A kinetic study on the development of porosity in porcelain stoneware tile sintering

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The aim of this work is to develop a mathematical model to study the mechanism of elimination of total porosity as a function of soaking time using the Navier-Stokes. Then, parameters of the model such as kinetic constants and apparent activation energy are calculated on the basis of experimental data for a standard porcelain stoneware tile composition. The theoretical data calculated from the model are in good agreement with the experimental data. Using the model developed, it is possible to estimate the best soaking time to obtain minimum total porosity at a given firing temperature . The effects of nepheline on sintering process of porcelain stoneware tile is investigated. It was found that when the nepheline syenite content of the starting mix was increased to 10%, the constant k_p of the kinetic equation also increased. The results showed that addition of nepheline to composition of porcelain stoneware bodies was influenced remarkably suitable soaking time to obtain the minimum total porosity and increased shrinkage and bulk density while total and closed porosity fall down.

Keywords: porosity; Kinetic Model; Liquid Phase.

Estudio cinético de la evolución de la porosidad durante la sinterización de gres porcelánico

El propósito de este trabajo es desarrollar un modelo matemático tipo Navier-Stokes para estudiar el mecanismo de eliminación de la porosidad en función del tiempo de maduración en cocción. Los parámetros del modelo tales como las constantes cinéticas y la energía de activación aparente se calcularon a partir de datos experimentales para una composición de gres porcelánico estándar. Los datos teóricos obtenidos a partir del modelo están en buena concordancia con los datos experimentales. Se investigaron los efectos de la nefelina en el gres porcelánico, encontrado que cuando se aumenta el contenido hasta un 10%, la constante de la ecuación cinética k_p aumenta. Empleando el modelo desarrollado, es posible estimar el tiempo de maduración en cocción para obtener la porosidad mínima (se alcanza la eliminación de la porosidad debido a la presión capilar) una temperatura dada. Los resultados mostraron que la adición de nefelina en la composición del gres porcelánico afecta fuertemente el tiempo de maduración en cocción requerido para alcanzar la mínima porosidad y aumenta la contracción y la densidad, mientras la porosidad total y cerrada disminuyen.

Palabras clave: porosidad; modelo cinético; fase líquida.

1. INTRODUCTION

Porcelain stoneware is an high performing material with water absorption less than 0.1%. It is characterized by high mechanical strength and chemical resistance. The sintering process of this material is complex, because a lot of phenomena simultaneously occur during sintering at about 1200-1300°C. Raw materials react and new crystalline phases are formed (1,2). The melting process of raw material produce a liquid phase whose viscosity decreases by increasing the sintering temperature so that it can enter the pores and eliminate them. The quartz tend to dissolve in this liquid phase. A characteristic shrinkage is observed when the metakaolin formed from the clay minerals at high temperature transforms into needle-shaped mullite crystals and silica glass at 950 to 1000 °C. A liquid phase forms between 1100 and 1150 °C when the feldspar present is in contact with silica (eutectic point) (3). The above considerations clearly illustrate that it is impossible to develop a theoretical kinetic model only on the basis of the chemical reactions that occur during sintering of porcelain stoneware tile. There are a few models, however, dealing with the kinetics of mullite formation from the decomposition of pure kaolinite (4).

Very few models are developed for the case in which the solid phase partially reacts with the liquid phase but theoretical models are developed by considering the pore size and the shrinkage variations. In those models (5,6,7) some geometrical assumptions are exaggerated to model the total microstructure of clay bodies. Therefore, the results of these kinetic equations have an approximate validity in reference to the influence of kinetic parameters such as temperature and soaking time on sintering rate.

In the sintering of porcelain stoneware tile, the viscosity of the liquid phase changes continuously by increasing soaking time due to the formation of new crystalline phases and melting of quartz. The average pore size increases

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progressively during the sintering process and kinetic models are proposed to describe the isothermal sintering of floor tile based on the average pore size of the tiles (8,9,10).

In the present study a kinetic model is developed to describe the changes in the porosity of porcelain stoneware tile during the soaking time, using the Navier-Stokes equation. Then the values of the constants for a porcelain stoneware tile composition are found and the validity of the model is verified with experimental data.

The typical fluxes for porcelain stoneware are soda feldspar and potassium feldspar. The role of fluxes in ceramic bodies is to form a glassy matrix that will bond together the all the constituents of the sintering process (11,12,13,14). The fluxes are low melting materials that react with other raw materials and fall down the temperature of liquid phase formation, in the ceramic system. The sintering process is due to the liquid phase diffusion, by capillary pressure, in the interconnected pores. The characteristic of feldspars as fluxing agent depends on their chemical composition and in particular on their high alkali content. The substitution of the typical fluxes in porcelain stoneware with other kind of material with the same properties, is an important goal to achieve for the tiles producers (15,16,17). So that glass or other materials are used in order to obtain lower sintering temperatures, good microstructure and white products.

The nepheline syenite is the feldspathoid used in the sanitaryware production as it increases the whitness of the products (18). The nepheline syenite is used in the sintering process of sanitaryware, electrical porcelain and chinaware bodies as it exhibit a greater fluxing activity in comparison with potassium feldspar (19,20). Nepheline syenite is composed of the mineral nepheline ($Na_3KAl_4Si_4O_{16}$), sodium and potassium feldspars and possesses a higher percentage of alkali: silica ratio (4:9) than the feldspars (1:6).

The aim of this work is to study the effects of this flux in the kinetic of the porcelain stoneware sintering process by using the just developed kinetic model employed for the standard formulation in the part I. In this work the nepheline syenite is used in a porcelain stoneware tile slip by substituting the potassium feldspar.

2. MATERIALS AND METHODS

A standard porcelain stoneware mix is prepared by wet milling for 8 h in a laboratory jar mill (1kg capacity) the raw materials to obtain slips at 33wt% of water content. At the same conditions some different slips of porcelain stoneware are prepared by substituting the K-feldspar with different amount of nepheline in a standard industrial formulation as reported in the table I.

The determination of the particle size distribution is carried out on the slips using laser light diffraction (Malvern

TABLE II. CHEMICAL ANALYSIS OF THE RAW MATERIALS

Oxide (%)	Raw Materials				
	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
ZrO_2	0.00	0.07	0.00	0.00	0.00
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
SO_3	0.00	0.00	0.00	0.00	0.00
L.O.I.	5.41	6.62	0.50	0.38	0.55

Mastersiser 2000) (see table I). Chemical and mineralogical analyses are performed on raw materials because sintering conditions are strongly influenced by these factors. Chemical analysis is performed by inductively coupled plasma optical emission spectrometry (ICP OES model 3200XL Perkin Elmer) and mineralogical analysis is done by diffractometer model PW 1927 Philips. The results are reported in table II. The slips are dried at 110 °C and then milled in a laboratory milling equipment to obtain a particle size less than 125 μm. The powder obtained is brought to a moisture content of about 6 wt% and sieved at 800 μm to avoid agglomerates (21).

A series of test pieces in the shape of disks (40 mm diameter and 4 mm thick) are prepared by pressing at a forming pressure of 52 MPa. The test pieces are fired at three temperatures and different soaking times in an electrical gradient kiln (Ceramic Instrument Model 86V). To characterize the fired pieces, the total porosity is calculated as:

$$\varepsilon = 1 - (\rho_b / \rho_t)$$

where ρ_b and ρ_t are the bulk and true densities respectively, measured by the hydrostatic method (22,23).

2. 1 Proposed kinetic model

In the sintering of porcelain stoneware tile two types of pressure act on the pores during the process. One of those is the capillary pressure, P_c, that is produced in the fine pores. The other one is the gas pressure inside the pores, P_g. The capillary pressure and gas pressure work in opposite directions. Therefore the total pressure, P, is the difference between the two pressures ($P = P_c - P_g$). The general capillary pressure for spherical pores is given by $-2\gamma/r_1$ where r_1 is the average pore radius and γ is the surface free energy. In the first and intermediate stages of the sintering process the closed

TABLE I. FORMULATION OF MIX COMPOSITIONS USED IN THIS STUDY

Sample	Raw materials (%)					Particle size		
	Clay 1	Clay 2	K-feldspar	Na-feldspar	Nepheline Syenite	d(10) μm	d(50) μm	d(90) μm
STD	10,02	38,62	15,64	35,52	0,00	1.89	11.93	48.14
F1	10,02	38,62	10,64	35,52	5,00	2.17	12.50	44.83
F2	10,02	38,62	5,64	35,52	10,00	1.79	10.98	44.48
F3	10,02	38,62	0,00	35,52	15,64	1.86	11.45	46.35

porosity is much lower than the apparent porosity, so that the effect of gas pressure inside the pores on the sintering rate is assumed to be negligible as compared with the capillary pressure .

In the final sintering stage, where the pores are, almost all closed, the pressure of the gas inside the pores becomes high and influences the sintering rate. The minimum porosity is that where the gas pressure becomes equal to the capillary pressure. After this point the total and closed porosity both increase and the pieces expand with increasing soaking time. Since the sintering process is finished when minimum porosity is reached, in the present study the change in total porosity was investigated until this point.

In developing the model for this phenomenon we considered an average radius, r_1, for a total of pores which are surrounded by a spherical shell of an equal amount of real incompressible material with radius, r_2. When an external or a negative internal pressure is applied, the flow of the material inside the shell decreases the pore volume by radial movement. Also, it was assumed that the variation in density of the liquid phase is negligible. Therefore, the porosity of the system, ε, is expressed as:

$$\varepsilon = \left(\frac{r_1}{r_2} \right)^3 \qquad [1]$$

If we assume Newtonian behavior and creeping conditions for the system (Reynolds Number $\ll 1$), the mass and momentum balance can be written in spherical coordinates (Navier-Stokes equation) as follows (24)

$$\text{Mass balance} \qquad r^2 u_r = r^2 u_1 \qquad [2]$$

$$\text{Momentum balance} \qquad -\frac{\partial P}{\partial r} + \eta \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial u_r}{\partial r} \right) = 0 \qquad [3]$$

where u_r and u_1 are the velocity of real material at radiuses r and r_1 respectively, and η is the effective viscosity of the system. Substituting Eq. [2] into Eq. [3] and integrating between capillary and atmospheric pressures, we obtain the flow velocity at the boundary between the pore and real material, u_1, as a function of total porosity:

$$u_1 = -\frac{3\gamma}{\eta(1-\varepsilon)} \qquad [4]$$

In the sintering process the tiles are usually held at constant temperature and the porosity is measured as a function of soaking time. The volume of real material in the tiles is approximately constant and the total number of pores does not change, if they are all equal in size. But, when the pores are not equal in size the small pores will disappear more rapidly than the larger ones, so that the total number of pores decreases as soaking time increases.

Therefore, it is important to evaluate the number of pores per unit volume of real material, n, to find the relationship between the different parameters. In this case porosity is given by:

$$r_1 = \left(\frac{3}{4\pi} \right)^{\frac{1}{3}} \left(\frac{\varepsilon}{1-\varepsilon} \right)^{\frac{1}{3}} \left(\frac{1}{n} \right)^{\frac{1}{3}} \qquad [5]$$

and, since $u_1 = dr_1 / dt$, substituting Eq. (5) into Eq. (4) we find:

$$-\frac{d\varepsilon}{dt} = n^{\frac{1}{3}} \left(\frac{4\pi}{3} \right)^{\frac{1}{3}} \left(\frac{9\gamma}{\eta} \right) \varepsilon^{\frac{2}{3}} (1-\varepsilon)^{\frac{1}{3}} \qquad [6]$$

After simplifying Eq. [6] with Eq. [5], the relationship between the rate of change in porosity and the other parameters is the following:

$$-\frac{d\varepsilon}{dt} = \frac{9\gamma}{\eta r_1} \varepsilon \qquad [7]$$

The effective viscosity of the system largely depends on the amount and viscosity of the liquid phase formed from the quartz and alkaline oxides present in the mix. Consequently, evaluation of the effective viscosity is very complex.

According to Sack and Vora (25) the variations in effective viscosity of a system with time can be described by the following equation:

$$\eta = k_1 \eta_0 t^\alpha \qquad [8]$$

where k_1 and α are constants, and η_0 is the viscosity of the system at the beginning of the soaking time. It is assumed that the average pore size in isothermal conditions can be defined as:

$$r_1 = k_2 r_0 t^\beta \qquad [9]$$

where k_2 and β are constants, and r_0 is the initial average pore radius at the beginning of the soaking time.

The surface tension is assumed to be constant (26).

Substituting Eqs. [8] and [9] into Eq. [7], separating variables and integrating we obtain (27):

$$\varepsilon(T) = \varepsilon_0(T) \exp\left(-kt^n \right)$$

$$n = 1 - (\alpha + \beta) \quad , \qquad K = \frac{9}{nk_1k_2} \quad , \qquad k = \frac{K\gamma}{\eta_0 r_0}$$

$$[10]$$

where $\varepsilon_0(T)$ and $\varepsilon(T)$ are the porosity of the system at the beginning and during the soaking time, respectively.

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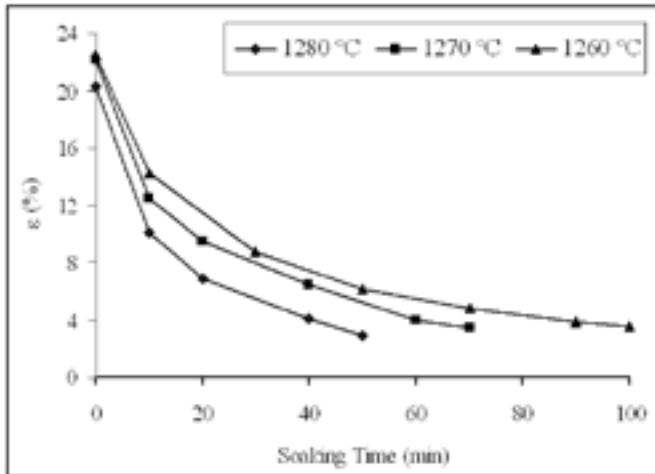

Fig. 1- Porosity vs. soaking time at three different firing temperatures (experimental data)

3. RESULTS AND DISCUSSION

3.1 Application of kinetic model

The porosity of the fired samples is plotted in Figure 1 versus soaking time, for three different firing temperatures. The porosity decreases as soaking time increases and the rate of densification decreases (curve slope) as the pieces are sintered. Also, the same minimum porosity is reached at the three different firing temperatures and the rate of densification to reach this point increases with increasing firing temperature.

In order to elaborate the kinetic parameters of the model, the experimental data are plotted with a logarithmic scale as log (ln (ε_0(T)/ε(T))) versus log (t).

The final equation to plot is:

$$\text{Log} \{\ln [\varepsilon_0(T)/\varepsilon (T)] \}= n\text{Log } k_p + n\text{Log } t \qquad [12]$$

The plot is linear when the variation in porosity is controlled by capillary pressure. In this case, the proposed model is acceptable. The plots for the experimental data at the studied temperatures are reported in Figure 2 where the equations are written. From this plot it is possible to obtain the values of n and k_p for three temperatures.

The n values are quite constant for each temperature, thus an average value can be used to calculate the other parameters. This parameter, n, can be considered as a densification index, i.e., it is proportional with the rate of densification. The values of "n" increases by increasing nepheline syenite content as reported in table III. The viscosity of the liquid phase decreases and the diffusion of the liquid phase is accelerated. Consequently, the rate of elimination of the porosity increases.

As previously discussed, the values of "n" obtained by the logarithmic method allow assessment of the kinetic model and choice of the best kinetic expression to describe the effect of nepheline syenite.

In order to evaluate how the kinetic constant k changes with the temperature, a plot with the data of kp found from the equation [12] in the function of temperature is done to find the value of apparent activation energy which is calculated from the Arrhenius equation:
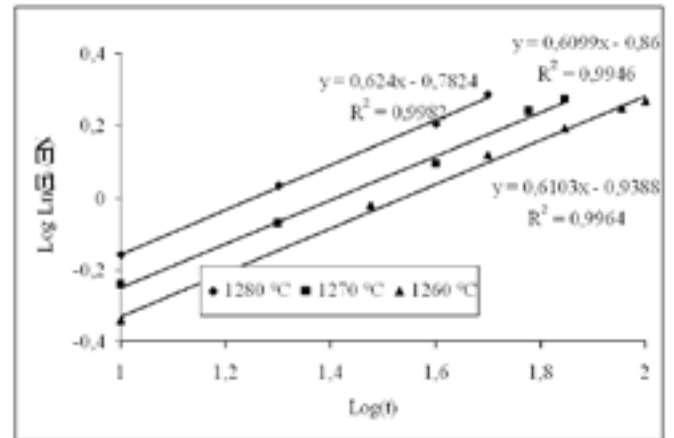
$$k_p = k_0 \exp (- E_a/RT) \qquad [13]$$

Fig. 2- Log (ln (ε_0(T)/ε(T))) vs. log (t) for the sample at different temperatures (experimental data) to evaluate the equation for kinetic parameters.

where :
k_0 is a constant
E_a is the apparent activation energy,
R is the gas constant
T is the absolute temperature

The values of the constant k_p, used in the plot of ln(k_p) versus 1/T (Arrhenius plot) which is the logarithmic form of the Arrhenius equation., are reported in figure 3. The values of kp increase by increasing the nepheline syenite content up to 10 % but higher nepheline syenite contents do not further affect the constant of the kinetic equation in the porosity formation kinetic. This phenomenon could be explained as the liquid phase, that fills the pores, is independent of the above 10 %. amount of nepheline syenite. The values of apparent activation energy are not so different for all the compositions and the activation energy increases when the mix contains nepheline syenite. This means that, as the flux content is greater, these compositions need a little more energy to form the liquid phase in comparison with the standard. The values of activation energy show a minimum when 10 % of nepheline syenite is used; this may be due to the eutectic point of this composition.

In Figures 4a and 4b the values of total porosity calculated by the kinetic model are plotted versus the experimental values of total porosity for the standard and for the added samples.

TABLE III. VALUES OF CONSTANTS AT DIFFERENT TEMPERATURES CALCULATED BY THE MODEL WHICH FITTED THE EXPERIMENTAL DATA AND ARRHENIUS PARAMETERS CALCULATED FROM THE PLOT.

Mix	T (°C)	Average n	Arrhenius parameters	
			A (min^{-1})	E_a (kJ/mol)
STD	1280			
	1270	0.62	1×10^{18}	572
	1260			
F1	1260			
	1250	0.83	6×10^{20}	645
	1240			
F2	1260			
	1250	0.94	1×10^{19}	591
	1240			
F3	1260			
	1250	1.08	3×10^{20}	634
	1240			

The agreement between the experimental and calculated data is good, indicating the validity of the kinetic model.

Obviously, the error of the model at the initial soaking time is higher than at the end of the sintering process because the rate of elimination of the porosity at beginning of the soaking time is much too high. Also, the value of initial porosity is not so different in this case.
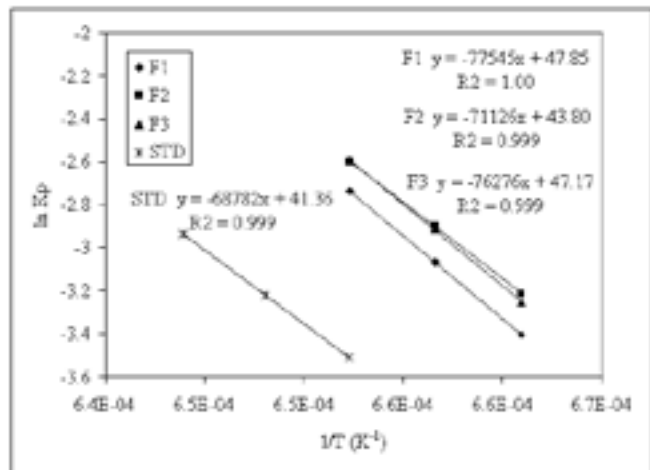

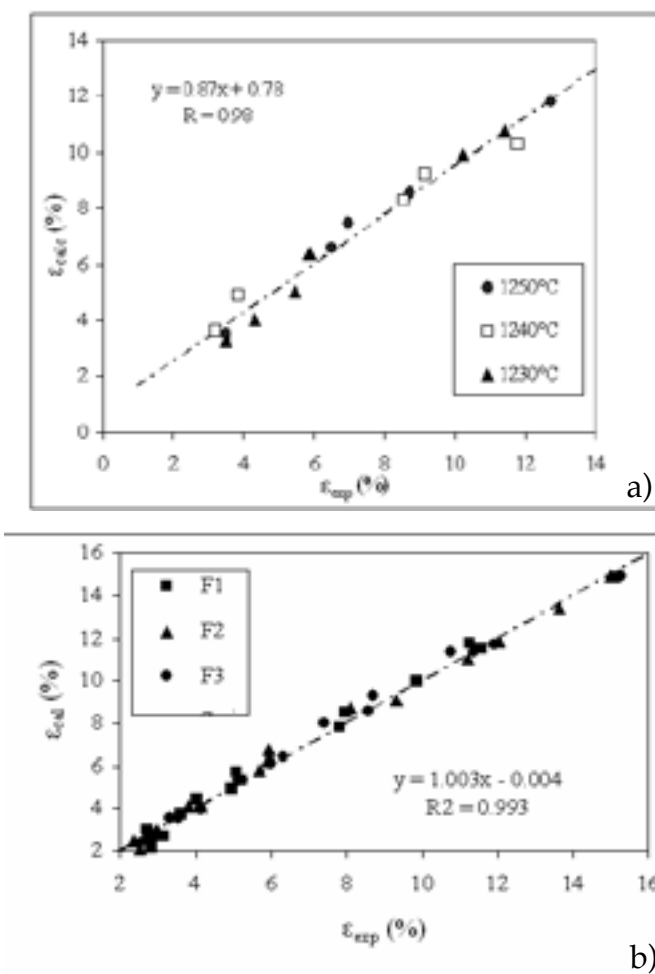Fig. 3- The equation evaluation to determine the parameters of Arrhenius equation.

Fig. 4- a) Relative porosity calculated from the model experimental one for the standard mix a three different temperatures; b) Relative porosity calculated from the model versus experimental one at 1260 ºC for the compositions used in this study.

4. CONCLUSIONS

The mechanism determining the elimination of porosity is characterized by capillary pressure and by the viscosity of the system that is controlled by the alkaline materials present.

A kinetic model is derived to express the variation in porosity of porcelain stoneware tile as a function of the soaking time and firing temperature. The model proposed is useful to determine the sintering conditions (soaking time) for porcelain stoneware tile mixes on the basis of the mix composition and firing temperature. The experimental data are in good agreement with the data obtained with the model so that it is possible to extrapolated data at different temperatures. It is so possible to estimate the proper soaking time to obtain minimum total porosity at a given firing temperature. The kinetic model is applied in the presence of different amount of nepheline and the results are very good in comparison with the experimental data so that the data of theoretical porosity are very similar to the experimental one.

The optimum soaking time is found to obtain minimum total porosity for each composition. In summary, nepheline, as expected, accelerate the sintering process, as it increases the value of n. In effect at constant temperature the soaking time is reduced by increasing the nepheline amount. Increasing activation energy by increasing flux amount is probably due to the greater quantity of flux which need a little more amount of energy to form the liquid phase.

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