The Influence of Particle Size Distribution on the Performance of Ceramic Particulate Suspensions

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In memoriam of Professor Dr. Brian Scarlett

Abstract

During the preparation of ceramic glaze suspensions it is necessary to guarantee that the suspension possesses the required properties, with several parameters having to be rigorously controlled, e.g., particle size and solids concentration, composition of the suspension and ionic charge of the liquid. This study focuses attention on the influence of particle size distribution on three important properties of glaze suspensions: rheological behavior, opacity and reflectance characteristics and tendency to dissolve. In this paper, results are presented for two glaze formulations prepared with two different commercial frits of distinct composition. The glazes were prepared in a laboratory ball mill and the grinding time was adjusted for each formulation, in order to obtain suspensions with different particle size (at least three different grinding times). The rheological behavior is strongly dependent on the particle size and also on changes in the interactions between the particles, caused by modifications in the cationic content of the suspending medium, as a result of frit dissolution, which is also influenced by the size of the particles.

Keywords: glaze, grinding, particle size distribution, reflectance, rheology

1 Introduction

Glaze suspensions are complex mixtures of different particulate materials, essentially frit and kaolin. The frits can have different compositions, but are always a solid mixture of oxides of several metals, depending on the final properties required for the glaze (hardness, optical properties, etc.). Therefore, in such a complex mixture, interactions between the particles are very intricate and are strongly affected by the size of the particles.

In addition, the preparation of ceramic glaze suspensions requires that an adequate flow behavior is maintained. Therefore, several parameters have to be rigorously controlled, e.g., particle size and solids concentration, composition of the suspension, ionic charge of the liquid, etc. On the other hand, it is quite usual in the ceramics industry for the glaze suspension to lose its suitable flow characteristics with time. That can be caused by the dissolution of the glaze or by the sedimentation of the particles, which result in agglomeration or deagglomeration of the solids. This can result in difficult problems for industry, mainly when the process is irreversible. These effects have been observed by several authors [1], but some authors have recently begun to study the relation between the release of cations by the frit and the changes detected in the rheological behavior of the glaze, in a more systematic manner [2,3].

This work focuses attention on the influence of the size of the particles on the quality and stability of glaze suspensions, since particle size has the strongest affect on the rheology and performance of these suspensions, aside from the frit composition.

In this paper, results are presented for two glaze formulations prepared with two different commercial frits of distinct composition. The glazes were prepared in a

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laboratory ball mill, and for each formulation, the grinding time was adjusted in order to obtain suspensions with different particle sizes (at least three different grinding times). Three quality parameters were evaluated: rheological behavior of the suspension, dissolution of the glaze and opacity of the final glaze. The main focus and effort was directed to the control of the rheology of the glaze suspension. Rheological behavior is strongly dependent on particle size and also on changes in the interactions between the particles, caused by modifications in the cationic content of the suspending medium, as a result of frit dissolution. Furthermore, the rate of cationic release is also influenced by the size of the particles.

Correlations are made between the rheology of the glaze and the particle size, and the manner in which particle size influences the aging of the glaze, i.e., deterioration of its rheological behavior with time, is also discussed.

It is obvious that adequate control of particle size in glaze production, can contribute to energy savings, since grinding is one of the most inefficient operations in industry, as far as energy is concerned. Thus, being able to control grinding time and avoid excessive grinding without affecting product quality, will be most important for the ceramics industry.

2 Slurry Rheology

When a fluid or slurry is subjected to a deformation by applying tangential stress (shear stress, τ) different behaviors can be observed. Usually, the resistance offered by the fluid element to deformation can be related to the fluid viscosity, μ, and more generally, to the rheological behavior of the fluid.

In general, one can write the relation between shear stress, τ, and shear rate, γ' as:

$$\gamma' = f(\tau) \tag{1}$$

where the form of the function depends on the nature of the fluid, i.e., on the rheological behavior of the fluid. The simplest case is a Newtonian fluid that corresponds to a linear relation between shear stress and shear rate, Eq. (2):

$$\tau = \mu\,\gamma' \tag{2}$$

where μ is the constant fluid viscosity.

However, Newtonian behavior is rarely found when analyzing slurries, unless the concentration of solids is very low.

The rheological tests that allow one to characterize the fluid in this manner are flow tests, which provide the shear stress versus shear rate curve. Moreover, there are fluids that exhibit a shear stress versus shear rate curve which is dependent on time. These fluids show a hysteresis loop when they are subjected to an ascendant shear ramp followed by a descendant one. That was the case for all of the suspensions tested in this work. These fluids can be either thixotropic or rheopetic, depending on whether the viscosity decreases or increases with time.

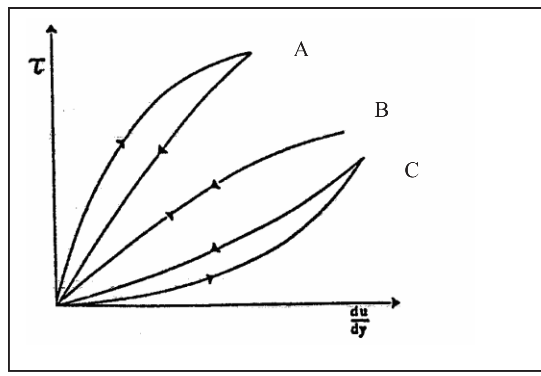


Fig. 1: Time dependent rheological behavior (A – thixotropic; B – pseudoplastic; C – rheopetic).

3 Experimental

This work involves the study of two different glazes based on two frits (transparent and matt, see Table 1 for compositions) and on a pre-fixed kaolin used as the suspending medium (Galiza kaolin) rich in kaolinite, presenting only small percentages of quartz. The glazes also had a small percentage of bentonite acting as a binding agent. The glazes average composition (w/w) was 40 % water, 56 % frit, 3.8 % suspending agent (kaolin), and 0.2 % bentonite. The water used to prepare the suspensions was also controlled (pH, hardness and conductivity). No significant variation of the water characteristics was detected while performing the tests (once a month during the duration of the study). All the suspensions

Table 1: Frits' composition.

	Chemical Composition (wt %)								
Frit	**Na_2O**	**K_2O**	**MgO**	**CaO**	**BaO**	**B_2O_3**	**PbO**	**Al_2O_3**	**SiO_2**
FFA 4	15	5	–	6	–	15	–	9	50
FMP 3505	4	1	–	19	3	13	2	5	53

Table 2: Suspension characteristics.

Suspension	Grinding Time (min)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	Residue (%)	Density (g/L)
FFA 4 glaze	18	4.24	20.04	50.01	6	1615
	21	3.42	16.84	43.07	4	1620
	25	2.93	10.48	23.44	1.3	1635
FMP 3505 glaze	18	2.11	16.11	61.20	5.5	1566
	22	1.95	13.88	49.68	3.5	1577
	28	1.66	10.47	24.59	1.7	1571

were prepared through wet grinding in a laboratory ball mill.

Different grinding times were tested (at least three times) in order to obtain suspensions of different particle size distribution. The grinding times were adjusted so that the residue varied between 1.5 and 6.5 in a 45 μm sieve. For each suspension the suspension density (25 °C) was measured and adjusted so that it fell between 1550 and 1700 g/L, according to industrial specifications. The particle size distribution was measured by laser diffraction spectroscopy (LDS). Table 2 summarizes the average values of the particle size distributions obtained (d_{10}, d_{50}, d_{90}) for the different grinding times.

Figure 2 presents an example of the size distributions obtained with frit FMP3505, for two grinding times.

The rheological characterization was performed in a *Brookfield* rotating viscometer DVII+ equipped with concentric cylinders, and the rotating speed was varied between 10 and 200 rpm. The temperature of the suspension was kept constant at 25 °C. Moreover, in order to monitor the frit dissolution, the ionic composition of the supernatant water from the glaze was analyzed over time. The ionic composition of the supernatant liquid from the suspension was measured by atomic absorption. Additionally, the conductivity of each suspension was also measured. All the measurements (rheology, dissolution and conductivity) were performed at t = 0, 24, 48 and 192 h, in order to control the aging of the suspension.

The influence of particle size on glaze opacity has also been checked, since texture is an essential quality parameter in glaze production and the opacity has to remain within certain limits. The glaze was applied as a thin coating in a ceramic body and then fired to two different temperatures (1080 and 1180 °C). The opacity of the final glaze was measured with a CM500 colorimetric spectrometer that measures the reflectance percentage of a light beam. Higher reflectance values mean higher opacity with this instrument.

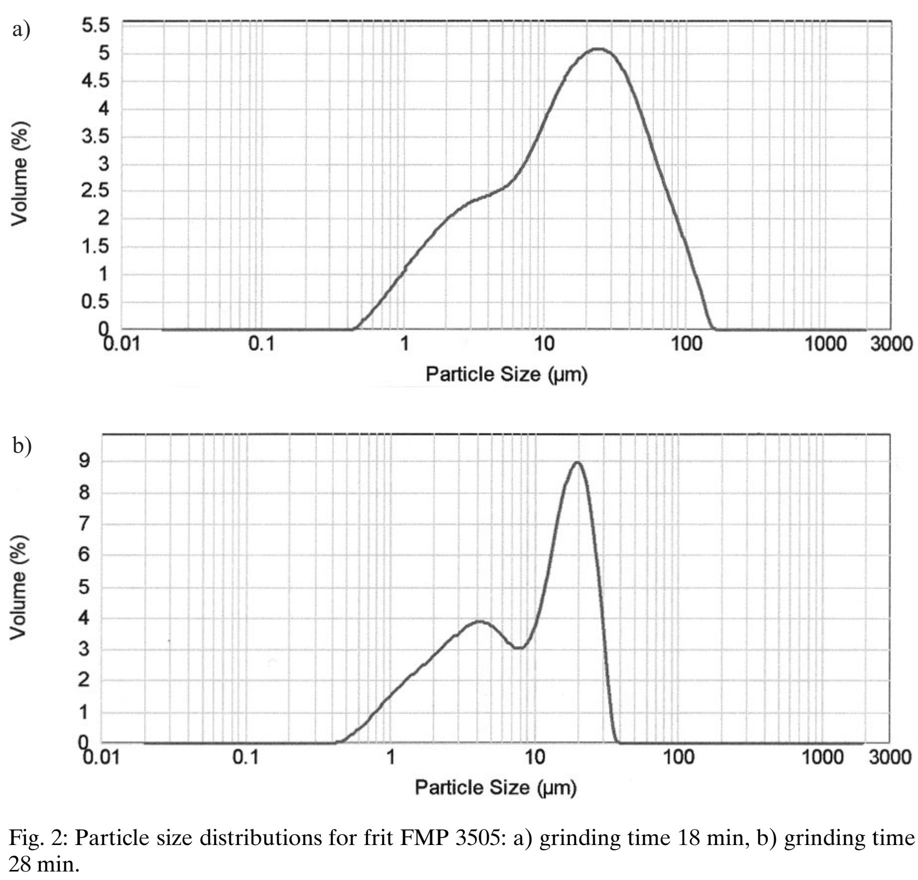
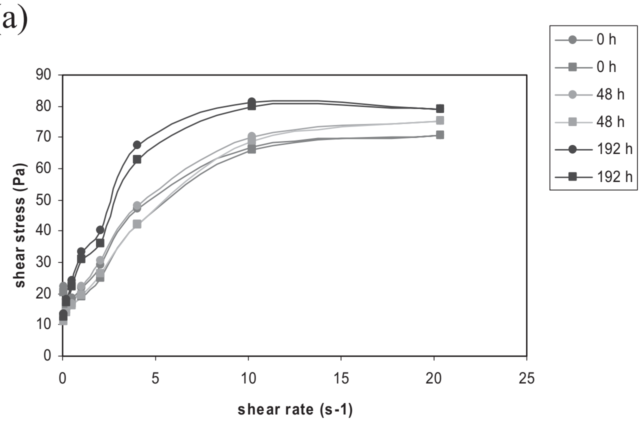


Fig. 2: Particle size distributions for frit FMP 3505: a) grinding time 18 min, b) grinding time 28 min.

4 Results

Figures 3 and 4 show the flow test results for the two frits studied, for the different grinding times and for three aging times (0, 48 and 192 h). From examination of the shear stress vs. shear rate curves, it is obvious that the suspensions are thixotropic.

(a)



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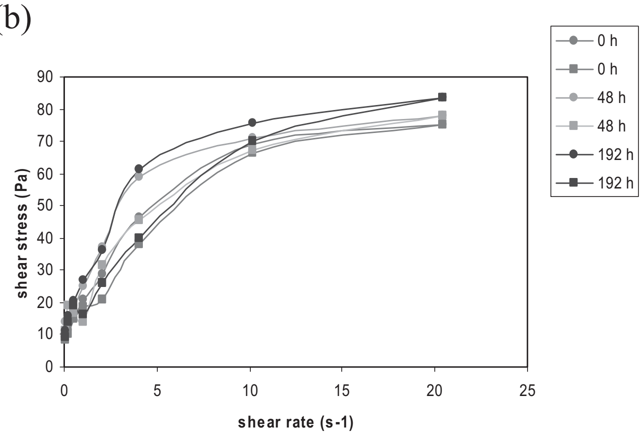

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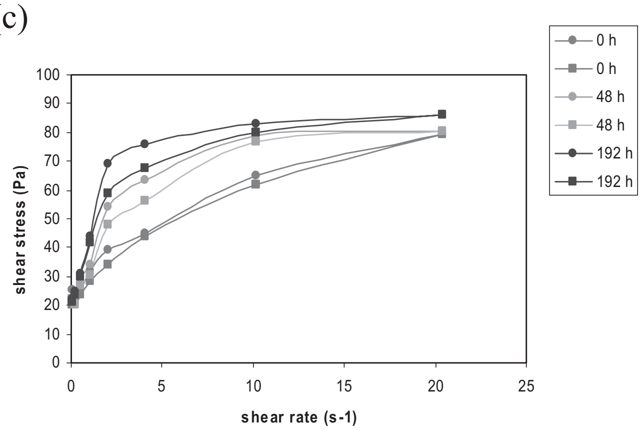
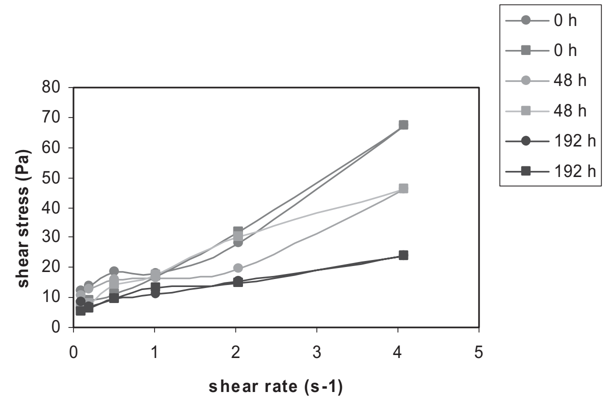


Fig. 3: Flow tests for frit FFA 4 (● – up ramp; ■ – down ramp). a) 18 min, b) 21 min, c) 25 min.

(a)



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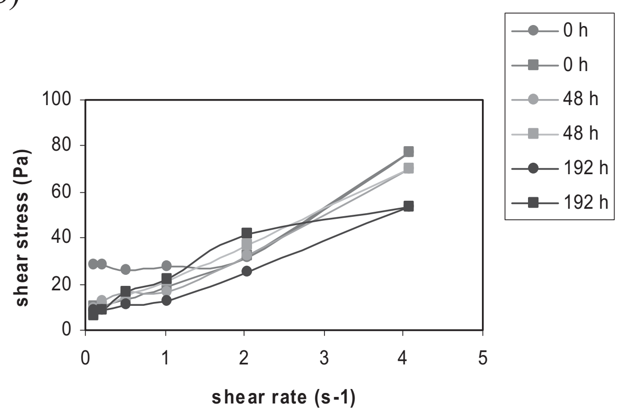

(c)

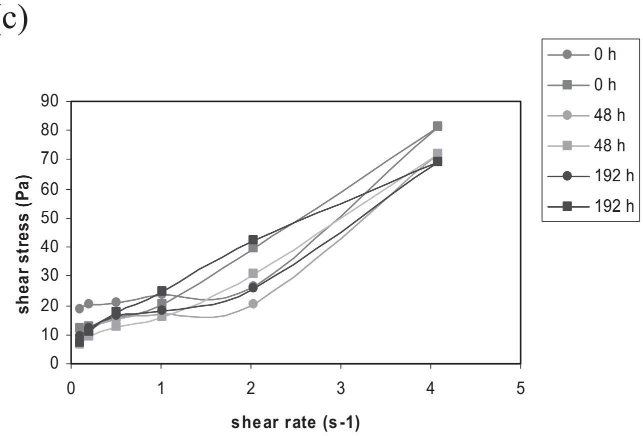

Fig. 4: Flow tests for frit FMP 3505 (● – up ramp; ■ – down ramp). a) 18 min, b) 22 min, c) 28 min.

It is also apparent from the analysis of these figures that both viscosity and hysteresis area tend to increase as the particle size (d_{50}) decreases. Furthermore, the initial yield stress also increases as the particle size decreases. On the other hand, thixotropy increases with glaze age, but this effect is more pronounced if the particles are smaller (higher grinding time).

From comparison of the results for the two frits, the FMP 3505 glaze presents the highest viscosity (see Table 3) and a more typical aging process (the hysteresis area increases more as time elapses) mainly for the smaller particles. However, the viscosity decreases with age, probably due to a sedimentation effect, which is more pronounced in the case of this frit since it is much denser.

Table 4 details the evolution of the suspension conductivity with aging time, while Table 5 presents the results of the analysis of the cationic content of the supernatant water from the suspensions, for the different aging times. The conductivity increases with aging time, being higher for the FMP 3505 suspension and showing a more pronounced increase with time when the particles are smaller. This agrees with the fact that the cationic concentration, in general, increases as the particle size decreases (see Table 5).

Moreover, the trends observed for the cationic content of the suspension agree with the trends detected for the evolution of the suspension viscosity. The higher viscosities correspond to the larger conductivities, since in

Table 3: Suspension viscosity at infinite shear rate.

Glaze	Grinding Time (min)	μ_∞ (cp)		
		t = 0 h	t = 48 h	t = 192 h
FFA 4	18	351	374	393
	21	375	388	417
	25	396	400	430
FMP 3505	18	1675	1145	749
	22	1930	1750	1340
	28	2025	1795	1720

Table 4: Suspension conductivity.

Glaze	Grinding Time (min)	Conductivity (μS/cm)		
		t = 0 h	t = 48 h	t = 192 h
FFA 4	18	555	590	618
	21	589	640	628
	25	635	678	675
FMP 3505	18	673	715	715
	22	752	746	764
	28	710	772	803

Table 5: Cationic content of the suspensions.

Ion	Concentration (mg/L) – FFA 4								
	Grinding Time – 18 min			Grinding Time – 21 min			Grinding Time – 25 min		
	0 h	48 h	192 h	0 h	48 h	192 h	0 h	48 h	192 h
Na	52.65	79.94	78.68	88.39	85.59	84.91	96.85	98.28	109.19
Ca	3.89	2.08	2.15	4.08	3.66	3.93	9.14	6.26	7.07
K	18.50	14.00	19.75	27.75	24.75	28.50	32.25	28.50	37.25
Pb	–	–	–	–	–	–	–	–	–
	Concentration (mg/L) – FMP 3505								
	Grinding Time – 18 min			Grinding Time – 22 min			Grinding Time – 28 min		
	0 h	48 h	192 h	0 h	48 h	192 h	0 h	48 h	192 h
Na	177.99	193.32	220.22	164.49	216.08	246.17	173.15	246.92	285.50
Ca	24.00	20.14	52.67	85.83	69.50	131.00	88.67	124.00	211.70
K	16.25	16.69	15.61	13.17	17.78	15.92	21.43	20.44	20.43
Pb	0.00	0.06	0.06	2.22	2.74	3.75	3.24	3.54	6.05

cases where the cationic content is higher, the electric double layer around the particles tends to be thinner, favoring aggregation of the particles [3], which leads to both higher viscosities and initial yield stresses.

It is also important to note that both frits release significant amounts of Ca^{2+}. Additionally, frit FMP3505 also releases Pb^{2+} due to its composition. It has previously been proven that these two cations are the ones presenting more difficult handling problems for glaze suspensions due to their strong impact on suspension rheology, and these results are detailed in another publication [4]. This agrees with the observation that aging is more obvious for frit FMP 3505, since, in this case, both Ca^{2+} and Pb^{2+} are being released into the suspending medium. Moreover, aging is more evident when the amount of these two cations in the suspension is higher, i.e., when the particles are smaller.

In Figure 5 one can see the reflectance curves for the two frits, for the different grinding times and for a firing temperature of 1180 °C. Table 6 summarizes the colorimetric results (reflectance percentages) for the two frits, giving information on the range of reflectance values (as a function of wave length) for the glazes studied.

It is evident from the examination of both Figure 5 and Table 6 that the reflectance, and hence, the opacity, increase slightly for frit FMP 3505 as the particle size decreases. However, this influence is not very pronounced. On the contrary, for frit FFA 4, the trend is the opposite, with the reflectance increasing as the particle size increases (see Table 6). In this case there is a second effect influencing the texture characteristics of the glaze. Since one is dealing with a predominantly vitreous frit and not a crystalline one, as in the case of frit FMP 3505, grinding may destroy the few small crystals in the frit leaving only amorphous structures, and therefore, the reflectance will be smaller for larger grinding times. In fact, it is for this frit that the influence of grinding time on the reflectance is most pronounced. Nevertheless, it can be said that reflectance is not very dependent on this parameter for the range of particle sizes studied.

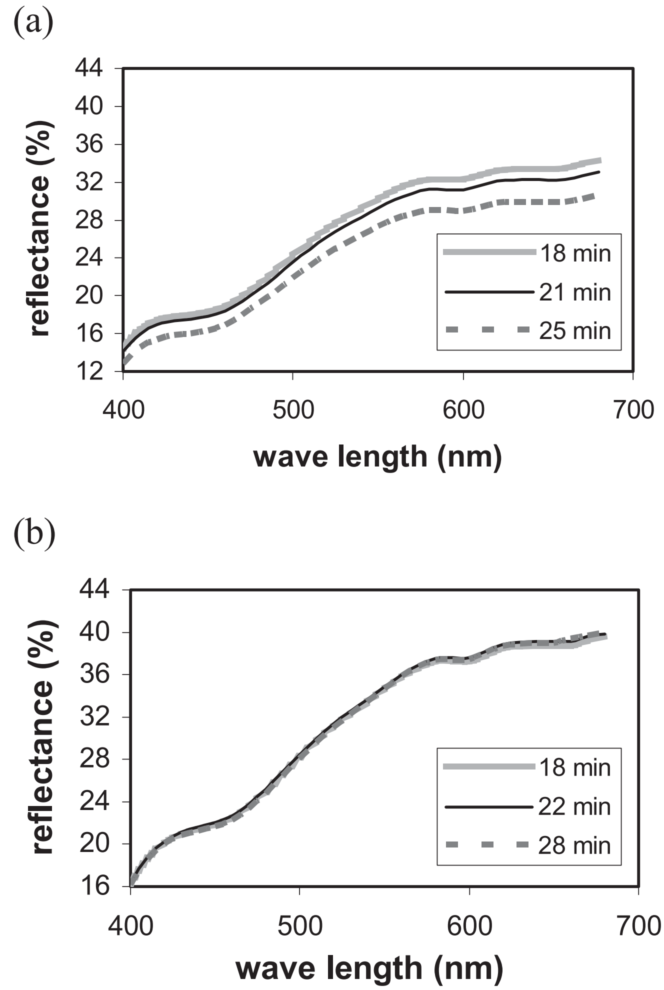

Fig. 5: Reflectance curves (firing temp. 1180 °C): a) FFA 4, b) FMP 3505.

5 Conclusions

Glaze suspensions are complex mixtures of different particulate materials. The interactions between the particles are very intricate and strongly dependent on their size in such complex mixtures.

Table 6: Glaze reflectance.

Glaze	Grinding Time (min)	Reflectance Range (%)	
		1080 °C	1180 °C
FFA 4	18	19.8 – 49.4	14.5 – 34.2
	21	19.7 – 49.2	14.1 – 32.9
	25	19.7 – 48.9	12.8 – 30.5
FMP 3505	18	23.6 – 57.4	16.3 – 38.9
	22	24.0 – 58.0	16.3 – 39.7
	28	24.0 – 58.8	16.4 – 39.9

In this study, it has been proven that particle size, which is dependent on the grinding time, has a strong impact on the rheological behavior of glaze suspensions, i.e., on the degree of thixotropy. Moreover, the particle size also influences the aging of the glaze suspension caused by the dissolution of the frit. In fact, the frits tend to release different cations as time elapses, depending on their composition, and the rate of release of the cations is dependent on the size of the particles. Aging is, nevertheless, highly dependent on the composition of the frit.

In addition, it has also been shown that the glaze opacity, as given by the reflectance percentage, can also be influenced by the size of the particles. However, there is a large range of particle sizes for which the dependence is not very prominent, though it is conditioned by the composition of the frit. In the case of vitreous frits, the influence of particle size on the glaze opacity is more obvious.

In conclusion, it is possible to say that the study conducted shows that a close control of the particle size in glaze preparation is essential to guarantee adequate properties, both during the application stage and in the final product.

6 References

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