HIGH TEMPERATURE VISCOSITY OF PORCELAIN STONEWARE BODIES

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1. ABSTRACT

The viscosity of porcelain stoneware at high temperatures is crucial to understanding the vitrification path, the viscous flow sintering kinetics, and the pyroplastic deformation of this material. The final viscosity of porcelain stoneware has to be determined considering both the viscosity of the liquid phase formed by the melting of feldspars – and other minerals – and the viscosity of the body made up of a suspension of crystals dispersed in the melt. A fundamental theoretical background along with semi-empirical constitutive laws on viscous flow sintering, glass densification, as well as on the high viscosity of liquids and melts already exists. Different approaches are needed to measure/estimate the two viscosities and the parameterization depends on both the chemical composition of the liquid phase and persistence of crystal phases in the melt. In this work, a first attempt to predict the viscosity of a porcelain stoneware liquid phase is proposed by means of a detailed overview of preexisting models for high temperature viscosities of glasses and melts. Although models developed for glasses take into account a large number of oxides and they can be applied to melts characterized by a wide compositional range, the maximum concentration of alumina expected by these models is too low compared with that of the systems investigated here. On the other hand, the models proposed for granitic melts, although based on a lower number of oxides, take into account alumina levels closer to those of the systems of interest. In this contribution it is demonstrated that the latter models can be used to predict the viscosity at high temperature of porcelain-like bodies. Comparative examples are provided for porcelain stoneware tiles, vitreous china, and porcelain bodies.

2. INTRODUCTION

The high temperature viscosity of porcelain stoneware tiles is a crucial parameter in several stages of industrial firing. In particular, it has an important role in the vitrification path [1, 2] and the kinetics of viscous flow sintering [2, 3]. In addition, the melt viscosity is the main cause for pyroplastic deformation occurrences [4, 5], and deviation from the expected sintering behavior [6].

A serious complication stems from the multiple scales at which the viscosity acts in porcelain stoneware tiles. As a matter of fact, the viscosity of the liquid phase formed by melting of feldspars and other minerals controls both the melt flow and the rearrangement of the crystal mush at the micrometer scale [7, 8], as well as the tile viscosity (intended for resistance to high temperature deformation), which depends on the amount, size and shape of crystals dispersed in the melt [9].

A fundamental theoretical background of viscous flow sintering based on semi-empirical constitutive laws of glass densification already exists [2, 3, 6]. On the other hand, predictive models of the high temperature viscosity, which take into account the chemical composition of the melt, are only available for glasses [10, 11] and silicate melts [12, 13]. The missing link is the knowledge about the chemical composition of the liquid phase present at high temperature in porcelain-like bodies [1, 14, 15] and the applicability of existing models to porcelain stoneware tiles.

In these cases, the occurrence of crystals suspended in a melt requires two different approaches: one aimed at estimating the viscosity of the liquid phase, depending on both its composition and temperature, and another one to evaluate the contribution of the solid fraction to the viscosity of the tile as a whole. Further variables, such as porosity, particles size and shape, can play a significant role and should be considered [6].

This work represents a step forward in the viscosity estimation of the melt present in porcelain-like bodies by its chemical composition. Literature data were used to compare, for the first time, the physical and chemical features of the viscous phase present in porcelain stoneware, vitreous china and porcelain. The main drawback of previous attempts [1, 16, 17] is that the predictive models for the viscosity of glasses [10] are valid for low alumina concentrations. In the case of the liquid phase of porcelain stoneware, the calculation can be performed just by extrapolation, thus resulting in a systematic viscosity underestimation. Nevertheless, the liquid phase of porcelain stoneware exhibits a remarkable compositional similarity with granitic melts. Therefore, it is demonstrated here that predictive models developed for magmas [12] could be successfully employed to estimate the viscosity at high temperature of the liquid phase in porcelain-like bodies.

3. EXPERIMENTAL APPROACH

The chemical and mineralogical composition of forty-five porcelain-like bodies was taken from the literature in order to estimate the viscosity and surface tension of the vitreous phase at high temperature. Since accurate determination of the phase composition is the crucial step, only studies with a Rietveld refinement of XRD patterns were taken into account.

Specifically, the chemical (Table 1) and mineralogical (Table 2) compositions of hard porcelain [18], porcelain [18], vitreous china [19], and porcelain stoneware [5, 20, 21] were taken into account.

(wt%)	HP	P	PS	VC
	mean	mean	mean	mean
SiO_2	49.2	66.5	68.7	70.1
TiO_2	0.5	0.6	0.3	0.3
Al_2O_3	46.1	28.6	22.3	25.0
Fe_2O_3	0.4	0.5	0.7	0.7
MgO	0.0	0.1	1.2	0.2
CaO	0.2	0.3	0.9	0.1
Na_2O	0.1	0.8	3.6	2.6
K_2O	3.4	2.6	1.1	1.1
ZrO_2	0.0	0.0	1.3	0.0

Table 1. *Chemical composition of Hard porcelain (HP), Porcelain (P), Porcelain Stoneware (PS), and Vitreous china (VC) products.*

The chemical composition of the vitreous phases was obtained by subtracting the chemical contribution of each mineralogical phase, considering their stoichiometric formulae, from the total chemistry of the bodies (Table 3).

To calculate the viscosity of a melt based on both its composition and temperature, two different models, developed for silicate glasses and for naturally-occurring silicate melts, were considered.

Primarily, Fluegel's model [10] has been evaluated. This model was developed using a global statistical approach and more than 2200 composition–viscosity data elements for silicate glasses, including soda–lime–silica container and float glasses, TV panel glasses, borosilicate fibre wool and different types of glasses, low expansion borosilicate glasses, glasses for nuclear waste vitrification, lead crystal glasses, binary alkali silicates, and various other compositions.

(wt%)	HP			P			PS			VC		
	min	max	mean	min	max	mean	min	max	mean	min	max	mean
Corundum	33.2	35.3	34.4	8.5	8.9	8.7	0.0	0.0	0.0	0.0	0.0	0.0
Quartz	8.4	12.1	9.9	22.6	23.8	23.1	10.1	29.8	17.5	13.0	28.3	20.4
Mullite	3.3	5.8	4.5	5.1	5.9	5.5	10.0	16.3	11.9	16.4	19.5	17.5
Na-Plagioclase	0.0	0.0	0.0	0.0	0.1	0.0	0.0	4.0	1.9	0.0	3.5	0.3
K-Feldspar	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.2	0.0	0.0	0.0
Rutile	0.0	0.2	0.2	0.0	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Zircon	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	1.4	0.0	0.0	0.0
Vitreous phase	50.7	51.1	50.9	61.2	63.6	62.5	57.6	76.0	67.0	51.8	70.6	61.7

Table 2. *Mineralogical composition of Hard porcelain, Porcelain, Porcelain Stoneware, and Vitreous china products. Abbreviation as in Table 1.*

The model is based on the Vogel-Fulcher-Tammann (VTF) equation:

$$\log_{10}\eta(T, x) = \log_{10}\eta_{\infty}(x) + A/(T-T_o) \qquad (1)$$

where T is temperature, x is composition, and the three VFT parameters (η_{∞}, A, and T_0) are obtained by fitting Eq. 1 to experimentally measured viscosity data.

Fluegel's model can be applied to melts characterized by a wide range of compositions, taking into account fifty-four oxides. To check the model results, a comparison between the experimentally calculated and the measured viscosities from the literature was performed for naturally-occurring silicate melts [22-26] and silicate glass [27-29]. This comparison demonstrated a significant error between the calculated and measured viscosity, generally related to an underestimation of the model based on glasses.

Moreover, the levels of alumina considered by Fluegel's model (maximum Al_2O_3 19 wt%) are too low for the systems being examined here (Al_2O_3 content from 14.5 to 26.0 wt%, see Table 3).

For all these reasons, an alternative model, among those developed on natural silicate melts, was also considered. The model proposed by Giordano and co-workers [12], was chosen. It was developed from more than 1770 experimentally measured viscosities of multicomponent anhydrous and volatile-rich silicate melts, of known composition, and, as the Fluegel's one, it is based on the VTF equation. Even though this model takes into account a lower number of oxides (eleven), it shows alumina levels closer to those of interest (Al_2O_3 up to 23 wt%) and a lower error when compared with experimental data.

Therefore, this latter model was applied to predict the viscosity of the vitreous phases of the different porcelain-like bodies, at high temperature.

The diagram in Figure 1 summarizes the methodological path followed, starting from the chemical and mineralogical composition of the bodies from literature, to determination of the vitreous phase viscosity.

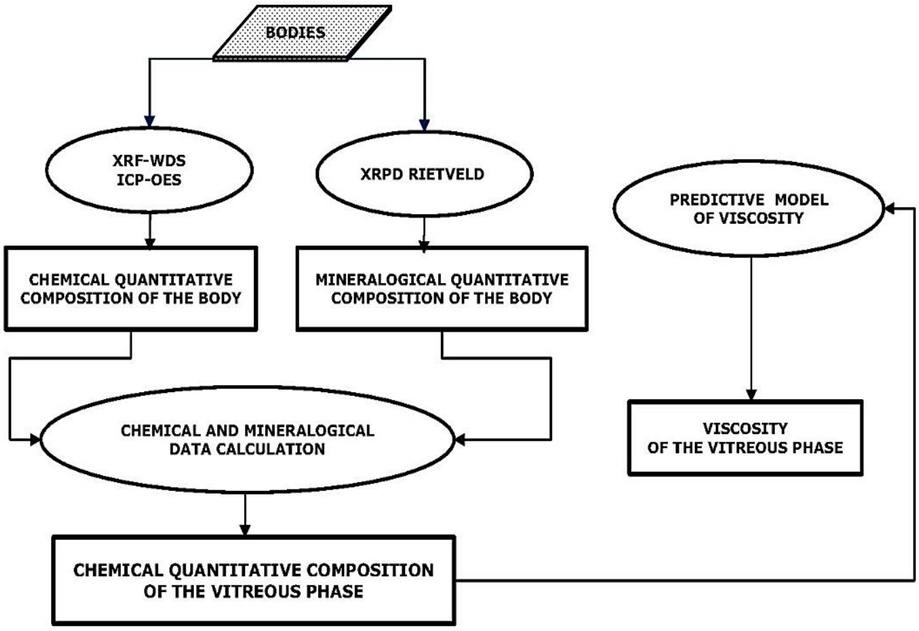

Figure 1. *The methodological path followed for determination of the vitreous phase viscosity.*

4. RESULTS AND DISCUSSION

The chemical compositions of the vitreous phase of porcelain stoneware tiles, vitreous china sanitary-ware, and porcelain ware, are reported in Table 3. The reliability of results strongly depends on the phase composition accuracy. For this reason, the proper application of full profile refinements of XRD patterns is of fundamental importance. It is worth noting that this is the first time that the composition of the liquid phase in porcelain-like materials has been approached.

(wt%)	Hard Porcelain			Porcelain			Porcelain Stoneware			Vitreous China		
	MIN	MAX	AV.	MIN	MAX	AV.	MIN	MAX	AV.	MIN	MAX	AV.
SiO_2	72.0	76.7	74.6	66.3	67.4	66.9	64.9	72.2	68.5	67.2	74.3	72.0
TiO_2	0.6	0.9	0.7	0.5	0.9	0.7	0.4	0.7	0.5	0.4	0.5	0.4
Al_2O_3	14.5	17.8	16.6	25.1	26.0	25.5	17.8	21.3	19.8	18.4	24.1	20.1
Fe_2O_3	0.8	0.9	0.8	0.6	0.8	0.7	0.5	1.5	1.0	0.9	1.3	1.1
MgO	0.0	0.0	0.0	0.0	0.5	0.2	0.1	2.9	1.7	0.2	0.3	0.3
CaO	0.3	0.4	0.4	0.5	0.6	0.5	0.6	2.1	1.3	0.2	0.3	0.2
Na_2O	0.0	1.0	0.3	1.3	1.4	1.4	1.7	8.1	5.1	3.7	4.7	4.2
K_2O	6.0	7.2	6.7	4.1	4.4	4.2	0.4	8.8	1.6	1.5	2.0	1.7
ZrO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	0.4	0.0	0.0	0.0

Table 3. *Chemical composition of the Vitreous Phase into Hard porcelain, Porcelain, Porcelain Stoneware, and Vitreous china products. Average, minimum and maximum values are reported.*

The chemistry of the vitreous phases pertaining to different porcelain-like materials somehow reflects the chemical composition of the starting bodies. In fact, those phases are characterized by high and variable contents of silica and alumina (65-76 SiO_2 wt%, 14.5-26 Al_2O_3 wt%). In addition, hard porcelain and porcelain exhibit a more potassic composition with respect to the porcelain stoneware and vitreous china, which show higher contents of soda. The variable amounts of silica and alumina depend basically on the persistence of quartz and mullite with the melt phase at the equilibrium. Faster dissolution of mullite leads to increasingly peraluminous melts, while quartz is buffering the silica oversaturation. These two mechanisms deeply affect the viscosity of the liquid phases. Interestingly, the alumina percentage in the melt is higher in porcelain than in vitreous china and porcelain stoneware. Hard porcelain seems to have a peculiar melt composition, i.e., a silica enrichment and an alumina deficiency, with respect to conventional porcelain. Another fundamental factor is the amount of glass network modifiers (GNM) that in porcelain-like materials are mainly represented by alkaline and alkaline-earth oxides. GNMs are most abundant in porcelain stoneware, followed by vitreous china and porcelain (Table 3).

Parameters	Hard porcelain			Porcelain			Porcelain Stoneware			Vitreous China		
	Firing Temperature (1400°C)			Firing Temperature (1300°C)			Firing Temperature (1170-1200°C)			Firing Temperature (1240-1280°C)		
	MIN	MAX	AV.	MIN	MAX	AV.	MIN	MAX	AV.	MIN	MAX	AV.
Viscosity ($Log_{10}Pa{\cdot}s$)	4.2	4.7	4.5	4.4	4.6	4.5	4.5	5.2	4.8	4.6	5.3	4.9
Surface tension (mN m-1)	292	298	296	332	336	334	331	360	349	327	344	333

Table 4. *Vitreous Phase Physical Properties of Hard porcelain, Porcelain, Porcelain Stoneware, and Vitreous china products.*

The vitreous phase compositions calculated were used to predict the physical properties of the liquid phases at the temperatures of maximum densification, through application of Giordano's model for viscosity, and Dietzen's and Appen's models for surface tension [1]. Results are reported in Table 4 and Figure 2.

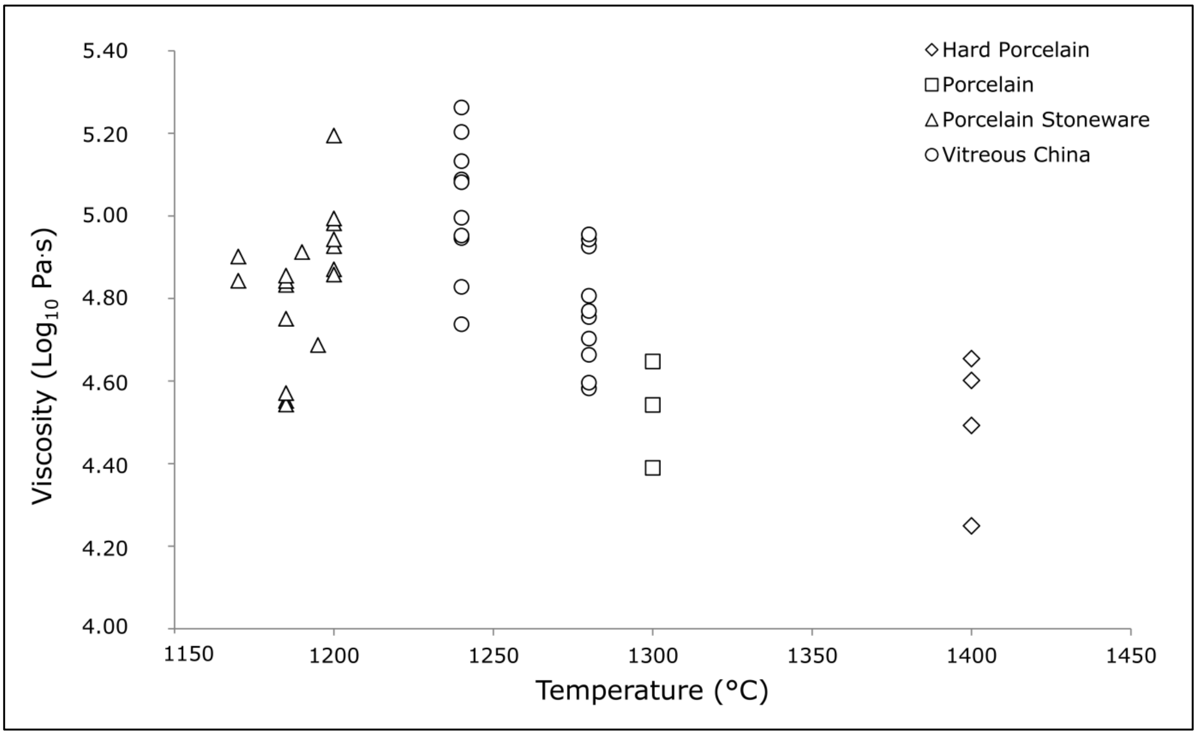

Figure. 2 *Correlation of viscosity versus firing temperature of Hard porcelain, Porcelain, Porcelain Stoneware, and Vitreous china products.*

In particular, three conclusions can be inferred from Figure 2. The first and expected one, is that the viscosity of the liquid phases decreases with increasing temperature. The second is that despite the four porcelain-like bodies being characterized by different firing temperatures, it seems that the viscous flow sintering occurs at a critical viscosity in a defined range from of 4.2 to 5 $\log_{10}$ Pa·s.

Finally, it can be observed that in order to control viscous flow sintering, the ratio between the vitreous phase amount and its viscosity is crucial. Specifically, in bodies where the amount of vitreous phase is low, as in hard porcelain (see Figure 3), a lower viscosity is needed. Conversely, where the amount of vitreous phase is abundant, as in porcelain stoneware, a higher viscosity is necessary.

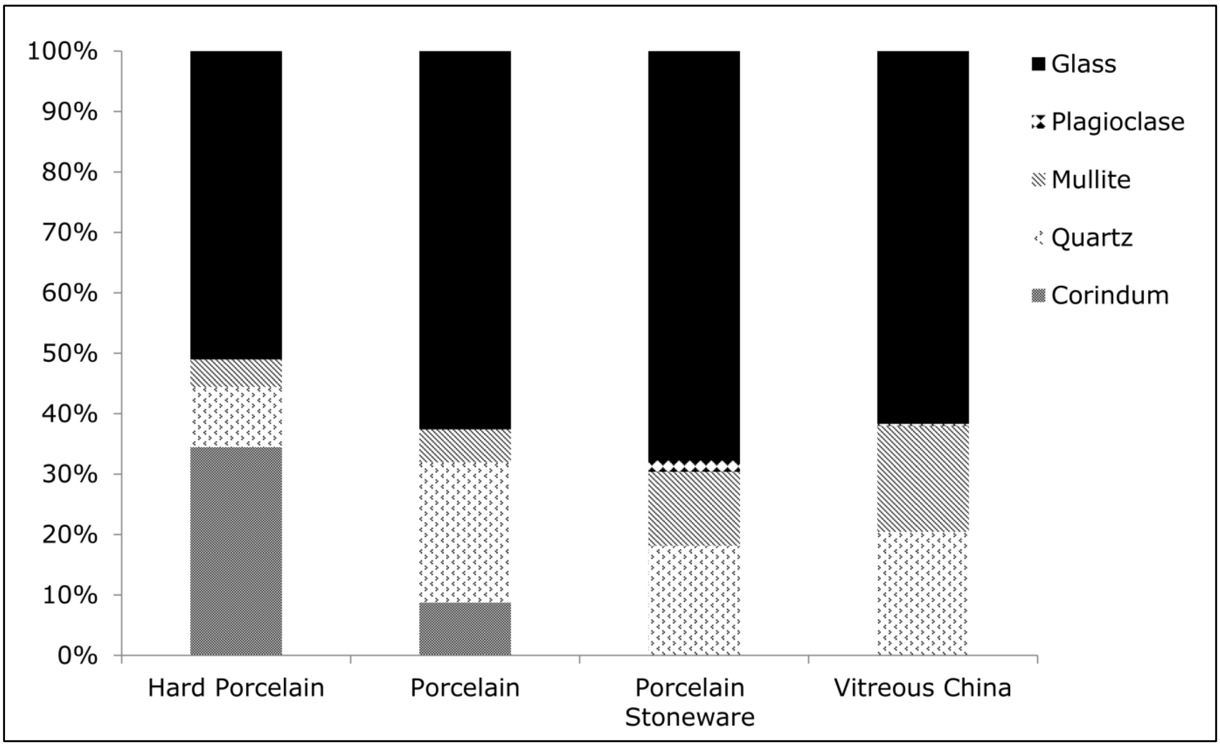

Figure 3. *The mineralogical composition of Hard porcelain, Porcelain, Porcelain Stoneware, and Vitreous china products.*

It is important to keep in mind that all these results are related only to the viscosity of the vitreous phase of porcelain-like bodies. In any case, in order to fully understand the phenomena acting during viscous flow sintering, the effects of crystals dispersed in the melt must to be also taken into account.

5. CONCLUSIONS

The goal of this work is a first attempt to estimate the viscosity of porcelain stoneware bodies at high temperature. Since porcelain-like materials (porcelain, porcelain stoneware, vitreous china,…) are composed of a vitreous phase as well as of a crystalline fraction, a first step involved the prediction of the vitreous phase viscosity at the temperature of viscous flow sintering. To do so, a method to calculate the chemical composition of the vitreous phase has been successfully applied to different porcelain-like bodies. In this contribution, it is demonstrated that starting from the quantitative chemical and mineralogical compositions of a porcelain-like body, it is possible to calculate the chemistry of the vitreous phase of the system. Then, a model to predict the viscosity at high temperature is needed. In this respect, based on the alumina contents and the good fit between the calculated and measured viscosities reported in literature, Giordano's model gave the most appropriate results.

The viscosities calculated for different vitreous phases suggest that despite hard porcelain, porcelain, porcelain stoneware, and vitreous china being characterized by different sintering temperatures, viscous flow sintering takes place in all of them at a critical viscosity of 4-5 $\log_{10}$ Pa·s.

The prediction of the vitreous phase viscosity discloses new opportunities for a fuller understanding of viscous flow sintering, which is becoming pivotal in the manufacture of increasingly larger products. The approach proposed here is followed up to better understand the role of melt viscosity in pyroplasticity, with feedback on batch formulation.

6. ACKNOWLEDGEMENTS

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