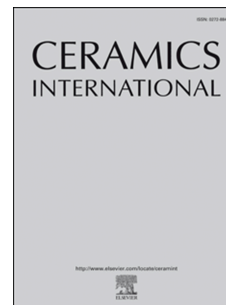


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Vitrification rate and estimation of the optimum firing conditions of ceramic materials from raw clays: A review

Eduardo Garzón^{a*}, Luis Pérez-Villarejo^b, Dolores Eliche-Quesada^c, Sergio Martínez-Martínez^{b,d}, Pedro J. Sánchez-Soto^d

^aDepartment of Engineering, University of Almería, 04120-Almería, Spain

^bDepartment of Chemical, Environmental and Materials Engineering, Higher Polytechnic School of Linares, University of Jaén, 23700-Linares, Jaén, Spain

^cDepartment of Chemical, Environmental and Materials Engineering, Higher Polytechnic School of Jaén, University of Jaén, 23071-Jaén, Spain

^dInstitute of Materials Science of Sevilla, Joint Center of CSIC (Spanish National Research Council) and University of Sevilla, 41092-Sevilla, Spain

*Corresponding author:

E-mail address: egarzon@ual.es (Prof. E. Garzón)

A B S T R A C T

The present work is a review concerning the previous investigations on the vitrification behaviour of clays containing kaolinite, feldspars, muscovite (illite/sericite) and pyrophyllite. These clays are silico-aluminous and have interesting properties as raw materials for structural ceramics. The mineralogical and chemical composition were determined. Then, the vitrification in these clay samples using pressed bodies was investigated by few researchers in the temperature range 800 - 1350 °C with 0.5 - 5.5 h of soaking times. The effect of heat treatments on the degree of vitrification in these clays was characterized by bulk densities of the ceramic bodies at the fired stage. It was found some variations of bulk density values for all these clays fired in the range 1000-1150 °C, with marked decreases of the values obtained at 1200 °C and 1300 °C. A first order reaction kinetics was applied to the analysis of vitrification of the ceramic bodies under isothermal heating. The method is based on experimental data of bulk densities, being proposed for the estimation of the relative degree of vitrification resulting from different firing schedules. The analysis considered the temperature dependence of the rate of vitrification following Arrhenius behaviour. Thus, the vitrification activation energy can be obtained. The activation energies for the physical process of vitrification in these clays ranged from 45 to 151 kJ/mol. The relative rates of vitrification or degree of vitrification attained during heating and soaking were calculated. The results suggested that the contribution of vitrification due to heating in all these clays was relatively small compared to the vitrification during soaking. However, it was evidenced that the influence of the particle sizes in the thermal behaviour of these clays cannot be neglected. The vitrification rate equations, as deduced in these previous studies, can be useful tools to estimate the optimum firing conditions of these clays, allowing the extension of this method to other clay types.

Keywords: clays, vitrification, activation energy, vitreous phase, ceramics, kaolinite, illite, pyrophyllite

1. Introduction

Vitrification is considered the result of heat treatment and fusion during which a glassy or non-crystalline phase is produced with a progressive reduction in the porosity [1-3]. The vitrification range is the temperature interval between the temperature at which a ceramic material begins to fuse and the temperature at which the ceramic begins to deform by melting [3]. Vitrification is considered complete when maximum density or zero porosity are achieved without deformation. The knowledge of the vitrification process using common kaolinite clays, as ceramic raw materials, is fundamental in ceramic processing of such as clays according to the great magnitude of consumption by the industry for tile and whiteware manufacture, in particular to achieve the optimum firing conditions. The effect of heat treatment on the degree of vitrification of ceramic bodies, in particular obtained by processing raw clays, can be characterized by important variations in physical properties, such as linear firing shrinkage (LFS, %), water absorption capacity (WAC, %), bulk density (BD, g/cm³), apparent (open) porosity (AP, %) and mechanical strength. There are some characteristic changes in these properties beyond the point of complete vitrification, as pointed out in previous works [1-7]: (1) WAC, AP and LFS increase and bloating effects of the ceramic bodies can be observed; (2) volume shrinkage ceases and swelling begins, as assumed by Bogahawatta and Poole [2], and (3) BD decreases and deformation begins.

Norris et al. [1] reported a method for the study of vitreous pottery bodies. These authors proposed the determination of the range curves starting from the raw materials. Then, with this method, it was possible to estimate the temperature of vitrification (T_v) or temperature where porosity becomes almost zero. As proposed by Bogahawatta and Poole [2], the point of complete vitrification was assumed to lie midway between incipient vitrification and fusion where critical changes in physical properties occur, as mentioned above. This was ascertained by the optima of physical properties when BD and volume contraction were at maxima values and AP was minimum. The optimum heat treatment was identified as coincident with the state of optimum properties. The evolution observed in experimental results of AP and BD were the most useful in identifying the optima precisely. Thus, a semiempirical approach to study the vitrification process has been reported [2]. The purpose of this approach was to establish optimum firing conditions for ceramic raw materials based on clays, in particular kaolinitic brick clays, based on kinetic features applied to the reactions

leading to the vitrification of these clays under isothermal heating. It is based on experimental observations of BD as a function of firing temperatures. Considering the temperature dependence of the vitrification rate, an Arrhenius analysis is involved in this approach. From these calculations, the vitrification activation energy can be obtained and the optimum firing conditions can be calculated. The optimum firing, according to Bohagawatta and Poole [2], refers to the extent to which a clay body must be fired in order to have an acceptable range of properties, such as strength and durability. These properties improve with the degree of heat treatment. The degree of vitrification, as the criterion for determining the optimum state of firing under isothermal heating, was considered in this previous investigation [2].

Monteiro and Vieira [4] proposed a model of close packed discs (diameter $< 2 \mu\text{m}$) and nanoscale thickness ($< 0.1 \mu\text{m}$) to explain a much more efficient the sintering process for clay minerals than the classical spherical particle model [5]. These authors studied the nanoscale solid-state sintering of kaolinite. Other authors, such as Khalfaoui et al. [6] studied the sintering of clay samples. They investigated the sintering mechanism and ceramic phases of an illitic-chloritic raw clay. Freyburg and Schwarz [7] studied structural ceramics showing the influence of the clay type on the pore structure and microstructural development. These authors considered a group of clayey raw materials (51 samples) of different geology. They distinguished four clay types: kaolinitic, illitic-kaolinitic, mixed layer clays containing expandable minerals and carbonate-containing clays. These authors found significant differences of sintering behaviour in these four clay types.

Concerning vitrification, Wattanasiriwech et al. [8] investigated the vitrification of an illitic clay ($\sim 23 \text{ wt.}\%$ illite, $\sim 41 \%$ kaolinite, $\sim 30 \text{ wt.}\%$ quartz) via phase and microstructural changes in the temperature range $800\text{-}1250 \text{ }^\circ\text{C}$. The densification should start around $900 \text{ }^\circ\text{C}$, being achieved at $1200 \text{ }^\circ\text{C}$. Illite in this clay sample is considered that acted as superb melting agent in the mixture upon elimination of pores in the matrix. The determination of the vitrification curve of stoneware tiles was studied by Melnick et al. [9] using a dilatometric method, with dwell time 1 h and $1100 \text{ }^\circ\text{C}$ as the final temperature. The samples were composed by a mixture of 50 mass % of clay-siltstone shale and capping siltstone. Kaolinite was predominant (49.8 mass %), with quartz (30.3 mass %), illite (10 mass %) and hematite (7.3 mass %). Lecomte-Nana et al. [10] investigated the sintering mechanisms of kaolin-muscovite mixtures (0-25 mass % muscovite). These authors used reference kaolin (sample KGa-1 from The Clay

Mineralogical Society, 96 mass % kaolinite) and a muscovite sample (Bihar, India, 99 mass % muscovite) as raw materials under non-isothermal conditions. They showed that the densification resulted of the same mechanism as the kaolin up to 1300 °C, and above this temperature up to 1500 °C, densification was also the consequence of dissolution limited liquid sintering, with an activation energy of less than 250 kJ/mol.

Other clay types, such as pyrophyllite and pyrophyllite clays with sericite and kaolinite, have been investigated several years as ceramic raw materials [11-17]. The sintering capacity of pyrophyllite and pyrophyllite raw materials was determined for quartz-pyrophyllite and quartz-sericite-pyrophyllite clays [11]. It has been investigated the influence of mechanical, by dry grinding, and thermal treatments on raw materials containing pyrophyllite and pyrophyllite clays, which contain kaolinite and sericite or illite [14]. Mukhopadhyay et al. [16, 17] investigated for the first time the effect of a raw pyrophyllite (with sericite/muscovite) on vitrification, mullitization and on physical properties of triaxial porcelain. Pyrophyllite was added as a replacement of china clay in a conventional whiteware ceramic body. It resulted in lowering its vitrification temperature. Several authors reported on the application of pyrophyllite clays, for instance in the processing of tubular ceramic for microfiltration membrane [18], diatomite-pyrophyllite porous membranes [19] and porous composites based on alumina-coated pyrophyllite [20]. The sintering temperatures were 1200 °C, 1300 °C and 1400 °C for 1h.

Palaeozoic weathered shales named as “Aluminum-clays” have also been investigated [21]. These clays contain kaolinite, muscovite mica (illite/sericite) and pyrophyllite, mixed with the marls traditionally used in Spanish structural ceramic production. The illite/sericite mica is very-fine grained (10-20 μm) and quartz is found in low relative proportion. Traditional ceramics used clays with high-illite content applied for the production of bricks, tiles, plates and stoneware tiles [22, 23]. However, vitrification analysis of such as clays has not been considered. In fact, sericite clays (without or with pyrophyllite) were proposed as new ceramic raw materials [24, 25]. According to their properties, these clays produce very high mullite content at relatively low firing temperatures, a very reactive glassy phase and an exceptional firing range [12, 13, 23-28]. Sericite has also been used to induce textural structures in the preparation of emulsion-templated high-porosity mullite ceramics, as demonstrated by Wang et al. [29]. According to this study, sericite acts both as a template and a sintering additive: it promotes the densification and mullitization of the matrix with formation of

mullite crystals in these ceramics. Hence, the use of sericite as a natural flux is interesting because the raw materials with higher sericite content and finer particle size provide very high mullite content at a comparatively low temperature (1000 °C or lower), with improvements in energy savings [24, 25].

Using the semi-empirical attempt to calculate heat treatment conditions using experimental observations of bulk density, as proposed by Bogahawatta and Poole [2], Faieta-Boada and McColm [3] performed a preliminary analysis of the thermal behaviour of an industrially used kaolinitic clay. Recently, the vitrification behaviour of pyrophyllite clays, containing sericite and kaolinite, has been studied using the same method [30]. It can be noted that all these clays have application as raw materials for structural ceramics. Thus, the aim of the present work is to review these previous investigations concerning the vitrification process of several kaolinitic clays, containing kaolinite, feldspars, muscovite (illite/sericite) and pyrophyllite. It is favoured that the same method was applied to the analysis of vitrification process in these clays. Then, all the results can be summarized, compared and discussed. From this analysis it can be obtained values of vitrification activation energy and equations of heat treatment with time, heating rate and temperature parameters for all these clays. They are established using a scientific method. These equations, as summarized in this work, are interesting because they are useful to calculate the optimum firing conditions when such as clay types are considered.

2. Materials and methods

2.1 Samples studied: mineralogical and chemical characteristics

The clays included in this study are described as follows:

(I) Two samples of kaolinitic clays of residual origin (Samples A and B), two samples of podzolic clays (Samples C and D) and a latosol (Sample E), as described by Bogahawatta and Poole [2]. According to these authors, these five clays represent the range of brick making clays in common use in Sri Lanka.

(II) An industrial Ecuadorian kaolin clay (ore from Ecuador), named as C-1 clay, as described by Faieta-Boada and McColm [3]. This kaolin clay is applied in the manufacture of ceramic whitewares and tiles.

(III) A sample of raw pyrophyllite clay (named as “Pizarrilla”, supplied by Alicún Prospecciones S.L.), as studied recently by Sánchez-Soto et al. [30]. This pyrophyllite clay is being studied with respect to its characteristics for applications in structural ceramics containing mullite.

Table 1 summarizes the mineralogical (Table 1a) and chemical (Table 1b) data of all these clay samples [2, 3, 30]. Samples A-E are similar in mineralogical composition, with variations in the percentages of kaolinite and feldspars being the percentage of quartz the same [2]. The sample of Ecuadorian clay contains ~ 35 wt.% of kaolinite (disordered kaolinite), with quartz plus cristobalite and feldspars (albite-orthoclase) in similar proportion [3]. Finally, the pyrophyllite clay contains kaolinite, quartz, illite/sericite and pyrophyllite as the main mineral phases deduced by X-ray diffraction [30]. Table 1b includes the RO, R₂O and the total flux content calculated from the chemical data for all these clay samples. However, chemical data of Ecuadorian clay sample C-1 were not reported [3]. It was relevant to indicate that, in sample A, if RO is the sum of CaO + MgO and R₂O is the sum of Na₂O to K₂O, the values of these parameters are 2.86 and 0.73 and the total flux content is 21.43 %.

The chemical analysis of the pyrophyllite clay was determined in a previous paper [30] using atomic absorption spectrometry taking into account the problems of pyrophyllite determination in mineral samples using acid mixtures [31, 32]. The total flux content for the pyrophyllite clay is 4.18 wt.%, as calculated from the chemical data [30]. From these results, the value found in this sample is the lower as compared to those reported for Samples A-E. The total flux content of all these clay samples ranges from 4.18 to 26.76 wt.%.

2.2 Preparation of samples for firing experiments

As described by Bogahawatta and Poole [2], samples A-E were ground to pass a 125 µm sieve. They were dried to a pre-pressing moisture content of ~ 10 wt.%. The clay powders (~ 8 g each) were then isostatically pressed using a hydraulic press at 500 psi (i.e., 3.44 MPa). After oven-drying at 110 °C/24 h, the pressed samples were fired in an electric furnace in air at temperatures from 1025 to 1100 °C at a heating rate of 5.6 °C/min (i.e., 336 °C/h). The intervals between the different firings was a temperature of 25 °C. Depending on the characteristics of each clay sample, a range of soaking times at peak temperatures from 0.5 to 5.5 h was selected. After the completion of firing trials,

the properties which determine the degree of vitrification of fired specimens, in particular bulk density (in g/cm^3), were measured in accordance with British Standards (or American Society for Testing of Materials, ASTM) specifications as mentioned by Bogahawatta and Poole [2].

For the analysis of vitrification behaviour of Ecuadorian clay [3], the clay was ground mechanically for one and a half hours. Samples of the ground clay (with 8 % moisture) were pressed in a hydraulic press at 283 MPa and dried at 110 °C/24 h. The pressed samples were subjected to a range of heat treatments up to the desired temperature in the range 1025 to 1375 °C for soaking periods of 1-4 h. The heating rate was 5 °C/min (i.e., 300 °C/h). Bulk densities of fired samples were determined following the ASTM method [3].

Finally, pressed samples of powdered pyrophyllite clay [30] were obtained at 150 MPa using dry pressing (~ 30 g of powder moisturized with ~ 5 wt.% of deionized water). First of all, these samples were air-dried (24 h) and secondly dried at 60 °C/4 h. The dried samples were heated to several temperatures in the range 800-1500 °C using an electric laboratory furnace in air. However, the heating rate was higher than in the case of precedent samples. It was 8 °C/min (i.e., 480 °C/h) with 0.5-5 h of soaking times at each temperature. Then, the samples were cooled under the furnace up to 200 °C and stored in an oven at 110 °C. The determination of bulk density (in g/cm^3) was performed following the Spanish method proposed for this test, as previously described [24, 26, 33, 34].

2.3 Vitrification analysis

A first order kinetic model reported using kaolinite [35] was applied to the reactions leading to the vitrification of all these clays. The details of the procedure have been described [2]. A summary is as follows.

The temperature dependence of the rate of vitrification can be expressed by the Arrhenius equation as:

$$k = A \exp (-E_a/RT) \quad (1)$$

where k is the rate of reaction (rate of vitrification in the present study), A is a constant (pre-exponential factor or frequency factor), E_a is the activation energy (vitrification

activation energy), R is the gas constant and T is the absolute temperature. The logarithmic form of the equation for k is:

$$\ln k = - (E_a/RT) + \ln A \quad (2)$$

Redfern [35] studied the thermal decomposition of kaolinite (a purified kaolinite sample supplied by English China Clay Ltd.). This author showed that the time required to attain a certain degree of vitrification (t) under isothermal conditions is proportional to $1/k$, i.e., $t=c/k$ where c is a constant. Therefore, from equation (1)

$$\ln t = (E_a/RT) - \ln A' \quad (3)$$

where the value of the new constant A' is A/c . Consequently, a plot of $\ln t$ versus $1/T$ gives E_a/R as the slope.

The equation (2) can be rearranged as:

$$\ln (k_1/k_2) = E_a/R [(1/T_2) - (1/T_1)] \quad (4)$$

where k_1 and k_2 are the rates of vitrification at temperatures T_1 and T_2 , respectively.

The rate of vitrification of a kaolinitic clay at a temperature above 850 °C (or incipient vitrification) relative to that at 850 °C [2] was considered to be a measure of the overall rate of vitrification at that particular temperature. Therefore, if k_t is the rate of vitrification of the kaolinitic clay at t °C relative to that 850 °C (1123 K), i.e., if $k_1 = k_t$ and $k_2 = k_{850} = 1$, the equation (4) reduces to

$$\ln k_t = E_a/R [(1/1123) - (1/t + 273)] \quad (5)$$

Isothermal firing trials of the clays containing kaolinite can be performed at different temperatures by varying the soaking period. Bogahawatta and Poole [2] selected four temperatures (1025, 1050, 1075 and 1100 °C). The soaking periods, which correspond to the optimum degree of vitrification as shown by the critical changes in properties, were used in the construction of $\ln t$ -reciprocal temperature or equation (2) plots. Then, the exponential factor determined for the plot was used in equation (3) to calculate the relative rates of vitrification at different firing temperatures.

If k_t is the relative rate of reaction (degree of vitrification) of a kaolinitic clay body at t °C, then the degree of vitrification attained during heating (V_{heating}), according to [2], is given mathematically by

$$V_{\text{heating}} = \int_{h_0}^h k_t dh \quad (6)$$

where h denotes time and $h-h_0$ is considered the time interval during which temperature was raised from T_0 (1123K) to the maximum firing temperature T (K) at a constant rate. This also represents the curvilinear area under the k_t -time diagram, as represented in Figure 1.

The degree of vitrification attained during soaking according to [2] is given by

$$V_{\text{soaking}} = k_t \cdot h_s \quad (7)$$

where h_s is the soaking time.

The overall degree of vitrification (V_{total}) attained during heat treatment of the clay body, according to a fixed firing schedule [2], is thus given by

$$V_{\text{total}} = V_{\text{heating}} + V_{\text{soaking}} \quad (8)$$

Thus, the optimum firing conditions of the raw clays can be estimated. As pointed out by Bogahawatta and Poole [2], the optimum heat treatment was identified as coincident with the state of optimum properties, being observed that apparent (open) porosity and bulk density were the most useful in identifying the optima precisely. However, the heat treatment exceeding an optimum value will produce a deterioration of bulk density. Fortunately, the temperatures of soaking of all the clay samples, previously studied concerning optimum firing conditions, were in the range 1025-1100 °C [2], 1050-1150 °C [30] and 1225-1325 °C [3].

3. Results and discussion

Figures 2 and 3 show the effects of isothermal soaking on the bulk density of fired clay samples: samples A-E from Bogahawatta and Poole [2] and pyrophyllite clay

from Sánchez-Soto et al. [30], respectively. For all these clay samples the onset temperature of vitrification process was considered 850 °C. In the case of Ecuadorian kaolin clay C-1 from Faieta-Boada and McColm [3], the resultant values were of the same order of magnitude although the onset temperature of the vitrification process was considered by these authors at 1025 °C (1298 K).

From these results studying the evolution of bulk density in the range 1025-1100 °C for samples A-E (Figure 2), it can be observed that samples A and B, two kaolinitic clays of residual origin (Table 1a), show a few differences in bulk density evolution with soaking period (Figure 2, A and B), with higher values of bulk density for sample B. However, samples C and D, two podzolic clays (Table 1a), show a similar trend in the values of bulk density as a function of soaking period (Figure 2, C and D). Finally, sample E, a latosol (Table 1a) with minor content of kaolinite and feldspars, shows an evolution very distinct of bulk density (Figure 2 E) as a function of soaking period, as compared with those observed in precedent samples A-D (Figure 2 A-D). Increasing the soaking period produced an increase in bulk density, being marked the changes as the beginning of the vitrification range was approached.

Similar trends were observed when other physical properties are considered [2, 30]. For instance, concerning the pyrophyllite clay sample [30], it was observed an increase of % LFS as increasing firing temperature up to a maximum value of ~ 3 % at 1200 °C after 4 h of soaking. The fired sample shows a progressive decrease of LFS from 1200 °C up to 1400 °C with 4 h of soaking at each temperature. At the same time, WAC (in %) decreased from a value of 12 % at 800 °C to 3.2 % at 1200 °C with soaking time of 4 h and reached 0.94 % at 1300 °C/1h with an increase to ~ 3 % after firing at 1300 °C/4h. The evolution of apparent porosity (AP) according to this previous investigation [30] showed a progressive decrease from ca. 24.5 % at 1000 °C to ~ 5 % at 1300 °C after 4 h of soaking at each temperature.

In general, taking into account the mineralogical and chemical composition of the clays (Table 1), the properties changed slightly until an optimum soaking period at which the reversal of properties occurred. It is observed at low temperatures, 1025-1050/1100 °C in samples A-E [2] and pyrophyllite clay sample [30], and at relatively higher temperatures, 1225-1350 °C, in Ecuadorian kaolinitic clay C-1 [3]. Increasing the soaking period (higher than 1.5 - 2 h) produced an increase in bulk density and a decrease in apparent (open) porosity. It is associated to an increased amount of glass, liquid at increasing temperature, and pores of the ceramic body are progressively

closing. At relatively higher temperatures (1075-1100 °C and higher) the properties changed rapidly at the optimum soaking period was approached. However, heat treatments exceeding the optimum produced a marked deterioration of properties, as showed Figures 2 and 3.

The results of Figure 3 show the effect of isothermal soaking (0.5-5 h) on the bulk density of the pyrophyllite clay. Increasing the soaking period produced an increase of bulk density values. Bulk density increases up to a maximum of $\sim 2.5 \text{ g/cm}^3$ at 1200 °C/4h. At 1150 °C with 3 h of soaking time, the bulk density of the ceramic body obtained after this thermal treatment is $\sim 2.4 \text{ g/cm}^3$. A fast decrease can be observed up to $\sim 1.7 \text{ g/cm}^3$ at 1300 °C/4h. Taking into account these results, it can be deduced that after firing at 1200-1300 °C for 1 h, this pyrophyllite clay is completely vitrified. In fact, there is a trend for samples fired at 1000 - 1150 °C showing slight increases of bulk density values of the ceramic bodies, but in samples fired at 1200 °C and 1300 °C there is a marked decrease of these values as increasing soaking times.

It should be noted that Norrish et al. [1], examining vitreous ceramic bodies, considered two experimental parameters: (a) T_v or vitrification temperature, defined as the temperature (determined by the range curves) at which the apparent porosity becomes almost zero, and (b) T_d or temperature for maximum bulk density. It has been deduced from previous results using the pyrophyllite clay sample [30] that $T_v \sim 1300 \text{ °C}$ and $T_d \sim 1200 \text{ °C}$ (Figure 3). However, in the case of samples A-E and Ecuadorian clay C-1 it was not possible to find these experimental parameters because the evolution of apparent porosity as a function of firing temperature was not reported [2, 3]. Furthermore, the effect of soaking time cannot be rejected (Figures 2 and 3).

The analysis of optimum firing conditions assumes the rate of vitrification relative to that of 850 °C (k_r). Then, isothermal firing trials can be performed at different temperatures by varying the soaking period, as described in methods. The soaking period corresponding to the optimum degree of vitrification, as observed by the critical changes in characteristic properties such as bulk density (Figures 2 and 3), can be used to the construction of \ln (optimum soaking period) against the reciprocal temperature or equation (2) plots. The slopes of the straight lines can be used to estimate the optimum firing conditions for these clays. The exponential factor calculated for the plot is used in equation (3) to determine the relative rates of vitrification at different firing temperatures. Hence, from the results presented in Figures 2 and 3, the plot of $\ln t$ versus

$1/T$ gives E_a/R as the exponential factor and, hence, the E_a values or vitrification activation energy for each clay sample.

Taking into account the exponential factor E_a/R determined from the $\ln t$ versus $1/T$ plot (Figures 4-6), the equations presented in methods allow estimate the relative rate of reaction and the degree of vitrification of the clay samples. According to Bogahawatta and Poole [2], these experimental points deviate from linearity at high temperatures due to non-isokinetic behaviour [35]. The equations deduced in each case are presented as follows.

In the case of samples A-E, according to Bogahawatta and Poole [2], the relative degree of vitrification for each stage of firing (heating) is calculated using equation (6) as follows:

$$V_{\text{heating}} (\text{sample A}) = e^{16.22}/[e^{18.214/(t+273)}] \quad (9)$$

$$V_{\text{heating}} (\text{sample B}) = e^{7.95}/[e^{8.928/(t+273)}] \quad (10)$$

$$V_{\text{heating}} (\text{sample C}) = e^{11.45}/[e^{12.857/(t+273)}] \quad (11)$$

$$V_{\text{heating}} (\text{sample D}) = e^{10.18}/[e^{11.428/(t+273)}] \quad (12)$$

$$V_{\text{heating}} (\text{sample E}) = e^{9.86}/[e^{11.071/(t+273)}] \quad (13)$$

In the case of pyrophyllite clay [30], the relative degree of vitrification for each stage of firing (heating) is calculated from:

$$V_{\text{heating}} (\text{pyrophyllite clay}) = e^{4.828}/[e^{5.422/(t+273)}] \quad (14)$$

In the case of Ecuadorian clay C-1 [3], the relative degree of vitrification for each stage of firing (heating) is calculated from

$$V_{\text{heating}} (\text{Ecuadorian clay C-1}) = e^{13.23}/[e^{17.171/(t+273)}] \quad (15)$$

These equations show the temperature dependence of the rate of vitrification (theoretical rate equation) for all the clays giving a measure of the degree of vitrification attained during heating.

The calculations can be simplified using an empirical rate equation, as deduced by Bogahawatta and Poole [2]. Then, in the case of sample A, the exponential form is:

$$k_t (\text{sample A}) = e^{0.012rh} \quad (16)$$

with r = constant rate (°C/h) and h = heating time above 850 °C.

For samples B – E, the exponential forms are:

$$k_t (\text{sample B}) = e^{0.06rh} \quad (17)$$

$$k_t (\text{sample C}) = e^{0.08rh} \quad (18)$$

$$k_t (\text{sample D}) = e^{0.0076rh} \quad (19)$$

$$k_t (\text{sample E}) = e^{0.0073rh} \quad (20)$$

In the case of pyrophyllite sample [30], the exponential form of the simplified rate equation is:

$$k_t (\text{pyrophyllite clay}) = e^{0.0058rh} \quad (21)$$

In the case of Ecuadorian clay sample [3], the empirical rate equation can be expressed as:

$$k_t (\text{Ecuadorian clay C-1}) = e^{0.0085rh} \quad (22)$$

Bogahawatta and Poole [2] demonstrated, by simple calculations, that the degree of vitrification predicted from the empirical equations described above resulted slightly lower than that calculated using the exact rate equation over the range of temperatures between 850 and 1075 °C.

The relative degree of vitrification resulting from soaking can be obtained multiplying the rate of vitrification at the maximum temperature of firing by the soaking time. The procedure for these calculations involves two steps:

(a) calculation of the degree of vitrification resulting from heating (V_{heating}), by integration of the empirical rate equation in each clay sample (within the required limits and constant rate), and

(b) calculation of the degree of vitrification resulting from soaking (V_{soaking}), using the rate of vitrification at the maximum temperature of firing obtained by the exact rate equation when multiplied by the soaking period according to equation (6).

As an example, in the case of sample A, according to [2], the relative degree of vitrification for each stage of firing (vitrification) is calculated from:

$$V_{\text{soaking}} (\text{sample A}) = \{e^{16.22}/[e^{18.214/(t+273)}]\} \cdot h_s \quad (23)$$

and similarly for samples B- E.

In the case of pyrophyllite clay [30], it is calculated from:

$$V_{\text{soaking}} (\text{pyrophyllite clay}) = \{e^{4.828}/[e^{5.422/(t+273)}]\} \cdot h_s \quad (24)$$

In the case of Ecuadorian clay C-1 [3], the relative degree of vitrification for each stage of firing (vitrification) is calculated from:

$$V_{\text{soaking}} (\text{Ecuadorian clay}) = \{e^{13.23}/[e^{17.171/(t+273)}]\} \cdot h_s \quad (25)$$

Then, the sum of these two partial degrees of vitrification gave the total degree of vitrification or overall degree of vitrification calculated by equation (7).

Table 2 includes the results of calculations of degree of vitrification for sample A, as an example [2], pyrophyllite clay [30] and Ecuadorian clay C-1 [3] subjected to various heat treatments. The total relative degree of vitrification is the sum of contribution of heating and soaking. Then, it can be calculated the percentage of contribution of heating to overall vitrification. From these results, it can be deduced that the contribution of vitrification due to the heating was relatively small compared to vitrification during soaking. Furthermore, it can be observed that sample A shows the higher degree of vitrification achieved by the heat treatment at 1050 °C with a soaking

period of 4 h. Then, the ceramic bodies obtained under these conditions had superior physical properties as compared to those subjected to other forms of heat treatments [2]. The highest degree of vitrification is achieved by heat treatment at 1100-1150 °C with 3-3.5 h for pyrophyllite clay. Finally, the highest degree of vitrification is achieved by the 1325 °C heat treatment with 2 h for Ecuadorian sample C-1. In this sample, the vitrification is considered that begins at 1025 °C [3], as mentioned above.

The degrees of vitrification calculated using the data for all the clays (samples A-E, pyrophyllite clay and Ecuadorian clay C-1) subjected to experimental firing schedules [2, 3, 30] is summarized in Table 3. The soaking periods at the maximum firing temperatures (Figures 2 and 3) are included. The temperatures of soaking of all these clay samples were in the range 1025-1100 °C [2], 1050-1150 °C [30] and 1225-1325 C [3]. It is remarked that, according to the investigation of Bogahawatta and Poole [2], the most favourable heat treatment for attaining the highest degree of vitrification and, therefore, the maximum mechanical strength for the sample clays B, C and E is accomplished at 1075 °C. For sample clays A and D a heat treatment at 1050 °C for 4 h seems adequate. The sample B attained near optima properties at 1025 °C and, hence, firing above 1025 °C is unproductive. Bogahawatta and Poole [2] indicated that since the contribution of heating to the overall degree of vitrification is small at all temperatures of firing (Table 2), the order or error involved in the assessment of the total degree of vitrification is relatively insignificant. The same consideration can be plausible for the other clays.

It should be noted that, according to Faieta-Boada and McColm [3], there is a very large experimental effort to achieve data for a vitrification equation, being confirmed the usefulness of the method firstly proposed [2]. These authors concluded that the proposed equations allow the most favourable heat treatment regime to be determined for each clay to optimize vitrification. The equations may also be used to determine any two of the three variables: (a) maximum firing temperature, (b) soaking period and (c) rate of heating. Then, it can be achieved a required degree of vitrification and, hence, mechanical strength.

For a more complete discussion, and as source of criticism, a factor of influence must be considered. It was not studied in previous investigations [2, 3]. It is the particle size, being reported only several data in the case of pyrophyllite clay sample [30]. For this sample, the values reported indicated 62 wt.% of 50 - 2 µm fraction and 21.8 wt.% of < 2 µm fraction, with the complete description of distribution of particle sizes. For

the other samples, only a few indications were mentioned: (a) In reference [2], the clay samples were ground to pass a 125 μ m sieve; (b) in reference [3], the clay sample was ground mechanically for one and half hours. However, the influence of this factor in the vitrification behaviour cannot be neglected and further studies will be necessary.

On the other hand, taking into account the mineralogical results of all these clay samples (Table 1a), there appears to be no direct relation between their mineralogical composition and their firing behaviour. However, it is clear that vitrification is produced by the increasing amount of liquid phase, which will produce the glassy or vitreous phase after cooling the ceramic bodies. The vitreous phase produced in these clays is liquid at high temperatures [6, 27, 28, 36-38] and almost all the oxides distinct of silica and alumina (Table 1b) are forming this phase. In the case of clay-based ceramics, such as triaxial whiteware bodies, the feldspars melt by progressive heating and dissolves fine quartz grains, increasing the liquid's Si content and, hence, its viscosity [38]. The presence of fluxes (see Table 1) influences the thermal behaviour, producing a vitreous or glassy phase, which is liquid from 985 °C (eutectic) [36, 37]. Thus, the incipient vitrification at 850 °C is a good approach in the method proposed by Bogahawatta and Poole [2]. Furthermore, the predictions deduced from the $K_2O-Al_2O_3-SiO_2$ ternary phase diagram [24, 36-39] are, in general, in agreement with the observed thermal behaviour of these clays because they are silico-aluminous. It was already discussed in previous investigations on thermal behaviour of sericite clays as precursors of mullite materials [27] and studies on the effect of vitreous phase on mullite and mullite-based composites obtained from sericite clays and kaolinite [28]. A greater amount of liquid by heating, i.e. glassy or vitreous phase, will be produced if several components, such as Na_2O , TiO_2 , Fe_2O_3 , CaO and MgO , considered as RO and R_2O , are also present besides SiO_2 and Al_2O_3 as showed in Table 1b. In the other clay samples, except pyrophyllite clay [30], the contents of SiO_2 and Al_2O_3 were not reported [2, 3]. Thus, in the present study there is a total flux content in the range 4.18 – 21.43 wt.%, being higher for sample A and the lowest for the pyrophyllite clay sample.

Table 4 summarizes the results of activation energies for the physical process of vitrification in these clays and the total flux content (data from Table 1b). Vitrification activation energies for all these clay samples range from 45 to 151 kJ/mol. The value reported for the Ecuadorian clay C-1 (143 kJ/mol) is in the range of 74 – 151 kJ/mol reported by sample clays A-E [2]. However, the lower value of E_a (45 kJ/mol) was determined for the isothermal data of pyrophyllite clay sample [30], being the sample

with the lowest value of total flux content (4.18 wt.%, Table 1b). It can be remarked that there is not any relation between E_a and the total flux content. As pointed out by Faieta-Boada and McColm [3]: “the activation energy of vitrification may bear no relation to any specific kinetic chemical process. It is in fact a kinetic physical process and is related to capillary and liquid phases present, liquid viscosities and their changes, etc.”. In fact, these authors suggested, by comparison, that the controlling mechanism of vitrification is simply one of viscous flow [2]. Finally, as pointed out by the previous studies on this subject [2, 3], the vitrification rate equations, better as semi-empirical firing equations, can be useful tools for clay manufacturers to calculate the optimum firing cycles.

4. Summary and conclusions

Clays containing kaolinite, feldspars, muscovite (illite or sericite) and pyrophyllite have interesting properties as raw materials for structural ceramics. The present work reviewed the previous investigations on the vitrification of such as clays, considering two kaolinitic clays of residual origin, two podzolic clays, one latosol, one industrial kaolinitic clay, besides a clay containing kaolinite, muscovite (illite or sericite) and pyrophyllite [2, 3, 30]. The mineralogical and chemical composition of these clays were summarized (Table 1). Thus, the kaolinitic nature of all these clays was evidenced and their silico-aluminous characteristics. The total flux content of these samples, using the chemical data, ranges from 4.18 to 26.76 wt.%.

The vitrification process of all these clay samples, as a first approximation, was studied using a method previously described in the literature for kaolinitic clay samples [2]. The method considered an Arrhenius approach under isothermal conditions, based on the temperature dependence of the vitrification rate, and assuming a first order kinetic, as studied using pure kaolinite [35]. It was a semiempirical attempt to analyse vitrification in kaolinitic clays. The method started on experimental data of bulk densities obtained by firing of the clays under isothermal heating. The vitrification in the clay samples was investigated in the range 800 - 1350 °C with 0.5 - 5.5 h of soaking times. It was found variations of bulk density values for all these clays fired in the range 1000-1350 °C, with marked decreases of the values for the samples fired at 1200 °C and 1300 °C. Thus, the activation energies for the physical process of vitrification in these clays or vitrification activation energy (E_a) can be obtained assuming first order kinetic.

The values obtained of E_a range from 45 to 151 kJ/mol with differences in the whole of these clays. The lower value (45 kJ/mol) can be associated to the lower value of total flux content (4.18 wt.%), being obtained for the pyrophyllite clay sample with ~ 15 % kaolinite and ~ 35 % of pyrophyllite [30]. The vitrification in these clay samples follows an Arrhenius behaviour suggesting, by comparison, a viscous flow as the controlling mechanism as proposed in a previous investigation on a kaolinitic clay sample [3].

The relative rates of vitrification or degree of vitrification attained during heating and soaking period were calculated using the theoretical equations or, alternatively, a simplified empirical rate equation. Thus, it was determined the overall degree of vitrification attained during heat treatment of all these clay samples according to a fixed firing schedule. The results allow conclude that the contribution of vitrification due to heating in all these clays was relatively small compared to the vitrification during soaking. Then, it is deduced from these investigations along time (1991, 1993 and 2021) a better knowledge of the characteristics of vitrification of kaolinitic and pyrophyllitic clays applied as ceramic raw materials.

It can be concluded the utility of this scientific methodology to look for the optimum firing conditions. Thus, the vitrification rate equations, as deduced in these previous studies [2, 3, 30] and summarized in this paper, can be useful tools to estimate the optimum firing conditions of these kind of kaolinitic and pyrophyllitic clays applied as ceramic raw materials. It is important to remark the interest of this method, allowing its extension to other clay types applied in the ceramic industry, such as chloritic-kaolinitic clays and smectite-kaolinite clays. These will be matter for future studies.

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Figure captions

Figure 1.- Schematic representation of the reaction rate – time of firing dependence for the clay samples A - E, as described by Bogahawatta and Poole [2]. Adapted from reference [2].

Figure 2.- Variation of bulk density with soaking period (0.5 – 5.5 h at different temperatures (1025 – 1100 °C) for the clay samples A, B, C, D and E (adapted from reference [2]).

Figure 3.- Variation of bulk density with soaking period (0.5 - 5 h) at different temperatures (1000 - 1300 °C) for the pyrophyllite clay sample (adapted from reference [30]). The values of soaking period at the maximum value of bulk density, t (máx), obtained at each temperature following the model proposed in reference [2] are indicated in the insert.

Figure 4.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the clay samples A – E following the isothermal kinetic model (adapted from reference [2]). The correlation coefficients of the straight lines are in the range 0.984-0.997.

Figure 5.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the pyrophyllite clay sample following the isothermal kinetic model (adapted from reference [30]). The correlation coefficient of the straight line is 0.9980.

Figure 6.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the Ecuadorian clay sample C-1 following the isothermal kinetic model (adapted from reference [3], but the correlation coefficient of the straight line was not provided).

Table 1 (a). Mineralogical data of the clay samples: K = Kaolinite; Q = Quartz; F = Feldspars; I = Illite; Py = Pyrophyllite.

Sample	% K	% Q	% F	% I	% Py
A*	>30	>30	15-30	-	-
B*	>30	>30	15-30	-	-
C*	15-30	>30	5-15	-	-
D*	15-30	>30	5-15	-	-
E*	5-15	>30	5-15	-	-
Ecuadorian Clay C-1**	30-35	30-35 ⁺	30-35 ^x	-	-
Pyrophyllite clay***	15	20	<5	25	35

Table 1 (b). Chemical data of the clay samples: Total Flux Content = RO + R₂O + Fe₂O₃ + TiO₂; RO = CaO + MgO; R₂O = K₂O + Na₂O; NR = Not Reported.

Sample	Total Flux Content (%)	RO (%)	R ₂ O (%)
A*	21.43	2.86	0.73
B*	20.17	1.72	0.40
C*	16.31	1.25	1.58
D*	15.37	0.96	1.49
E*	16.45	0.91	1.23
Ecuadorian Clay C-1**	NR [§]	NR	NR
Pyrophyllite clay***	4.18	0.24	1.75

*Bogahawatta and Poole [2]

** Faieta-Boada and McColm [3]

⁺ Quartz and Cristobalite, according to [3].

^x Albite-Orthoclase Feldspar, according to [3].

*** Sánchez-Soto et al. [30], using the chemical data of calcined sample (in wt. %) with SiO₂ = 63.17; Al₂O₃ = 32.45; Fe₂O₃ = 0.68; TiO₂ = 1.51; MgO = 0.18; CaO = 0.06; Na₂O = 0.25; K₂O = 1.50, then RO = CaO + MgO = 0.06 + 0.18 = 0.24, R₂O = Na₂O + K₂O = 0.25 + 1.50 = 1.75, and Total Flux Content = 4.18.

[§] Taking into account the mineralogical content of samples A and B, which are very similar to the Ecuadorian Clay C-1, the Total Flux Content for this clay sample could be estimated in the range 21.43-20.17 %.

Table 2.- Results of calculation of degree of vitrification for sample A [2], Pyrophyllite clay [30] and Ecuadorian clay C-1 [3] subjected to various heat treatments.

Maximum firing temperature (°C)	Soaking period-hs (h)	Calculated Relative degree of vitrification Heating (arb. units)	Calculated Relative degree of vitrification Soaking (arb. units)	Total relative degree of vitrification* (arb. units)	% Contribution of heating to overall vitrification**
SAMPLE A					
1025	5.0	1.8	44.6	46.4	3.9
1050	4.0	2.4	46.4	48.8	4.9
1075	3.0	3.3	45.1	48.4	6.8
1100	1.5	4.7	28.9	33.6	14.0
PYROPHYLLITE CLAY					
1050	4	1.2	8.3	9.5	12.6
1100	3.5	1.4	8.4	9.8	14.6
1150	3	1.7	8.3	10	17
ECUADORIAN CLAY C-1					
1225	4	2.2	23.4	25.6	2.2
1250	3	2.7	21.2	23.9	11.2
1275	3	3.3	25.4	28.7	11.5
1300	2	4.1	20.2	24.3	16.8
1325	2	5.0	24.0	29.0	17.2

* $V_{total} = V_{heating} + V_{soaking}$

** Data from references [2] and [30] and calculated by the present authors for Ecuadorian clay C-1.

Table 3.- Degree of vitrification for the clay samples subjected to various heat treatments (soaking period at the maximum firing temperature is given in parenthesis). Results of samples A-E from reference [2]; Ecuadorian clay sample C-1 from reference [3] and pyrophyllite clay from reference [30].

Maximum Firing Temperature (°C)	A	B	C	D	E	Ecuadorian Clay C-1	Pyrophyllite clay
1025	46.4 (5.0)	14.0 (4.5)	23.4 (5.0)	18.9 (4.5)	21.8 (5.5)	-	-
1050	48.8 (4.0)	14.4 (4.0)	24.2 (4.0)	20.0 (4.0)	21.9 (4.5)	-	9.5 (4.0)
1075	48.4 (3.0)	14.6 (3.5)	25.4 (3.5)	19.5 (3.25)	22.5 (4.0)	-	-
1100	33.6 (1.5)	8.1 (1.5)	14.5 (1.5)	11.8 (1.5)	12.7 (1.75)	-	9.8 (3.5)
1150						-	10 (3.0)
1225						25.6 (4)	
1250						23.9 (3)	
1275						28.7 (3)	
1300						24.3 (2)	
1325						29.0 (2)	
1350						29.2 (2)	

Table 4.- Summary of results of vitrification activation energies (E_a in kJ/mol) for the clay samples and total flux content. Samples A-E from Bogahawatta and Poole [2], Ecuadorian Clay C-1 from Faieta-Boada and McColm [3] and Pyrophyllite clay from Sánchez-Soto et al. [30]. NR = Not Reported (from the results presented in Table 1, the total flux content in this sample could be estimated in the range 21.43-20.17 %).

Sample	E_a (kJ/mol)	Total Flux content (wt. %)
A	151	21.43
B	74	20.17
C	107	16.31
D	95	15.37
E	92	16.45
Ecuadorian Clay C-1	143	NR
Pyrophyllite Clay	45	4.18

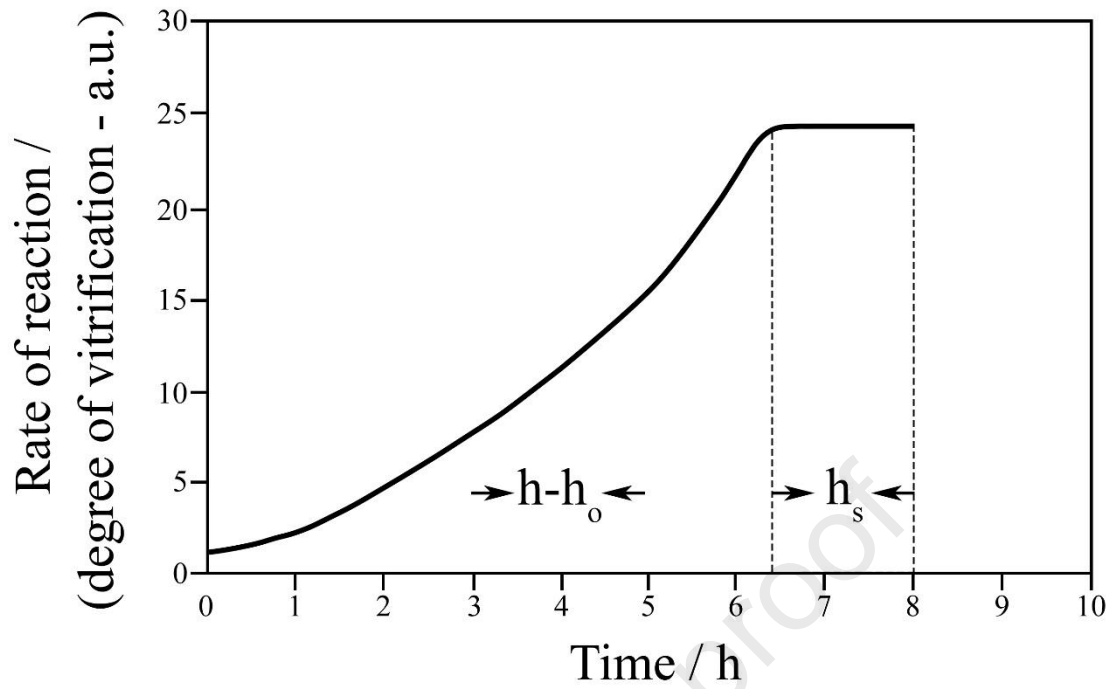
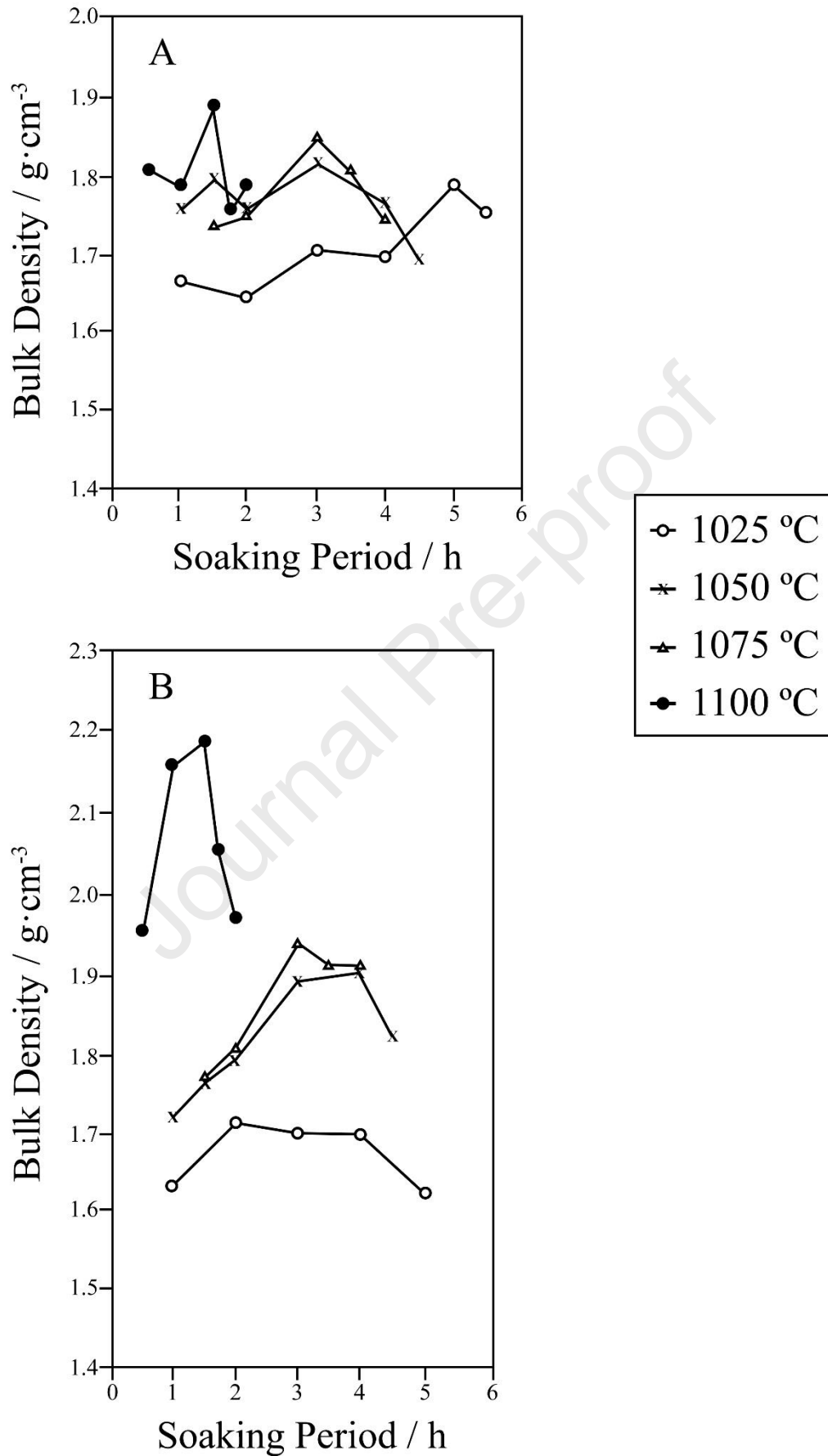
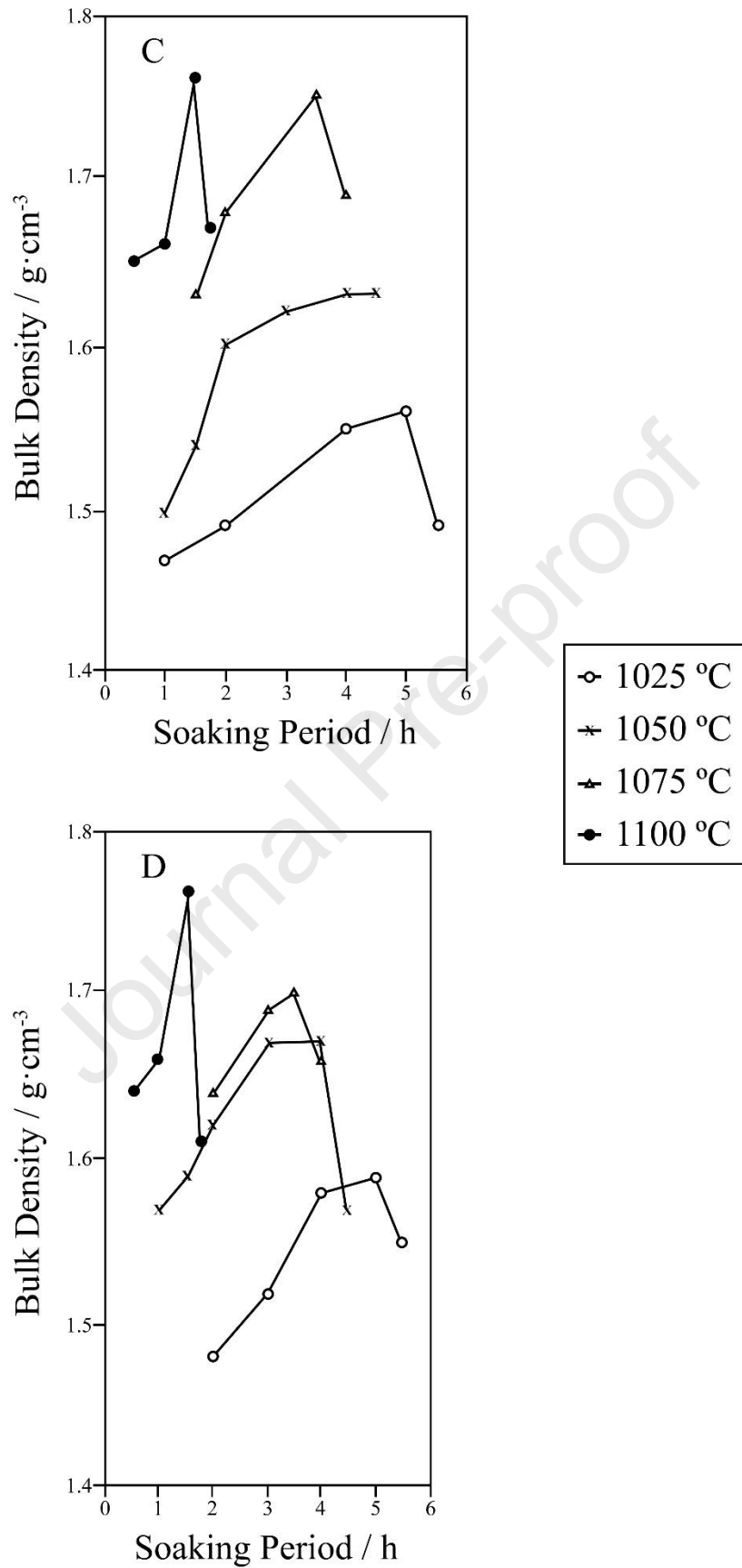


Figure 1.- Schematic representation of the reaction rate – time of firing dependence for the clay samples A - E, as described by Bogahawatta and Poole [2]. Adapted from reference [2].





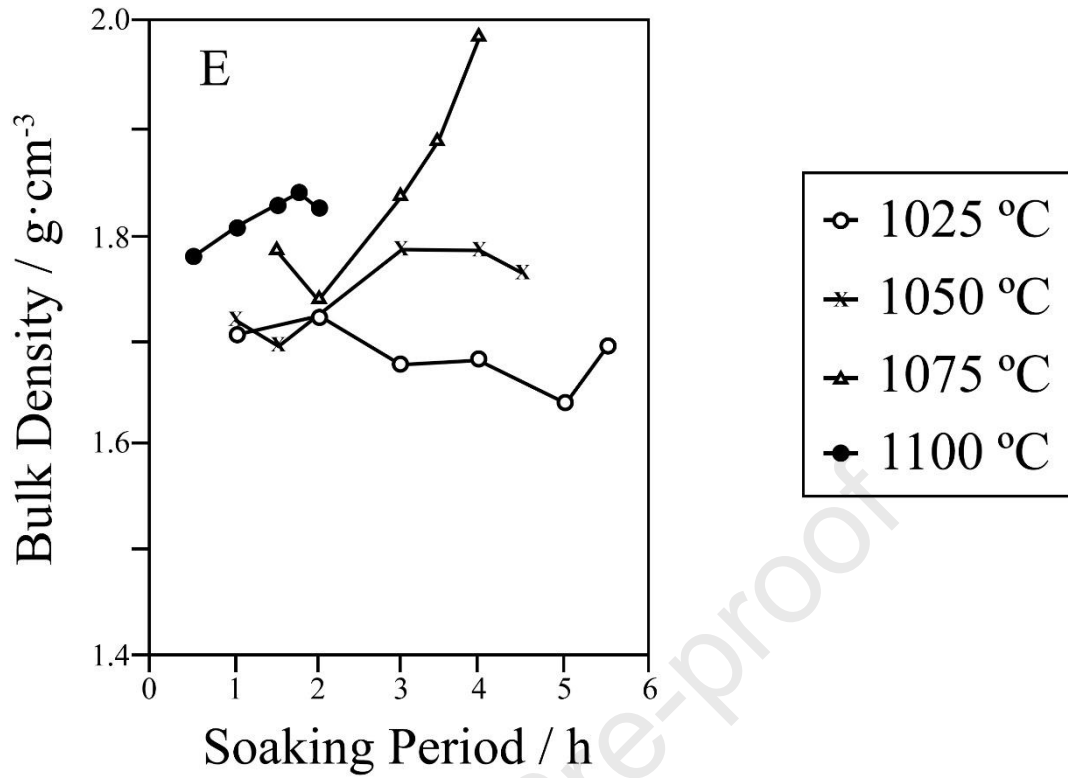


Figure 2.- Variation of bulk density with soaking period (0.5 – 5.5 h at different temperatures (1025 – 1100 °C) for the clay samples A, B, C, D and E (adapted from reference [2]).

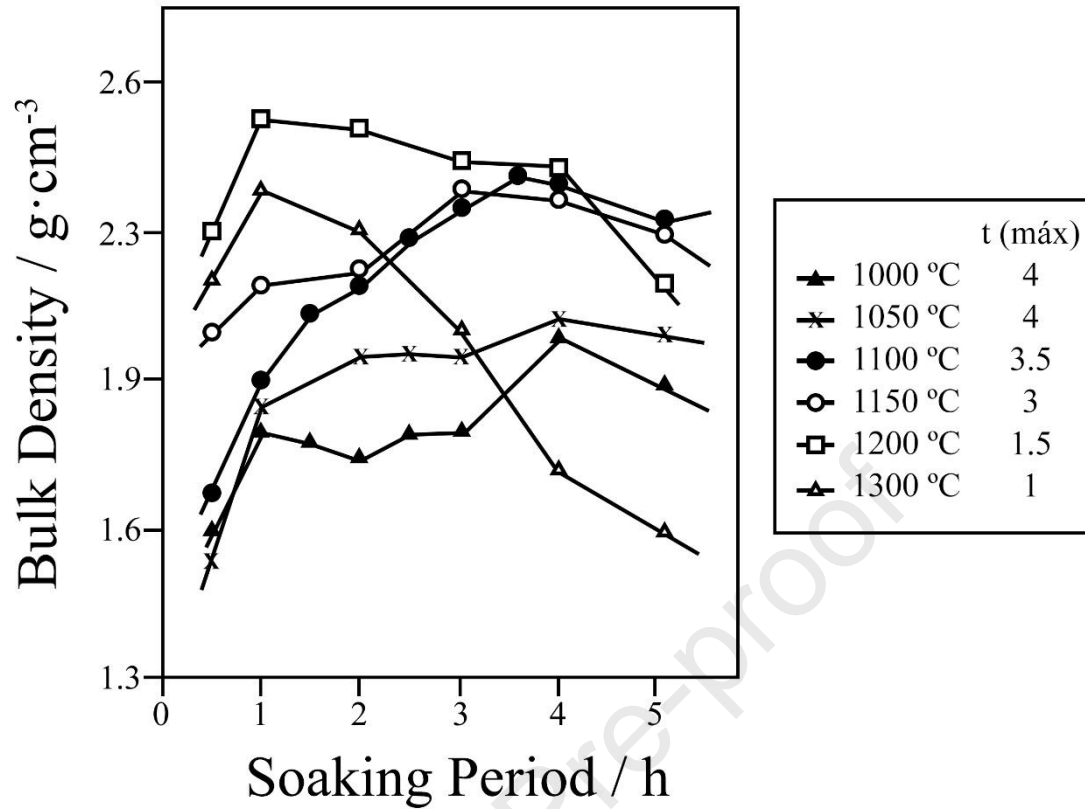


Figure 3.- Variation of bulk density with soaking period (0.5 - 5 h) at different temperatures (1000 - 1300 °C) for the pyrophyllite clay sample (adapted from reference [30]). The values of soaking period at the maximum value of bulk density, t (máx), obtained at each temperature following the model proposed in reference [2] are indicated in the insert.

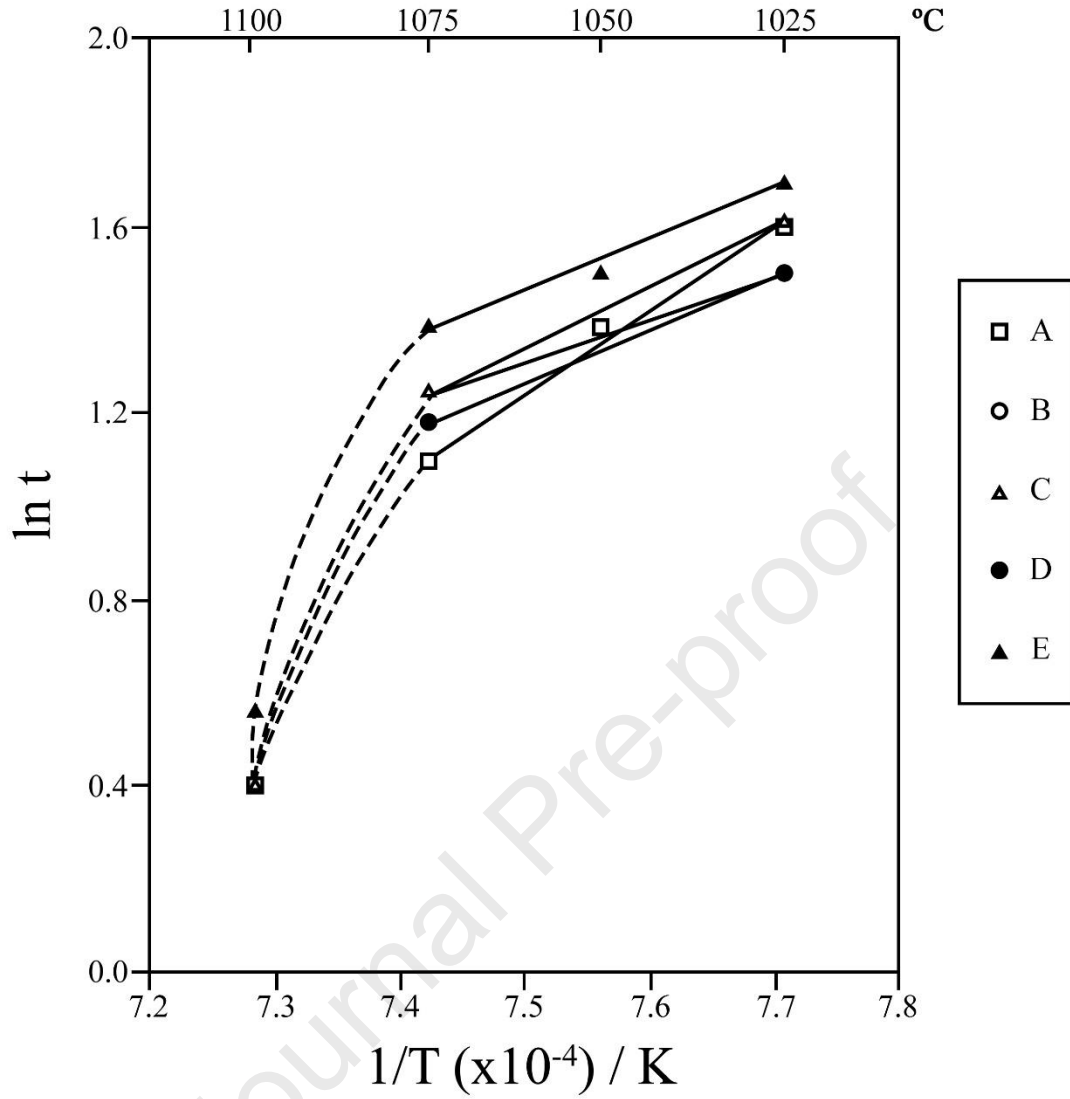


Figure 4.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the clay samples A – E following the isothermal kinetic model (adapted from reference [2]). The correlation coefficients of the straight lines are in the range 0.984-0.997.

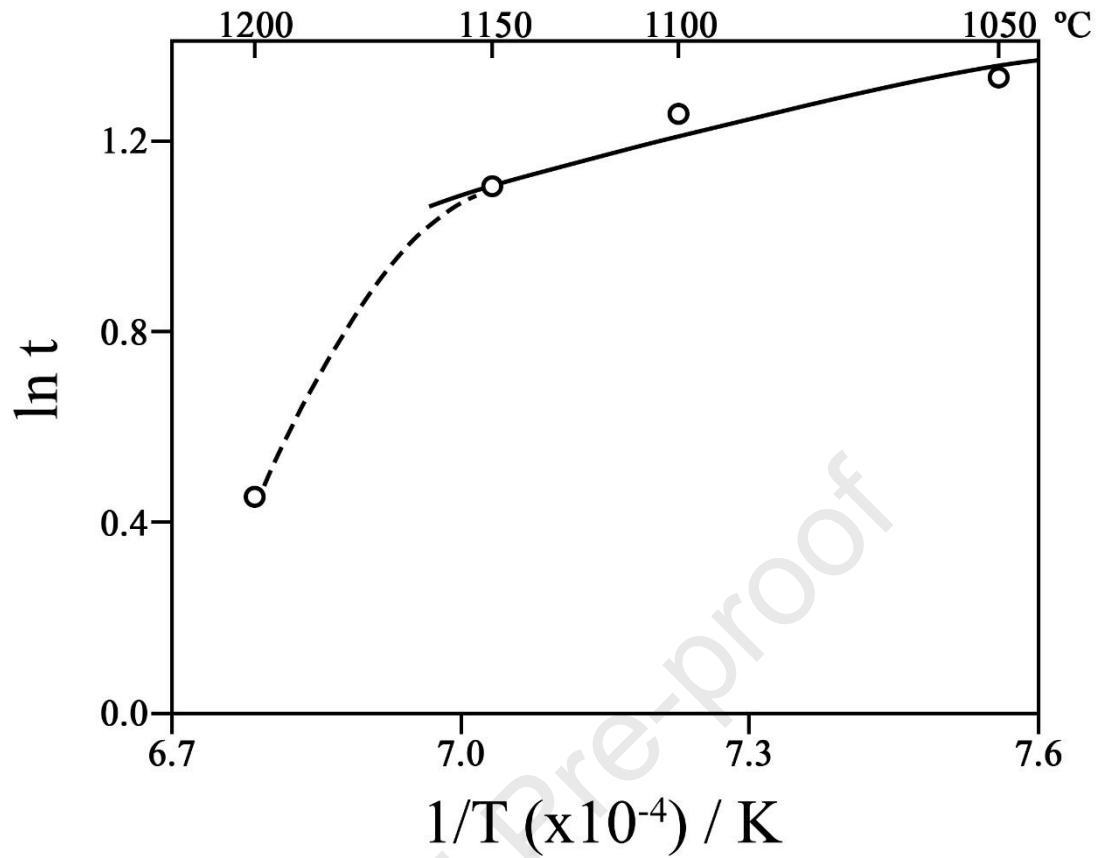


Figure 5.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the pyrophyllite clay sample following the isothermal kinetic model (adapted from reference [30]). The correlation coefficient of the straight line is 0.9980.

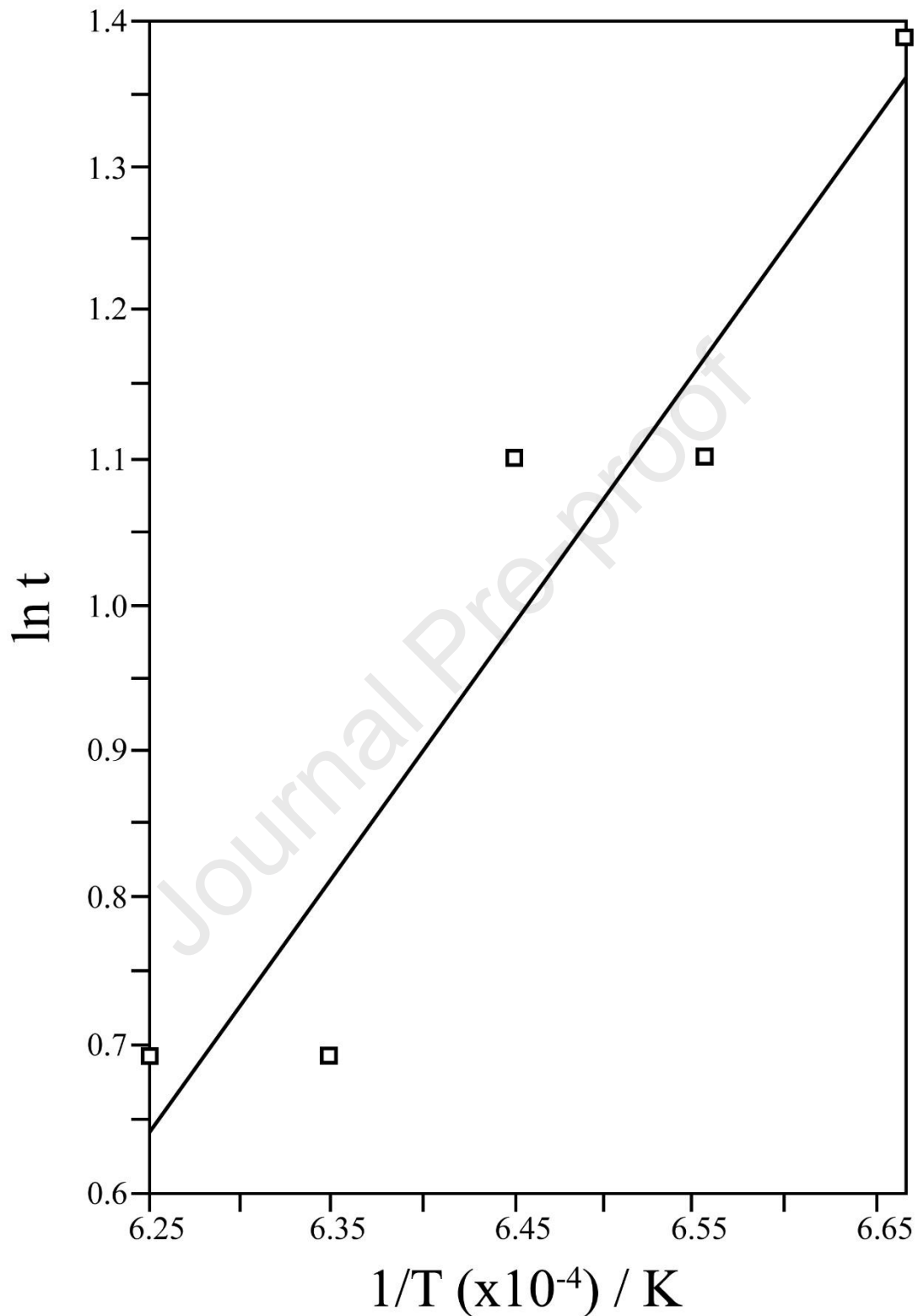


Figure 6.- Plot of $\ln t$ versus the reciprocal of firing temperature for isothermal heating of the Ecuadorian clay sample C-1 following the isothermal kinetic model (adapted from reference [3], but the correlation coefficient of the straight line was not provided).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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