

FORMULATION OF PORCELAIN TILE GLAZES USING A NEW BORON RAW MATERIAL. STUDY OF THE PHYSICO-CHEMICAL TRANSFORMATIONS THAT DEVELOP IN FIRING

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ABSTRACT

New fritless glaze compositions have been developed for porcelain tile from a new boron raw material obtained by calcination. Their fired properties were compared with those obtained using traditional glaze compositions. It was verified that the chemical and mechanical properties and the aesthetic characteristics of these new glazes were satisfactory. The complexity of this type of composition also translates into complex behaviour during firing in which, concurrently or in partially overlapping form, very different processes take place, such as crystalline phase dissolution, the crystallisation of new phases, and sintering phenomena. This study analyses the physico-chemical transformations that develop during the firing of these new glaze compositions, focusing in particular on the sintering process and its kinetics. A multi-step kinetic model was developed for this purpose, from which the effective viscosity of the glaze melt was obtained. This property was compared, on the one hand, with the effective viscosity determined experimentally using hot stage microscopy (HSM) and, on the other, with that estimated theoretically from the chemical and mineralogical composition of the material, at different temperatures. The results obtained by these methods exhibited very good agreement.

1. INTRODUCTION

The first part of this study examined the feasibility of using a new synthetic borate raw material, E4972 [1], as a constituent in the formulation of new fritless glaze compositions that yield appropriate porcelain tile glazes with glossy, satin, or matt finishes.

The second part analysed the physico-chemical transformations that develop in this type of glaze composition, focusing in particular on the sintering phenomenon. This study was undertaken for the following reasons:

1. These glazes have complex compositions, which also translates into complex behaviour during firing when, concurrently or in partially overlapping form, these compositions give rise to very different processes, such as crystalline phase dissolution, the crystallisation of new phases, and sintering.
2. This complexity and the few available studies related to the subject make the scientific and efficient formulation of raw glazes extremely difficult.
3. Although the main function of the glaze is to seal the body, the glaze sintering phenomenon, which is responsible for this property, has hardly been studied.

In order to address these aims, first, the following sintering model was developed [2]:

The overall sintering process and consequently the degree of progress of the process, X , are the sum of the partially or fully overlapping "m" contributions or individual steps that develop in parallel. At constant-rate heating, a , the sintering rate, caused by each contribution or step "i", is given by:

$$\left(\frac{dX}{dT}\right)_i = \frac{A_i}{a} \exp\left(\frac{-E_i}{RT}\right) f_i(X) \quad (\text{eq. 1})$$

where: $f_i(X)$ is the sintering model (which expresses the influence of X on the process rate), and A_i and E are the pre-exponential factor and the apparent activation energy, respectively.

Separating the variables and integrating then yield the integral form of the sintering model, $g(X)$, and its dependence on temperature. That is:

$$g_i(X) = \int_0^X \frac{dX}{f_i(X)} = \frac{A_i}{a} \int_0^T \exp\left(\frac{-E_i}{RT}\right) dT = \frac{A_i R T^2}{a E_i} \exp\left(\frac{-E_i}{RT}\right) \quad (\text{eq. 2})$$

Each individual step can be appropriately described by means of the Avrami–Erofeev sintering model, with a constant value of n , ranging between 0 and 1. In integrated form:

$$g_i(X) = \left[-\ln\left(1 - \frac{X}{w_i}\right) \right]^{\frac{1}{n}} \quad (\text{eq. 3})$$

where w_i is the maximum contribution of step “i” to the overall sintering process.

The sintering degree of progress, X , of Equations 2 and 3 is given by the expression:

$$X = \sum_{i=1}^m w_i \left\{ 1 - \exp\left\{ - \left[\frac{A_i R T^2}{a E_i} \exp\left(\frac{-E_i}{RT}\right) \right]^n \right\} \right\} \quad (\text{eq. 4})$$

where w_i , A_i , and E_i are the values of the kinetic triplet in each step.

By analogy with the rate law, which describes the processes that develop in an individual step, an effective or overall rate constant of the process is defined:

$$K_{\text{eff}}(T) = \left(\frac{dX}{dt} \right) \frac{1}{f(X)} = \frac{dX}{dT} \frac{a}{f(X)} \quad (\text{eq. 5})$$

where $f(X)$ is the differential form of the kinetic model given by Equation 3 with $w_i=1$.

The theoretical glass sintering models [3] and the models based on the continuum theory of viscous sintering [4] then yield the expression for effective viscosity, η_{eff} :

$$\eta_{\text{eff}}(T) = \frac{3\gamma}{2K_{\text{eff}}(T) \ln\left(\frac{1}{\rho_0}\right) r_0} \quad (\text{ec. 6})$$

where: γ , is the surface tension of the glassy phase, r_0 is the average particle radius, and ρ_0 is the compactness of the unfired glaze.

This last information will provide a better understanding of the role that the glaze constituents and the firing conditions play in sintering. Indeed, $\eta_{\text{eff}}(T)$ is a property of the material that depends, in addition to temperature, on the material’s microstructural characteristics (percentage of crystalline and glassy phases, composition, crystal size and shape, etc.), and a relationship has been established, albeit in an approximate form in many cases, between $\eta_{\text{eff}}(T)$ and some of the aforementioned microstructural characteristics.

2. EXPERIMENTAL

Different glaze compositions were prepared for porcelain tile, using a new boron raw material obtained by calcination, E4972 [1], with a view to selecting the most appropriate compositions (Table 1). The surface properties of the applied glazes, fired at 1180°C, were determined by standard methods.

Three glaze compositions were selected and thermally treated in a hot stage microscope at heating rates of 0.5, 5, 25, and 60°C/min. The surface area of the test piece silhouette, A , was used to calculate its surface shrinkage, $\varepsilon_A = \ln(A/A_0)$, from which the sintering degree of progress, $X = \varepsilon_A / \varepsilon_{A, \max}$, was then determined. The percentage of crystalline phases present in the test pieces fired at a rate of 25°C/min were determined by X-ray diffraction (XRD), using the Rietveld method [5].

Raw materials	Glossy	Matt	Satin
Kaolin	8	8	8
Calcined borate	28	24	27
Zinc oxide	9	4	6
Sodium feldspar	38	-	41
Nepheline	-	24	-
Wollastonite	9	19	9
Zircon	8	7	3
Corundum	-	10	6
Quartz	-	4	-

Table 1. Batch formulas of the selected new glaze compositions

3. RESULTS Y DISCUSSION

3.1. CHARACTERISATION OF THE SELECTED NEW GLAZE COMPOSITIONS

Table 2 summarises, for the three selected types of glaze, the crystalline phase contents (wt%) in the unfired glazes and in the glazes fired at 1180°C.

Phases	Glossy		Matt		Satin	
	Unfired	Fired	Unfired	Fired	Unfired	Fired
Kaolinite	8	-	8	-	8	-
Zincite	9	-	4	-	6	-
Albite	35	-	14	2	40	1
Nepheline	-	-	6	-	-	-
Wollastonite	10	-	19	-	10	-
Zircon	9	8	7	4	-	-
Corundum	-	-	9	5	6	6

Quartz	7	1	9	1	8	2
Anorthite	-	1	-	15	-	8
Gehlenite	-	-	-	1	-	-
Gahnite	-	1	-	1	-	1

Table 2. Crystalline phases of the selected new glaze compositions (% by wt).

The most important surface properties of the new fired glazes are detailed in Table 3, together with those of the commercial glazes used as references. It may be observed that, in every case, their properties were similar.

Property	Glaze	Glossy	Matt	Satin
Gloss	Selected	91-94	7-8	10-14
	Reference	92-94	7-8	10-12
Hydrochloric acid	Selected	GHA	GHB	GHB
	Reference	GHA	GHB	GHB
Lactic acid	Selected	GHA	GHB	GHB
	Reference	GHA	GHA	GHB
Potassium hydroxide	Selected	GHA	GHA	GHA
	Reference	GHA	GHA	GHA
Vickers (GPa)	Selected	4,8±0,1	5,3±0,3	4,6±0,2
	Reference	4,7±0,1	5,5±0,3	4,7±0,3
Berkovich (GPa)	Selected	10,4±0,8	9,3±0,8	9,8±0,8
	Reference	9,6±0,8	9,5±0,8	9,7±0,8
Elastic modulus (GPa)	Selected	100±15	87±21	101±10
	Reference	102±8	101±10	94±8
Toughness (MPa·m ^{1/2})	Selected	1,07±0,11	1,0±0,11	1,05±0,11
	Reference	1,05±0,10	1,1±0,08	1,15±0,20

Table 3. Surface properties of the new glazes and of the reference glazes.

3.2. EVOLUTION OF CRYSTALLINE PHASES BY X-RAY DIFFRACTION

All these glazes exhibited similar behaviour with regard to their physico-chemical transformations. By way of example, only the results corresponding to the matt glaze are presented below, as this was the most complex glaze composition (Figure 1).

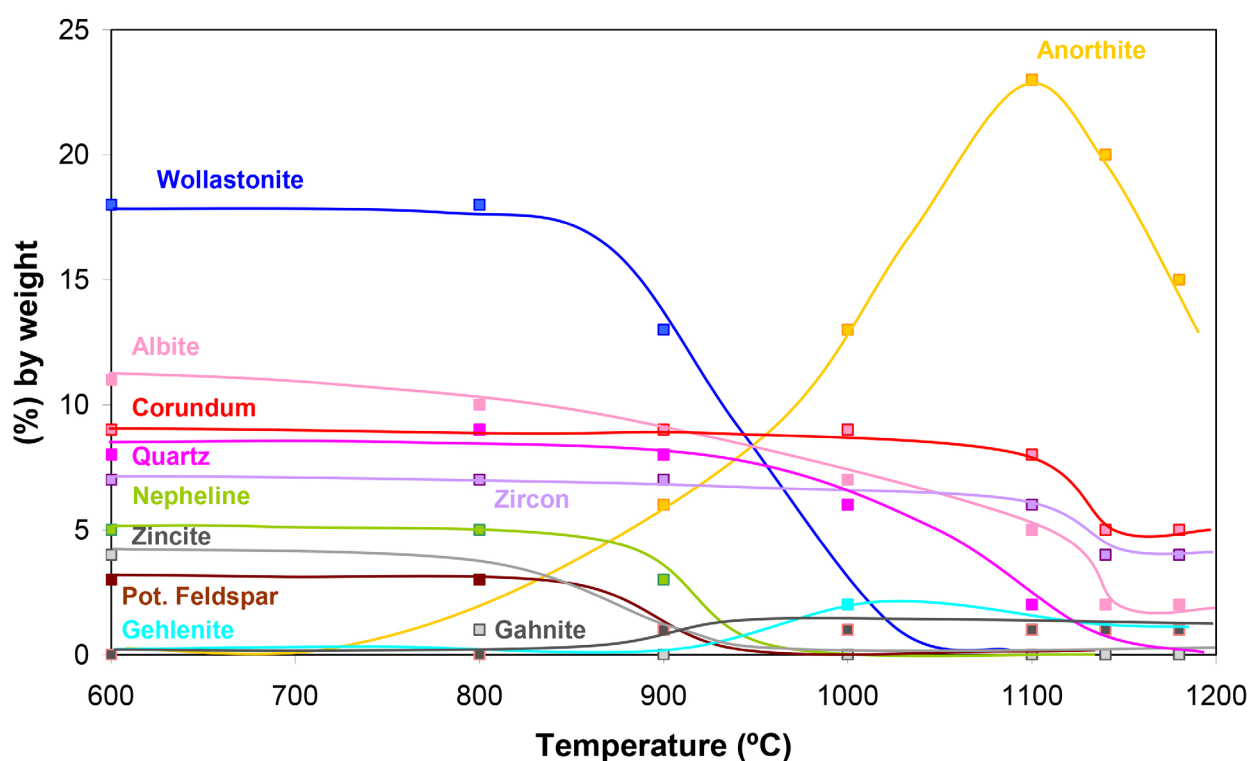


Figure 1. Evolution of crystalline phase contents (wt%) with temperature in the matt glaze. Heating rate: 25°C/min.

As occurred with the other studied glazes, at low temperatures, the only important transformation was kaolinite decomposition at temperatures below 600°C. At about 800°C, the zincite had already started to react in considerable quantities, and at 900°C it was no longer detected by X-ray diffraction. As in the other glazes, anorthite was also the first crystalline phase to form. At low temperatures it formed by crystallisation in the calcined borate (Figure 2a) and as a result of the reaction at the contact points between the feldspathoids, wollastonite, and calcined borate. In contrast, at higher temperatures (1100°C) the predominant formation mechanism was by crystallisation in the glassy matrix in the regions richest in CaO and Al₂O₃. These regions were generally located close to the albite and/or nepheline and corundum crystals (Figure 2b and 2c) and rarely near the quartz particles (Figure 2b). Indeed, the partial dissolution of Al₂O₃ and albite and/or nepheline enriched the liquid phase with aluminium oxide, the liquid phase already being rich in calcium owing to wollastonite dissolution. Gahnite, which formed to a small extent, was only noted at high temperatures in the form of small light-coloured crystals surrounding the corundum particles (Figure 2c).

In regard to the most refractory crystalline phases introduced as raw materials (quartz, corundum, and zircon), their dissolution in the melt was practically negligible at temperatures below 1000°C (Figure 1), and the crystals exhibited clear surfaces and angular shapes, as may be observed in Figure 2d for zircon and corundum. At temperatures above 1100°C, the dissolution of these phases was already significant (Figure 1), the particle shape being more rounded and the surface less clear (Figure 2b and 2c). The reaction between the different less refractory phases, such as the calcined borate, feldspathoids, zincite, and wollastonite, began to become significant at temperatures above 800°C (Figure 1), but only between the particles in which real

contact was established, this reaction being minor at low temperatures (Figure 2d). At high temperatures (1100°C), the reactions between these constituents were practically completed and, of these reactive phases, only albite was observed in appreciable quantities (Figure 1), surrounded by glass and/or devitrified plagioclase crystals (Figure 2b).

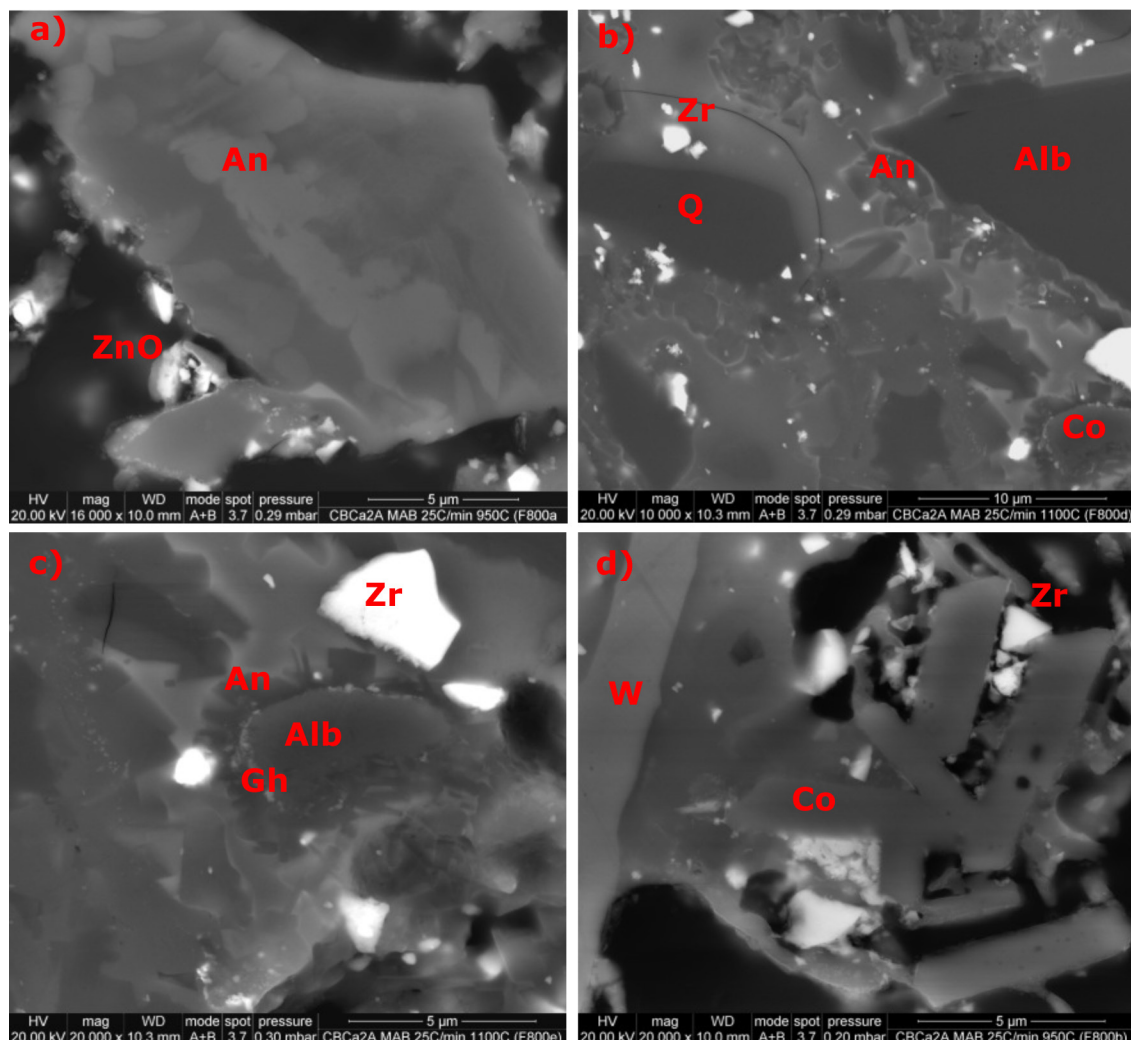


Figure 2. Microstructures of the matt glaze fired at different maximum temperatures, heating at 25°C/min. a) $T = 950^{\circ}\text{C}$. Formation of plagioclase, An, in the calcined borate. ZnO, regions with a high zinc content; b) $T = 1100^{\circ}\text{C}$. Formation of anorthite, An. Albite, Alb, corundum, Co, quartz, Q, zircon, Zr; c) $T = 1100^{\circ}\text{C}$. Formation of anorthite, An, and gahnite, Gh, around corundum, Co. Zircon, Zr; d) $T = 950^{\circ}\text{C}$. Wollastonite, W, corundum, Co, and zircon, Zr, crystals.

3.3. SINTERING

In order to describe the sintering curves, a three-step kinetic model was used in which the three steps develop in parallel, according to the procedure described in the introduction. In fitting the experimental values of X to the equations of the model, it was sought to minimise the number of parameters that depended on the heating rate, a [1]. As may be observed, the agreement between the experimental data and the calculated values is excellent (Figure 3a).

The first step consisted of a small shrinkage, mainly related, as in the other glazes, to viscous flow sintering as a result of the softening or partial fusion of the calcined

borate. The second step, which took place from 850 to 1050°C, as occurred with the other porcelain tile glazes, was characterised by scarce development of the densification process and by a small effect of temperature on this process, mainly owing to the concurrence of crystalline phase dissolution (wollastonite, feldspars, etc.) and anorthite crystallisation (Figure 1). The two processes led to a low amorphous phase content (about 40%) at this stage, and to its variation with temperature (Figure 4) also being low. Consequently, sintering by the dissolution–precipitation mechanism, which depends mainly on the glassy phase content, will hardly develop and do so at a low rate, even though amorphous phase viscosity decreases as temperature rises. At temperatures above 1000°C (step III), when the temperature rose, the amorphous phase content increased practically exponentially (Figure 4), which, together with the reduction in amorphous phase viscosity, also exponentially increased the densification and the densification rate (Figure 3) up to temperatures close to 1100°C (final sintering step).

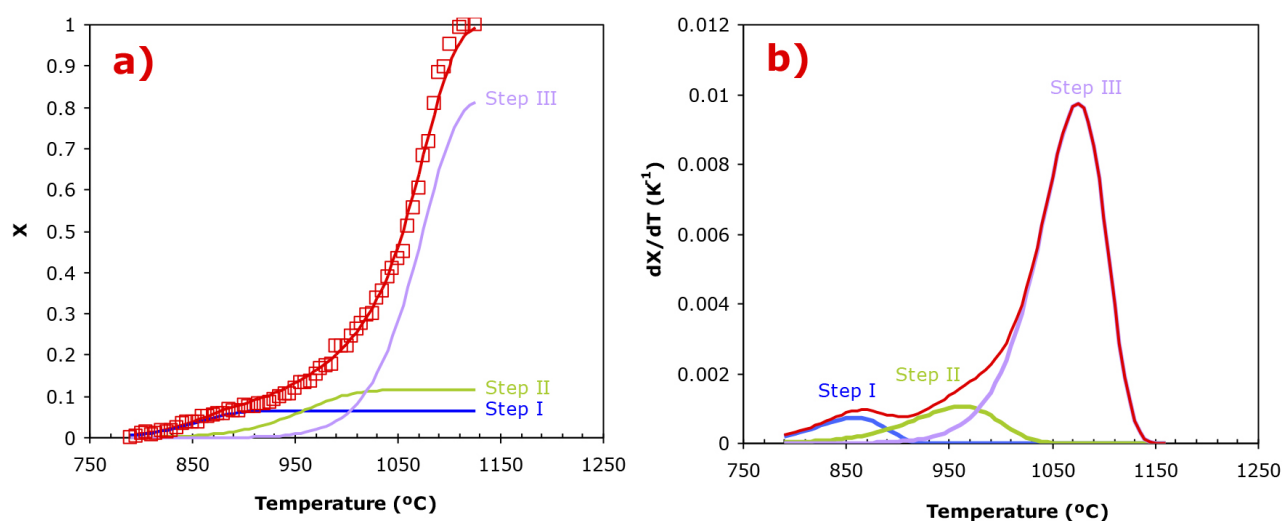


Figure 3. Sintering of the matt glaze at 25°C/min. Comparison of the experimental data with the values predicted by the model. a) Variation of the sintering degree of progress with temperature; b) Variation of the sintering rate with temperature.

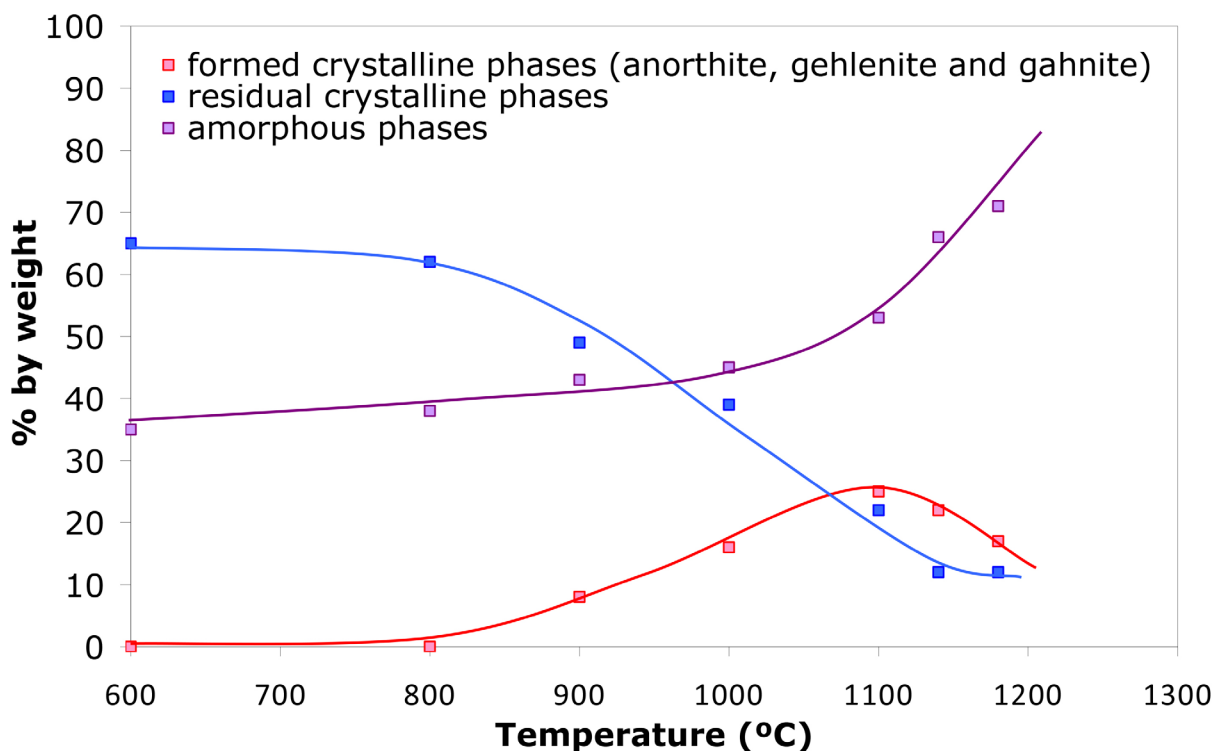


Figure 4. Evolution of crystalline phase content (residual and formed) and amorphous phase content with temperature in the matt glaze at 25°C/min.

3.4. EFFECTIVE VISCOSITY OF THE GLAZE MELT OBTAINED FROM THE SINTERING EXPERIMENTS, η_{eff}

a. Comparison of the fixed viscosity points with the experimental data.

The curve of the effective viscosity calculated from the proposed sintering model is plotted in the form $\log \eta_{\text{eff}}$ versus temperature in Figure 5. The figure includes the characteristic points corresponding to the following temperatures: shrinkage start (T_{IC} and T'_{IC}), shrinkage end (T_{FC}), reblandecimiento (T_{R}) and sphere (T_{E}), temperature, to which the literature on glassy materials [7][8][9] each assigns a certain viscosity. It may be observed that the estimated curve of the sintering model fits very well to the characteristic viscosity points except for T'_{IC} . These results confirm that the model used satisfactorily describes the sintering of complex glaze compositions.

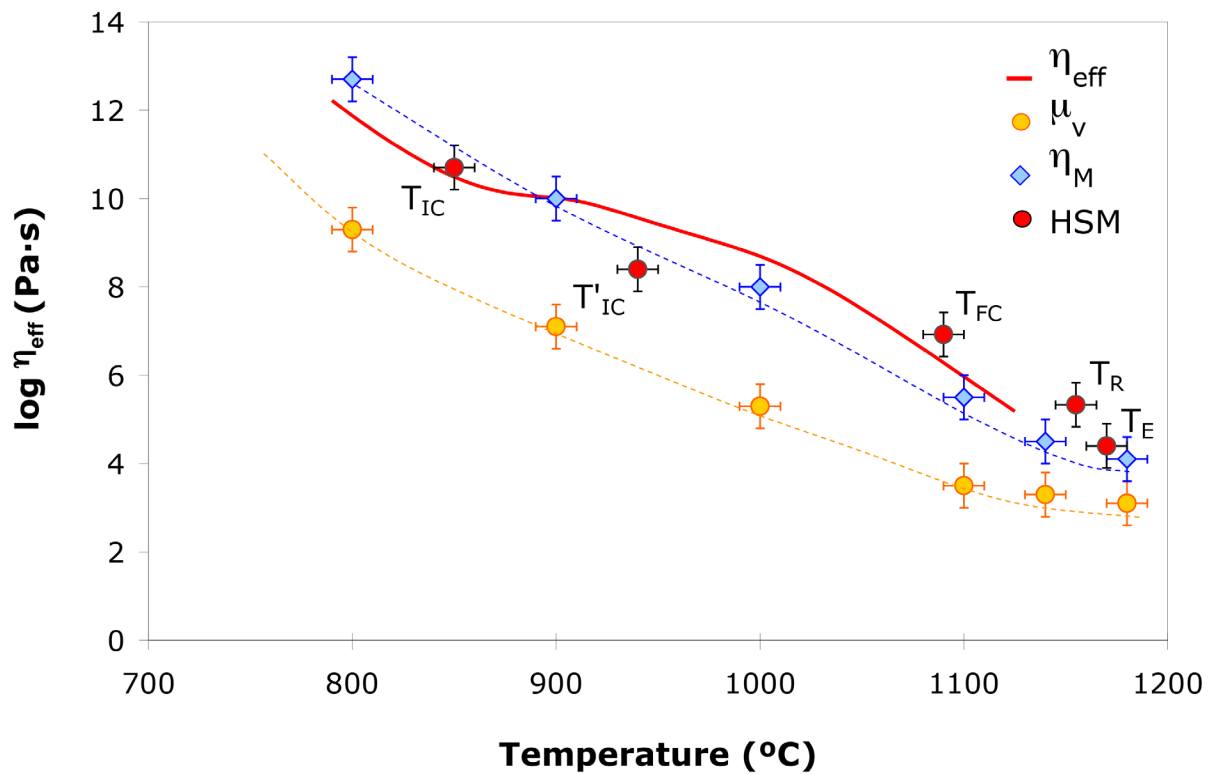


Figure 5. Variation of the matt glaze viscosities with temperature. μ_v , viscosity of the glassy phase; η_{eff} , effective viscosity calculated from the sintering model; η_M , viscosity estimated according to Müller; T_p , characteristic temperatures obtained by HSM.

- Comparison with the theoretically estimated values from the chemical and mineralogical composition of the material.

The viscosity of the glassy phase, μ_v , was calculated from its chemical composition by the Fluegel model [10]. This viscosity was obtained from the overall glaze composition and from the content and nature of the crystalline phases determined by X-ray diffraction in the test pieces fired at a heating rate of 25°C/min (Figure 1). The evolution of this characteristic, μ_v , with temperature is also plotted in Figure 5.

In order to calculate theoretically the glaze effective viscosity, η_M , the following, modified equation of Müller et al. [11] was used:

$$\eta_M = \mu_v \left(1 - \frac{\phi}{\phi_{\max}} \right)^{-4,5} \quad (\text{eq. 7})$$

where ϕ is the crystal volume fraction and $\phi_{\max}$ is the maximum compactness of the particle bed, which was taken as $\phi_{\max}=0.74$, instead of $\phi_{\max}=0.60$ que sugiere Müller.

The value of ϕ was calculated from the values of the mass fractions of the different phases, determined by XRD, from their true densities, drawn from the literature, and from the true density of the glassy matrix. This last value was estimated from the chemical composition, applying models from the literature. The values estimated from

Equation 7 are plotted in Figure 5. It shows that the values of the effective viscosity estimated from the Müller model, η_M , using the appropriate value of $\phi_{\max}$ are consistent with those obtained from the developed sintering model.

4. CONCLUSIONS

Using a new boron raw material (E4972 [1]), new fritless glaze compositions were obtained for porcelain tile, with properties similar to those of the glazes used customarily.

A multi-step kinetic model has been developed that appropriately describes the sintering degree of progress with temperature, in constant-rate heating experiments. Sintering was assumed to take place by means of three individual steps, which took place in parallel and were partially overlapping.

It was verified that the effective viscosity values, obtained from the sintering model, agreed very well with the experimental data (fixed viscosity points) and the values estimated from the modified Müller model.

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