STUDY OF OPACIFIERS IN CERAMIC MATERIALS

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1. ABSTRACT

Opacifiers are natural or synthetic raw materials that are added to ceramic compositions to increase opacity and the degree of whiteness of bodies, engobes, and glazes. The opacifiers used in the ceramic sector have evolved with time owing to the need to optimise the opacity/cost ratio. The two currently most widely used opacifiers are zirconium silicate and alumina.

The use of these opacifiers in ceramic compositions depends on numerous factors. Such factors include cost, type of composition into which the opacifier is introduced, opacifier reactivity with the ceramic matrix, and opacifier refractive index, particle size, chemical composition, and effect on the material's behaviour and resulting ceramic properties.

This paper describes a systematic study of the influence of various factors on opacification in porcelain tile bodies and glazes. The study examines the effect of opacifier particle size and quantity added on the whiteness and opacity of the ceramic material, as well as on the material's behaviour in the ceramic process and on its final properties.

When testing porcelain tile bodies, it was observed that the reduction in particle size had a much greater opacifying effect when zircon was used than when alumina was used. In addition, at small particle sizes (d_{50}=0,5 µm) the alumina partially dissolved, whereas the zircon remained stable. In the glazes, the main difference between both opacifiers was the high refractoriness and roughness that alumina contributed compared to zircon.

2. INTRODUCTION

Ceramic tile design and aesthetics are key characteristics when it comes to selecting a material for building decoration. These properties are obtained by using either natural or synthetic pigments, which are incorporated into ceramic materials by different methods [1][2]. For these pigments to develop colour satisfactorily, it is often necessary to have a white substrate, which makes white one of the main pigments used for bodies, engobes, and glazes.

Zirconium silicate or zircon is one of the most widely used white pigments in ceramics because of its high refractive index (1,92–1,97) [3] and high refractoriness (melting temperature ≅2100–2300 ºC) [4]. The particle size used differs as a function of the opacification mechanism targeted. Thus, when the mechanism is that of "inert particles", it is of interest to have zircon with a small particle size so that there is a greater surface area to interact with the light. One of the most commonly used sizes is the so-called "FIVE" size, which is used in porcelain tile bodies, engobes, and glazes, with a d_{50} value of about 1,8 µm [5][6][7][8]. There is a second mechanism, known as "devitrification", used in frit production, in which zircon with a larger particle size is used (d_{50}=15 µm). Here, the zircon becomes part of the glassy structure of the frit during its fusion process. When the frit is used as raw material in engobes and glazes, the zircon devitrifies during tile heating at temperatures above 900 °C [9][10][11]. The advantage of this mechanism is the small particle size of the devitrified zircon (d_{50} about 0,5 µm), which fosters white colour development (opacification).

In recent years, zircon use has decreased for several reasons, one being the great volatility in zircon prices [12]. The main substitute for zircon in ceramic tile manufacture is calcined alumina which, though it provides lower whiteness and modifies some tile characteristics, has a more competitive price [12][13][14].

In view of the above, a study was undertaken to quantify the advantages and disadvantages of using these two opacifiers in ceramic body and glaze compositions customarily used to manufacture porcelain tile, when opacifier content and particle size were modified.

3. EXPERIMENTAL

3.1. MATERIALS

The study was performed on a typical body and glaze composition used in porcelain tile manufacture. The body composition (base composition, expressed in wt%) consisted of 35% clay, 50% sodium feldspar, and 15% kaolin. The glaze composition (expressed in wt%) contained 32% matt frit (without zirconium), 21% wollastonite, 28% nepheline, 8% quartz, and 11% kaolin. Table 1 details the chemical analysis of both compositions.

	SiO_2	Al_2O_3	B_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	ZnO	P_2O_5	BaO	L.O.I.
Body	63,8	23,6	--	0,43	0,41	0,25	5,02	1,01	0,57	--	0,02	0,02	4,68
Glaze	58,9	16,5	0,15	0,20	13,5	0,30	4,90	2,0	0,05	1,55	0,05	0,01	1,86

Table 1. *Chemical analysis of the body and glaze compositions (wt%).*

Zircon and calcined alumina with a specific surface area of 7,5 m^2/g were used as opacifiers. Both opacifiers were wet milled in water either in a ball mill or a bead mill (depending on particle final size) until an average particle size (d_{50}) of about 5, 1,8, and 0,5 µm was reached. The particle size distribution of the milled opacifiers, together with the values of the characteristic diameters (d_{90}, d_{50}, and d_{10}), are shown in Figure 1.

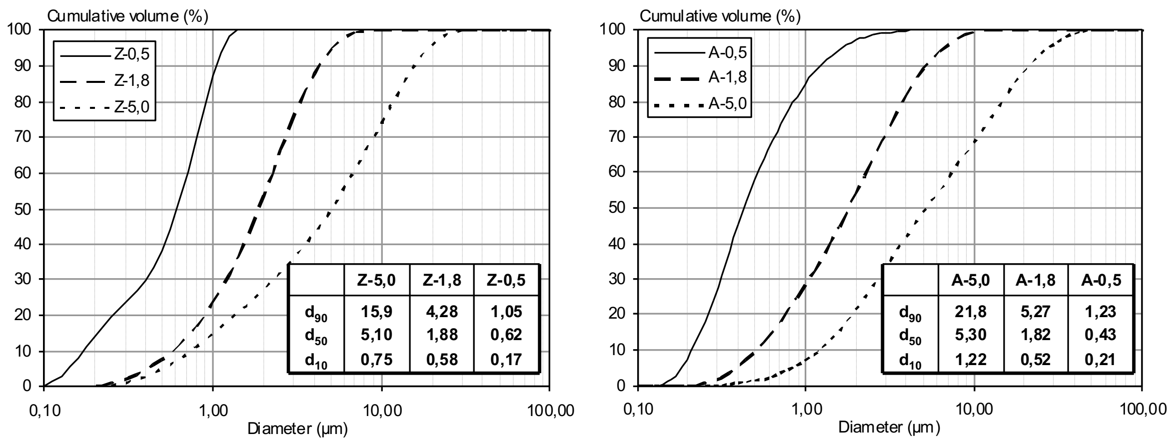

Figure 1. *Particle size distribution of the studied zircon (left) and alumina (right).*

3.2. PREPARATION AND CHARACTERISATION OF THE BODY COMPOSITIONS

The body composition without the opacifier was prepared first, by mixing the raw materials indicated in the previous section and milling them in water in a planetary ball mill until a reject of about 1% was reached on a 40 µm sieve. Increasing quantities of zircon, namely 3, 6, and 9% (percentage additions), were then added to the base composition. With a view to determining the alumina content that provided the same whiteness as that obtained with zircon, for each particle size, further compositions were prepared by adding alumina to the base composition. The alumina additions ranged from 2 to 18%.

To study pressing and firing behaviour, cylindrical test pieces (4 cm in diameter and about 7 mm thick) were formed by uniaxial pressing at a pressing moisture content of 5,5% (dry basis) and a pressing pressure of 400 kg/cm^2. The test pieces were dried at 110 °C in an electric laboratory oven with air recirculation. Their bulk density was determined by the mercury displacement method, after which they were fired with a fast firing cycle and 6-minute dwell at peak temperature in an electric laboratory kiln. The heating rate was 25 °C/min.

The chromatic coordinates, bulk density (by the mercury displacement method), and water absorption (measuring the weight gained by the test pieces after immersing them in boiling water for two hours) of the fired test pieces were then determined. Vitrification diagrams were constructed to determine the maximum densification temperature (Tmax), which was close to that of industrial firing. The chromatic coordinates were subsequently calculated at this temperature to compare the effect of opacifier content and particle size.

3.3. PREPARATION AND CHARACTERISATION OF THE GLAZE COMPOSITIONS

The body composition without the opacifier was prepared first, by mixing the raw materials indicated in the previous section and milling them in water in a planetary ball mill until a reject of about 1% was reached on a 40 µm sieve. Increasing quantities of zircon, namely 3, 6, and 9% (percentage additions), were then added to the base composition. With a view to determining the alumina content that provided the same whiteness as that obtained with zircon, for each particle size, further compositions were prepared by adding alumina to the base composition. The alumina additions ranged from 2 to 18%.

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4. RESULTS

4.1. BODY COMPOSITIONS

The evolution of dry bulk density with opacifier content is shown in Figure 2. It may be observed that zircon increased the dry bulk density of the pieces except when zircon particle size was small (d_{50}=0,5 µm), whereas alumina reduced bulk density at all tested particle sizes. The effect of both opacifiers on dry bulk density depended on two factors. On the one hand, the greater true density of both opacifiers with relation to the base composition (4,62 and 3,98 g/cm^3 for zircon and alumina, respectively, compared to 2,65 g/cm^3 for the base composition) tended to increase the bulk density of the pieces. On the other, opacifier particle size influenced particle packing in the composition. When alumina was introduced, the packing factor predominated over the true density factor, which decreased bulk density. However, when zircon was used, the true density factor predominated at average particle sizes (d_{50}) of 5,0 and 1,8 µm. When fine zircon (d_{50}=0,5 µm) was used, the magnitude of both factors was similar, leading to little variation in bulk density of the pieces.

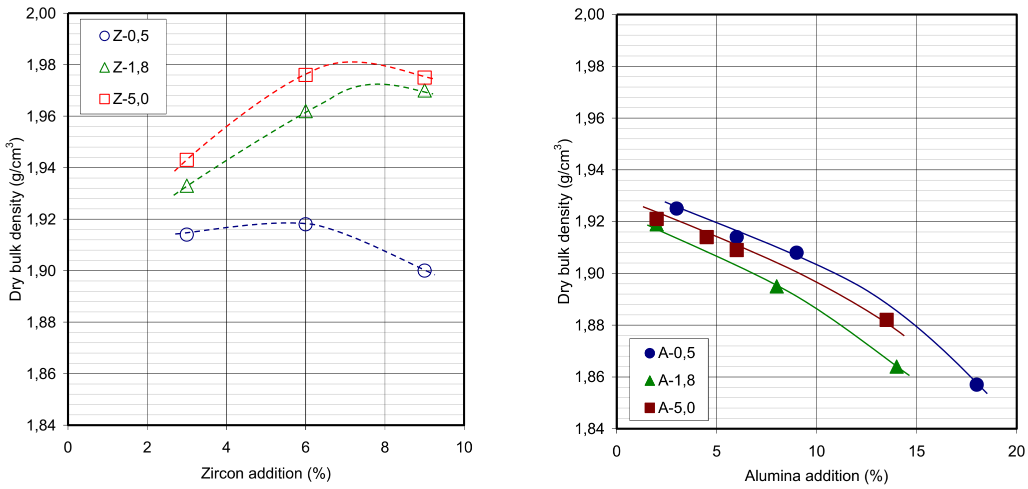

***Figure 2.** Evolution of bulk density with zircon (left) and alumina (right) content.*

With a view to eliminating the true density factor, the porosity of the dry pieces was calculated from the bulk density and true density values. The results are shown in Figure 3, which indicate that both opacifiers worsened base composition packing, this effect being heightened as opacifier content in the composition increased. This indicates that the base composition contained an excess of small particles.

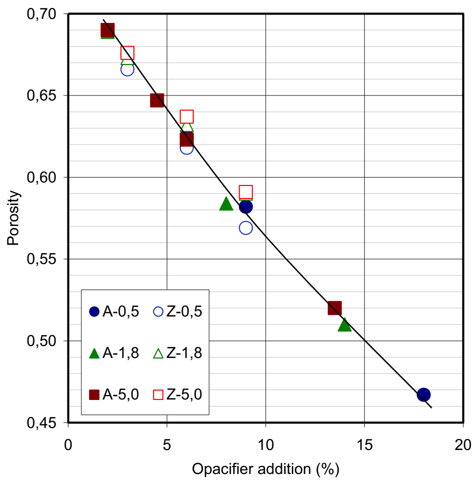

***Figura 3.** Evolution of porosity of the dry pieces with opacifier content.*

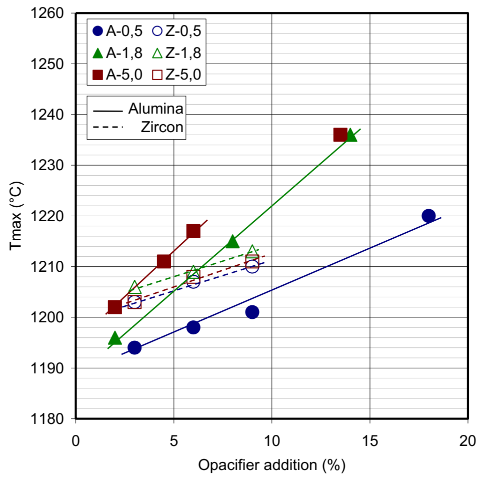

***Figura 4.** Variation of Tmax as a function of opacifier addition and opacifier particle size.*

The maximum densification (Tmax) temperatures obtained from the vitrification diagrams are shown in Figure 4. It may be observed that as opacifier content increased, maximum densification temperature rose as a result of the greater refractoriness of both materials compared to that of the ceramic matrix (base composition). When zircon was used, the increase in Tmax was not very pronounced (the slope of the lines was low) and the influence of zircon particle size was not significant. In contrast, using alumina raised Tmax to a larger extent (greater slope of the lines) and the influence of alumina particle size was higher.

The effect of alumina particle size might be related to reports in some studies [15] indicating that, in porcelain tile compositions, as particle size increased the resulting unfired microstructures contained a greater proportion of larger pores. The increase in pore size in the unfired piece delayed the sintering process, which required higher firing temperatures to attain the maximum densification state. However, as the zircon and alumina particle sizes were similar and no significant effect of zircon particle size on Tmax was observed on using zircon, the greater effect produced by alumina could be due to there being a certain dissolution of alumina during firing, which locally increased liquid-phase viscosity and adversely affected the sintering process. X-ray diffraction (XRD) tests were conducted which showed that there was a certain dissolution of alumina, which was not observed for zircon.

In Figure 5 (left), the values of the L* coordinate are plotted as a function of opacifier addition and opacifier particle size. The L* coordinate rose when zircon content increased and its particle size decreased as a result of the greater opacifier surface area that interacted with the light. When alumina was used, the L* coordinate also increased with opacifier content, but in this case particle size had little influence and a reduction in slope was observed as alumina content increased. This reduction was more pronounced when the smallest alumina particle size (d_{50}=0,5 µm) was used, which led to lower whiteness when the alumina addition was higher than 5% using the smallest alumina particle size.

With a view to understanding why the smallest alumina particle size provided lower whiteness compared to that of the other two tested aluminas, XRD tests were performed on some fired pieces that contained alumina, specifically on the pieces of compositions A-5,0/6%, A-0,5/6%, and A-0,5/18%. The presence was observed of a small alumina dissolution when the particle size was large (d_{50}=5,0 µm) and a considerable dissolution at the small particle size (d_{50}=0,5 µm), in particular when the alumina content in the piece was very high and Tmax was consequently also very high. Figure 5 (right) shows the evolution of the L* coordinate as a function of the real opacifier content in the fired pieces: the red diamonds plot the values determined by XRD. It may be observed that the lines that plot the variation of the L* coordinate with alumina content run parallel instead of crossing each other as in Figure 5 (left).

Comparison of both opacifiers reveals that at large particle sizes (d_{50}=5,0 µm), alumina provided a higher L* coordinate value than zircon, owing to the greater presence of colouring impurities in the latter. However, the greater influence of zircon particle size on the L* coordinate caused zircon to provide a higher L* coordinate value at intermediate and small particle sizes (d_{50}=1,8 and 0,5 µm).

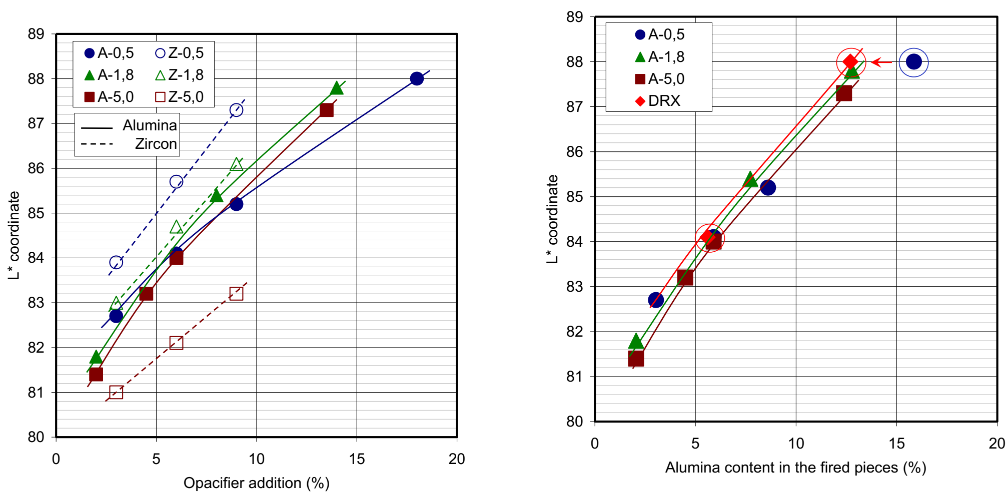

Figure 5. *Evolution of the L* coordinate with opacifier content and particle size. Left: experimental data. Right: data corrected by XRD.*

The values of the a* and b* coordinates are plotted in Figure 6. The figure shows that the increase in content of both opacifiers reduced the value of the two coordinates as a result of their opacifying effect on the base composition, which exhibited a slight reddish and yellowish hue. With regard to particle size, the trend was similar to that discussed for the L* coordinate: zircon particle size had a significant effect on the value of both coordinates, whereas no significant differences were observed when alumina particle size was modified. Similarly, at large opacifier particle sizes (d_{50}=5,0 µm), alumina provided lower chromaticity (lower values of the a* and b* coordinates), whereas at smaller particle sizes (d_{50}=1,8 and 0,5 µm) zircon exhibited a greater opacifying power.

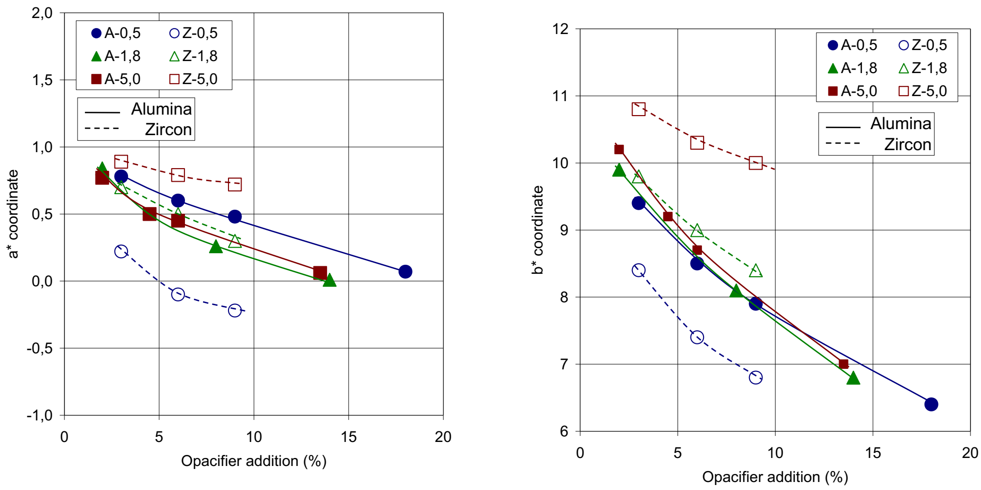

Figure 6. *Evolution of the a* (left) and b* (right) coordinates with opacifier content and particle size.*

To round off this section, for each studied opacifier particle size, the quantity of alumina was calculated that needed to be added to obtain the same whiteness (L* coordinate) as that provided by zircon (Figure 7). A comparative analysis was also performed of the properties of pieces with the same whiteness using opacifiers having the particle sizes currently used in industry (d_{50}=5,0 µm for alumina and d_{50}=1,8 µm for zircon). The composition with 6% zircon was used as reference.

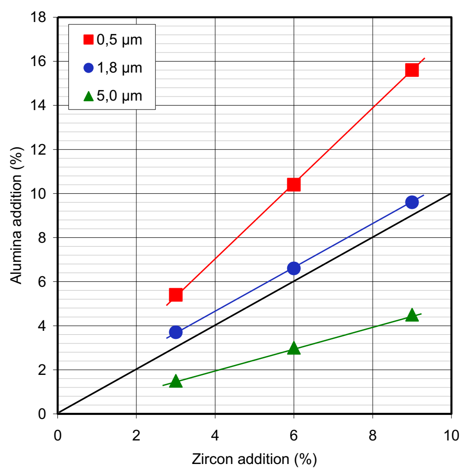

Figure 7. *Alumina addition that provided the same L* coordinate as that shown by zircon for each tested particle size.*

Opacifier	Zircon	Alumina
Addition (%)	6,0	7,3
Tmax (ºC)	1209	1218
Linear shrinkage (%)	8,5	8,6
a*	0,5	0,4
b*	9,0	8,4

Table 2. *Properties of the compositions with alumina (d_{50}=5,0 µm) and zircon (d_{50}=1,8 µm) that exhibited the same value of L* (84,7) at Tmax.*

4.2. GLAZE COMPOSITIONS

In the case of the glazes, the main variables used in the study were the L* chromatic coordinate, related to the opacity and whiteness of the glaze coating, and gloss. Firings were performed at 1180 and 1200 ºC. The glazes prepared with zircon as opacifier all sealed, even at the lower test temperature. However, the introduction of alumina increased refractoriness so much that the glazes with the greatest alumina content did not seal at the higher test temperature. The compositions that did not seal at 1200 °C are shown in Figure 8 (left). As may be observed, the increased refractoriness produced by alumina was more pronounced as particle size decreased. At a particle size of 5 µm the maximum quantity that could be added was about 9%, whereas at a particle size of 0,5 µm the maximum quantity dropped to about 4%.

The results obtained at 1200 °C when alumina and zircon were added are compared in Figure 8 (right). It shows that zircon particle size 5 µm gave rise to glazes that were not very opaque, their opacity being lower than that obtained when the same alumina particle size was used as opacifier. The results obtained using particle size 1,8 µm were very similar, though it should be noted that the glazes with alumina contents larger than 6% were not sealed. In the case of the smallest particle size, 0,5 µm, alumina gave rise to more opaque fired glazes than zircon, its use being limited to about a 4 wt% addition.

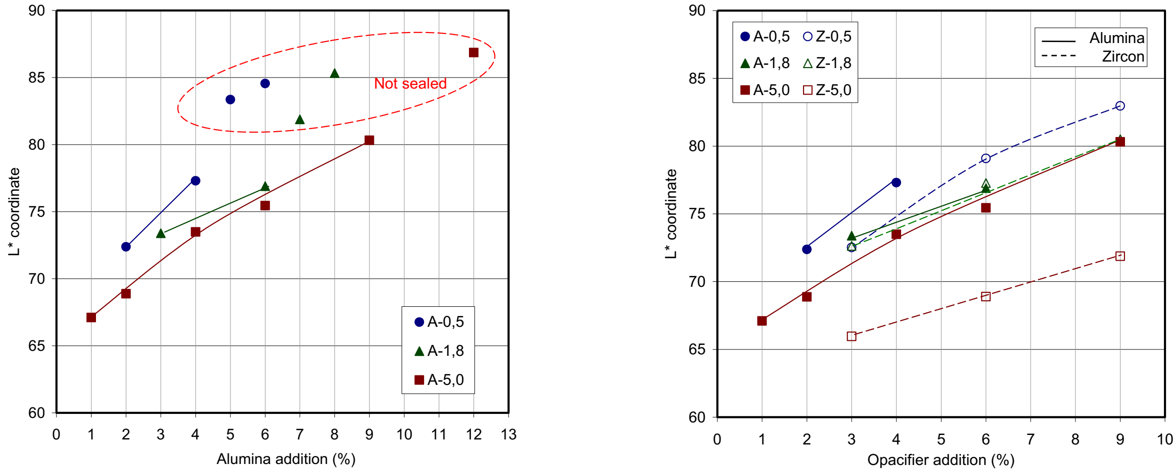

Figure 8. *Variation of the L*chromatic coordinate of the glazed pieces fired at 1200 ºC as a function of the opacifier addition.*

The gloss of the glazes sealed at 1200 °C is plotted as a function of the opacifier addition in Figure 9 (left). In general it may be observed that the zircon addition provided fired glazes with greater gloss compared to that obtained with the alumina addition as a result of the reaction of alumna with certain glassy phase constituents [14], whereas zircon behaved as an inert material. In addition, as particle size decreased, lower gloss values were obtained for both opacifiers.

The pairs of values L*–Gloss at 1200 °C for each tested glaze are plotted in Figure 9 (right). The addition of zircon particle size 5,0 μm gave rise to relatively high glosses; however, the L* coordinate values were very low, yielding glazes that were not very opaque. The opacifying strength of alumina particle size 5,0 μm was higher; however, as the value of the L* coordinate increased, a very pronounced reduction in gloss took place, yielding glazes with high opacity (L*) and low gloss (less than 5 units). The 4% addition of alumina particle size 5,0 μm gave rise to fired glazes with opacities and glosses similar to those obtained with zircon particle sizes 1,8 and 0,5 μm. The tested alumina samples with the smallest particle size yielded fired glazes with an intermediate opacity and very low gloss, it not being possible to obtain glazes with properties similar to those obtained with zircon, owing to the constraints stemming from the increase in refractoriness and reduction in gloss.

The L* (opacity) values that could be reached using the zircon opacifier were higher and the fired glazes displayed higher glosses and smoother textures than when the alumina opacifier was used. With a view to illustrating the differences in texture observed, Figure 10 shows the topographic charts of the samples with a 9% content in zircon particle size 1,8 μm and with the same content in alumina particle size 5,0 μm, which exhibited similar L* coordinate values. It clearly shows the greater roughness of the alumina-containing glaze.

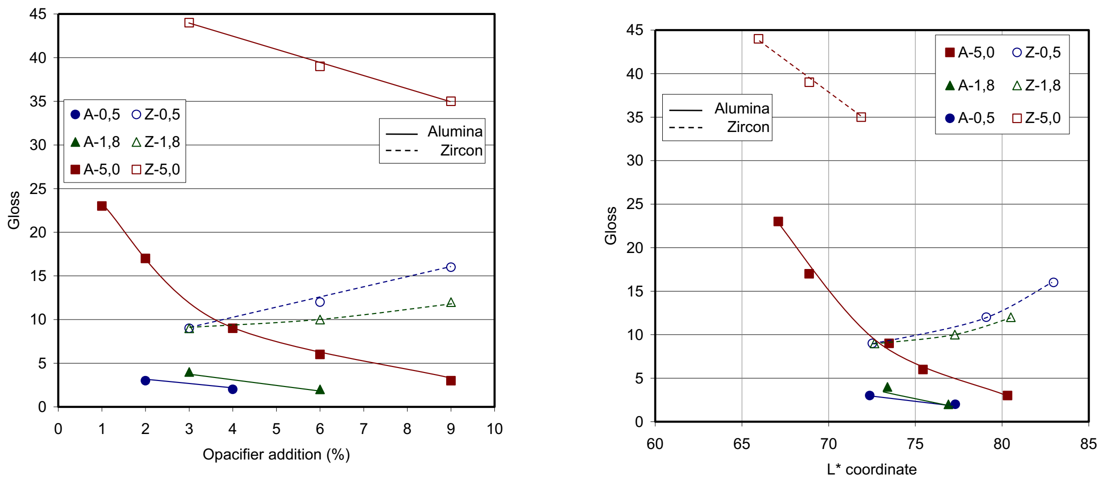

Figura 8

Figure 9. *Variation of gloss with opacifier addition (left) and with the value of the glaze L* coordinate (right). 1200 ºC*

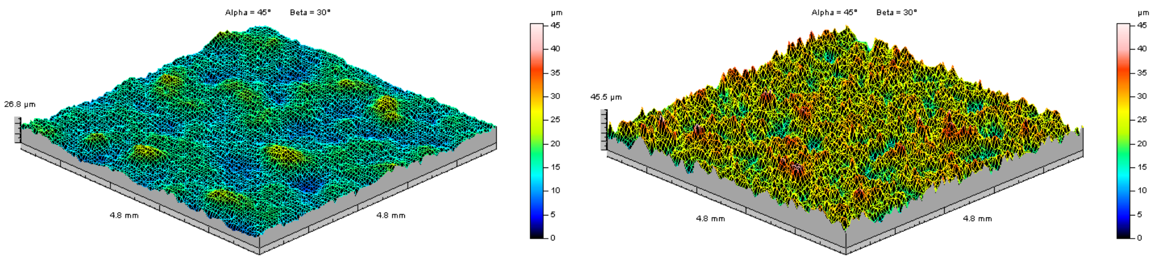

Figure 10. *Topographic chart of glazes prepared with a 9% content in zircon particle size 1,8 µm (left) and with a 9% content in alumina particle size 5,0 µm (right), which provided the same value of L*. 1200 ºC*

5. CONCLUSIONS

The study allowed the following conclusions to be drawn for the body compositions:

- Zircon did not unduly affect the value of Tmax when zircon content and particle size were modified. In contrast, alumina had a greater influence on Tmax when alumina content increased and its particle size decreased. This difference was associated with the partial dissolution of alumina during firing.
- The decrease in zircon particle size allowed a high degree of whiteness to be reached without modifying Tmax. This procedure could not be used with alumina because of the little influence of alumina particle size on the degree of whiteness.
- The replacement of the zircon used customarily (d_{50}=1,8 μm) with alumina (d_{50}=5,0 μm) allowed similar whiteness to be obtained, but it required increasing the quantity of opacifier and the firing temperature and led to increased firing shrinkage.
- The conclusions drawn for the glaze compositions are summed up below:
- The opacifying effect of zircon was more effective when 1,8 and 0,5 μm particle sizes were used, an almost zero opacifying effect being displayed at 5,0 μm particle size. Zircon allowed considerable quantities of opacifier to be introduced: up to a 9 wt% was tested, without this significantly modifying glaze fusibility. The zircon opacifier gave rise to opaque fired glazes with glosses between about 10 and 15 units. It is therefore deemed an appropriate opacifier for obtaining satin or matt glazes with a smooth texture.
- The use of alumina as glaze opacifier significantly raised refractoriness, this increase being more pronounced as alumina particle size decreased. This effect limited the use of alumina to lower percentages than those of zircon.
- The tested alumina samples of particle sizes below 5,0 μm produced a very pronounced reduction in gloss, it not being feasible to obtain opaque matt fired glazes with glosses higher than 5 units.

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