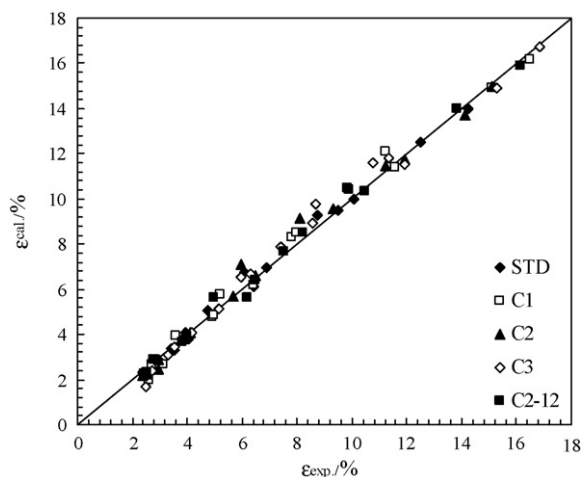


Fig. 10. Statistical evaluation of total porosity for reference and modified porcelain stoneware compositions.

The values of activation energy of C<sub>2</sub> composition prepared at two different milling times show that the increase in milling time changes the activation energy values considerably, indicating that the mechanism of sintering in these particular cases are different due to changes in surface tension/viscosity ratio. It is well known that an increase in the specific surface area of particles is sufficient to increase the sintering rate. The particle size distribution of raw materials is more important factor in densification rate and plays a beneficial role on specific surface area of materials to absorb energy. This is evident from the fact that the value of frequency factor which is the function of specific surface area is more in the composition milled for 12 h. The increase in milling time ensures a higher surface area to improve the densification rate.

The following equation which relates the total porosity of reference and modified porcelain stoneware compositions to temperature and soaking time was obtained by taking into account Eq. (7) and average value of  $b$  for each composition:

$$F(x) - F(x_0) = a_0 \exp\left(-\frac{Q}{T}\right) t^{\bar{b}} \quad (11)$$

where  $\varepsilon = x^3/(1+x^3)$ .

The values of total porosity computed by Eq. (11) have been plotted versus those determined experimentally in Fig. 10. To compare the experimental data with model prediction, the percent deviations,  $D_v$ , were calculated between experimental points and theoretical predictions by following equation:

$$D_v = \left[ \frac{\varepsilon_{cal} - \varepsilon_{exp}}{\varepsilon_{exp}} \right] \times 100 \quad (12)$$

From these percent deviations overall percent root mean square,  $rms$ , deviations were then calculated as follows:

$$rms = \left[ \sum_{i=1}^N \frac{D_v}{N} \right]^{\frac{1}{2}} \quad (13)$$

Very good agreement can be observed between the experimental data and calculated values with acceptable  $rms$  reported in Table 3, which substantiates the validity of new kinetic model. In order to well understand the validity of kinetic model, we calculate the values of total porosity at different temperatures and soaking times for reference composition as reported in Table 5.

According to data shown in Figs. 2–5 and 9, the average value of minimum total porosity was approximately considered 3.0% for reference and modified compositions. After rearranging Eq. (11), the

Table 6

The parameters of Eq. (14) for reference and modified porcelain stoneware compositions.

Composition	A (min)	B (K min)	r
STD	-4444.6	697.7	0.999
C <sub>1</sub>	-2858.8	442.6	0.999
C <sub>2</sub>	-1198.0	187.7	0.999
C <sub>3</sub>	-1923.1	297.9	0.999
C <sub>2</sub> -12	-1912.6	295.6	0.999

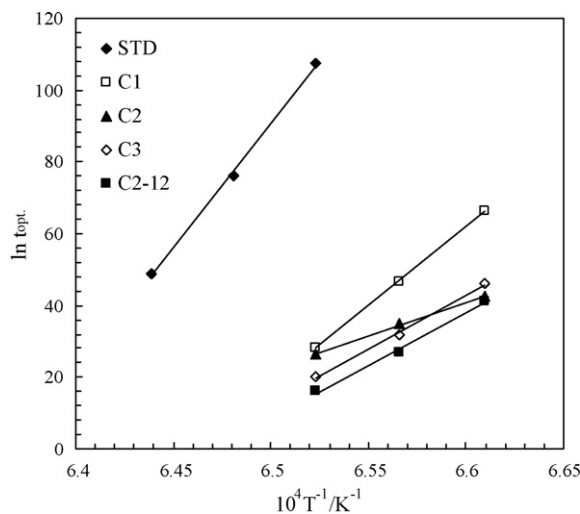


Fig. 11. Variations of optimum soaking time versus temperature for reference and modified porcelain stoneware compositions.

following equation was developed to relate the optimum soaking time to temperature:

$$\ln t_{opt} = A + \frac{B}{T} \quad (14)$$

where  $t_{opt}$  is the optimum soaking time to achieve minimum value of total porosity and  $A$ ,  $B$  are the model constants that are reported in Table 6. Also, Fig. 11 shows the variation  $\ln t_{opt}$  versus inverse temperature for each composition. The acceptable agreement can be observed between the experimental data and calculated values. The validity of kinetic model for obtaining optimum soaking time in other temperatures for reference composition was summarized in Table 5. The agreement between experimental data and model predictions was again excellent with  $rms$  of 7.86.

## 5. Conclusions

Sintering of porcelain stoneware body is typical example of densification process proceeding through liquid phase formation. Since the surface tension/viscosity ratio controls total porosity during the sintering process, addition of 5.0 wt% nepheline syenite enhances the removal rate of total porosity. Nepheline syenite was found to increase sintering rate which produces dense porcelain stoneware body compared to reference composition. A modified kinetic model was proposed to describe the variation of total porosity of porcelain stoneware bodies during the isothermal sintering with temperature and soaking time. The validity of model was substantiated for different porcelain stoneware compositions and the effect of nepheline syenite on kinetic parameters was evaluated. It is also observed that activation energy increases, reaching to maximum value in presence of 5.0 wt.% nepheline syenite because of rising surface tension/viscosity ratio in melted phase. Also, the value of frequency factor which is function of specific surface area, increases as the composition is prepared at high milling time. The proposed

model can be used for the bodies that are sintered in presence of melted phase to achieve minimum porosity at each temperature.

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