

Performance and Cost Optimisation in Ceramic Tile Production: Achieving Whiteness and Opacity through Zircon Opacifier

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In global ceramic tile production zircon remains, in the opinion of the Zircon Industry Association (ZIA), the material of technical choice for imparting opacification and whiteness. Despite the price volatility over the period 2011–2012, the crucial role of zircon in ceramic tile production appears to have been sustained, although substitution or thrifting of zircon by alternative whiteners, notably calcined alumina, became more prevalent. As with most raw materials, thrifting and substitution of zircon is incentivised when supply-demand dynamics push prices above trend levels. However, following the peak in 2012, a lower and more stable price level for zircon has been evident.

With this in mind, ZIA believes that it is now time for ceramic tile producers to re-evaluate the advantages offered by zircon in tile manufacture, most importantly, based on its relative economic value-in-use. Against this background, ZIA commissioned the Spanish Instituto de Tecnología Cerámica (ITC) to undertake a comparative study of the performance of zircon against alternative materials in ceramic tile applications, namely bodies, glazes, frits, and engobes. This paper presents the key findings, particularly the effect of opacifier particle size on performance in porcelain tile bodies.

Introduction

Micronised zircon is used as an opacifier in the production of engobes, opaque glazes, and porcelain tile bodies [1–2]. The price of zircon, as for other materials, is largely driven by supply-demand factors. Elevated price levels, as seen in 2011–2012 (Fig. 1), tend to incentivise thrifting and substitution of zircon by alternative materials. In most cases, substitution impairs product properties (mainly whiteness and opacity). However, for economic reasons these quality trade-offs have been accepted.

In porcelain tile body manufacture, zircon is used in compositions with varying degrees of whiteness, accounting for a significant proportion of the porcelain tiles made. An earlier zircon price spike in 2006 led to a considerable reduction in zircon content in body compositions (in certain cases up to 40 %) with accompanying reduction of whiteness. To offset the consequent loss in whiteness, efforts have been made to improve whiteness by using higher quality raw materials, reducing clay content, and using feldspars and sands with very low chromophore oxide contents [3–5].

Whitening raw material mixes have also emerged, made up of one or more opaci-

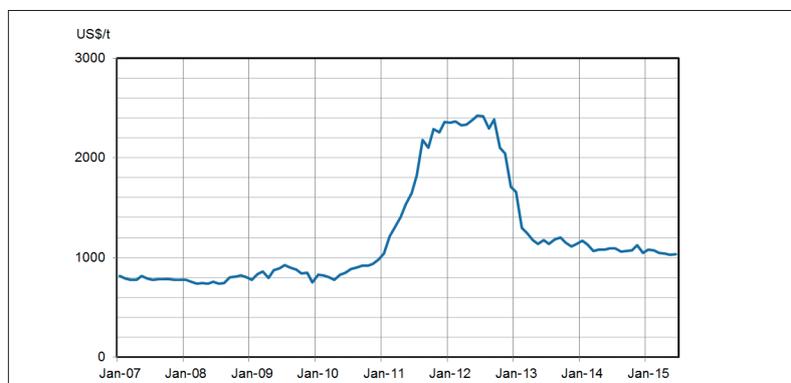


Fig. 1 Indicative zircon price trend, 2007 – 2015 (Source: Iluka/TZMI)

fiers (including alumina), together with various additives to offset the change in performance caused by the different properties of the opacifiers.

As with ceramic tile bodies, engobe and glaze producers have sought to reduce costs by using cheaper materials, as a result of which zircon has been substituted in some applications, typically by alumina.

A clear exception is the use of zircon in opaque frits for glazes – in this case, research and development work has shown that there are no viable substitutes for zircon in this type of frit. Some potential

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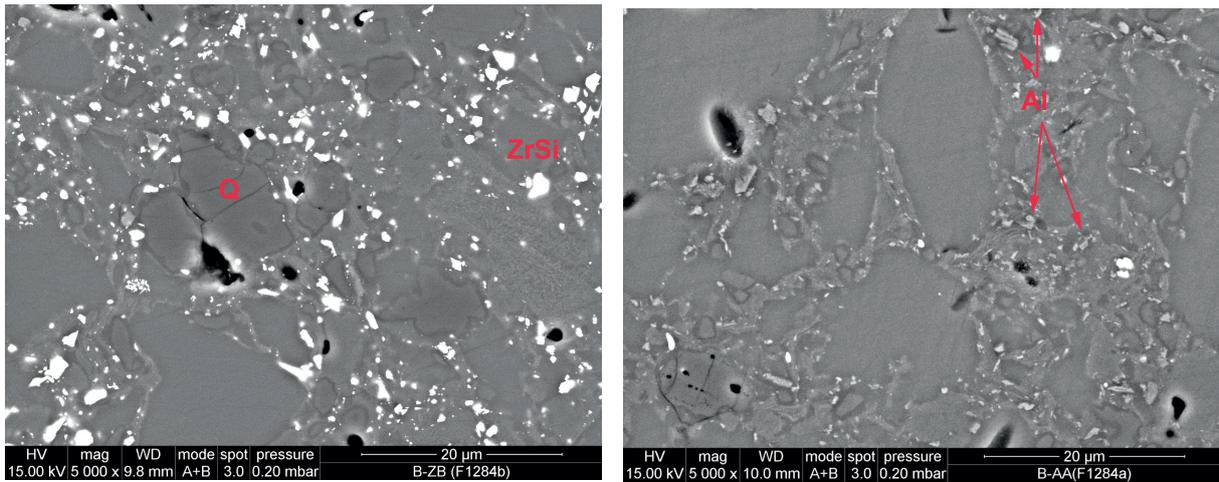


Fig. 2 Cross-sections of the porcelain tile specimens: B-ZR (l.), B-AL1 (r.); Identified phases: ZrSi) micronised zircon (white particles); Q) quartz; and Al) alumina (grey particles)

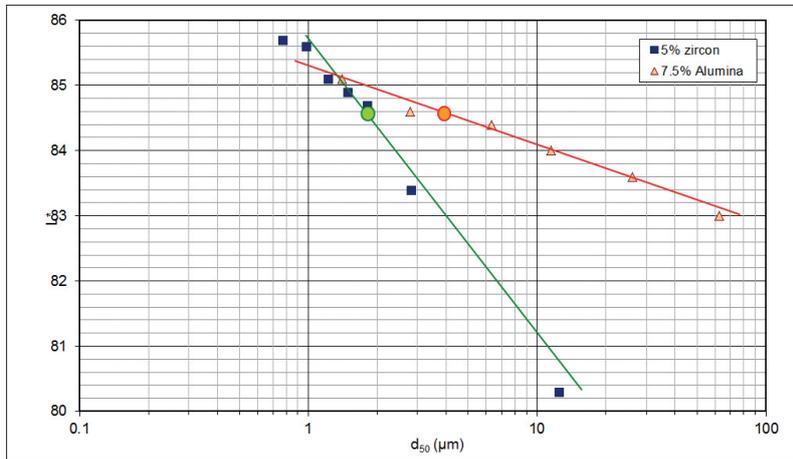


Fig. 3 Evolution of the L^* coordinate with the opacifier particle size for porcelain tile body compositions with 5 mass-% zircon and 7,5 mass-% alumina, respectively

substitutes do exist, but they are unsuitable for either technical or economic reasons, or both.

Since the price spike of 2011–2012, prices for zircon opacifiers have fallen sharply to a much more stable level which has been sustained ever since, as shown in Fig. 1.

This should prompt ceramic producers to revisit the advantages and, most importantly, the relative value-in-use of zircon opacifiers relative to alternatives, such as calcined alumina-based whiteners.

The ITC study aims to determine performance of micronised zircon relative to calcined alumina in porcelain tile body, engobe, and glaze applications.

Porcelain tile body compositions

The aim of this section was firstly to determine the influence on the processing

behaviour and properties of porcelain tiles when the zirconium silicate in the body composition was entirely replaced with alumina. For this study, a standard body composition (B-ZR) consisting of [mass-%] 30 % Ukrainian clay, 50 % Turkish feldspar, 15 % quartz, and 5 % zircon ($d_{50} = 1,4 \mu\text{m}$) was used as reference. The zircon was entirely replaced with two types of calcined alumina commonly used in the manufacture of porcelain tiles: AL1 ($d_{50} = 5,2 \mu\text{m}$) and AL2 ($d_{50} = 5,1 \mu\text{m}$). Secondly, compositions with different levels of alumina were tested in order to determine the alumina content that provided the same whiteness (L^* coordinate) as the zircon-containing reference composition.

To conduct the study, the different raw materials were mixed in the appropriate percentages and wet milled in water until

Tab. 1 Deflocculation behaviour

Composition	B-ZR	B-AL1	B-AL2
Solids content [%]	71	71	71
Minimum viscosity [cP]	420	550	550
Deflocculant content [%]	0,29	0,25	0,26
Thixotropy [diff. °G]	14	22	30

a reject of 2,0 % was reached on a 40- μm sieve. The resulting suspensions were dried under infrared lamps and dry milled.

Data on deflocculation curves of the compositions tested are shown in Tab. 1. The composition with zircon provided the best deflocculation behaviour, with the lowest viscosity and thixotropy. The data obtained with the aluminas were quite similar to each other.

Cylindrical test specimens (4 cm in diameter and approximately 7 mm thick) were formed by uniaxial pressing, at a pressing moisture content of 5,5 % (dry weight basis) and a pressing pressure of 30 MPa. The test specimens were dried at 110 °C to constant weight and then fired with a fast firing cycle and 6-min hold at peak temperature in an electric laboratory kiln. The heating rate was 25 °C/min.

Tab. 2 summarises the properties of these compositions (bulk density, linear shrinkage, water absorption, and chromatic coordinates) at the maximum densification temperature (T_{max}), this being the firing

Tab. 2 Properties at maximum densification temperature (T_{max})

Composition	B-ZR	B-AL1	B-AL2
T_{max} [°C]	1219	1224	1227
Bulk density [g/cm ³]	2,492	2,474	2,474
Linear shrinkage [%]	8,5	8,8	8,7
Water absorption [%]	<0,1	<0,1	<0,1
L^*	84,2	82,0	82,3
a^*	0,5	0,8	0,9
b^*	8,9	9,3	9,0
Bending strength [kg/cm ²]	700 ± 10	720 ± 10	690 ± 10

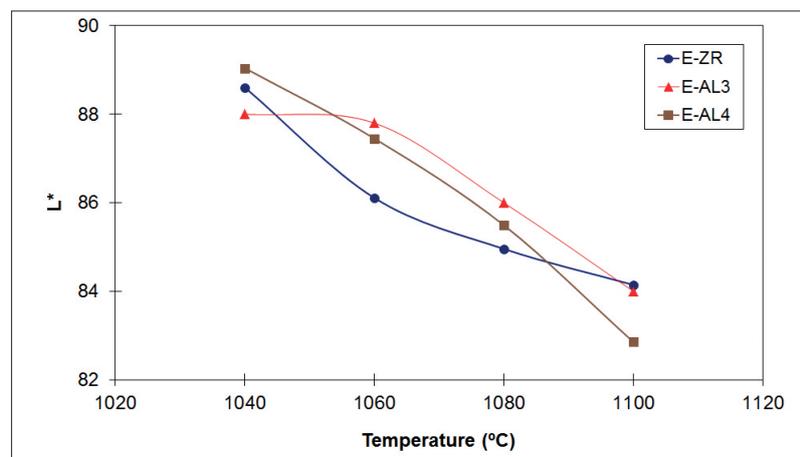


Fig. 4 Variation of the L^* chromatic coordinate with temperature for engobed tiles

temperature at industrial scale. The main inferences to be drawn from these results were as follows:

- The use of alumina increased maximum densification temperature and shrinkage, which modified final tile size. The higher shrinkage values could be related to the higher porosity in the dry compacts when the two aluminas were used.
- Both aluminas provided the tiles with a lower L^* coordinate than that of the zircon-containing composition. The a^* and b^* values were a little higher.
- The zircon-containing composition exhibited the lowest closed porosity, while the compositions with the two aluminas displayed similar closed porosity. SEM observation (Fig. 2) revealed significant differences between the zircon and the alumina particles: the zircon particles were very small (<5 μm), whereas the alumina particles were much larger in some cases (<10 μm).
- Stain resistance is related to closed porosity: consequently, the zircon-containing composition provided slightly better stain resistance.

In conclusion, when 5 mass-% calcined alumina was added to the porcelain tile body, the differences between zircon and alumina were not critical. However, the need to increase the alumina content in order to achieve a similar whiteness to that of the zircon-containing composition would augment these differences.

To determine the effect of the opacifier particle size and to obtain porcelain tiles with alumina, with a whiteness similar to that provided by the 5 mass-% zircon-containing composition, further tests were conducted with other body compositions, in which the zircon and alumina particle size and content were changed. Fig. 3 summarises some of the results obtained.

Typically, zircon for porcelain tile bodies ("five" quality, green circle on the chart) has a particle size (d_{50}) of about 1,5 μm , although many commercially available micronised zircon are finer, with d_{50} in the range 1,0–1,3 μm . On the other hand, commercially available calcined alumina for zircon substitution in porcelain tile bodies has a particle size (d_{50}) between 3–5 μm (orange circle on the chart).

Tab. 3 Properties of the fired pressed engobe compositions; water absorption = 0 %

Composition	E-ZR	E-AL3	E-AL4
Temperature [°C]	1080	1090	1100
Bulk density [g/cm ³]	2,305	2,130	2,119

From Fig. 3, it can be observed that 5,0 mass-% loading of zircon ($d_{50} = 1,5 \mu\text{m}$) corresponds to about 7,5 mass-% loading of alumina ($d_{50} = 4 \mu\text{m}$) to provide porcelain tile bodies with a similar L^* value (84,6). Furthermore, the slope of the L^* vs particle size lines are quite different for zircon and alumina. For zircon, the slope is significantly steeper, so that there is a significant benefit in performance if the opacifier is milled to a smaller size. For alumina the benefit of finer milling is much smaller.

Consequently, for finer zircon ($d_{50} = 1,2 \mu\text{m}$) the alumina loading required to match the same level of whiteness is higher, close to 8,5 %. Therefore, to achieve the same L^* value, the alumina added to the porcelain tile body formulation must be between 50–70 % higher than when finer micronised zircon is used, depending on the zircon particle size.

Engobe compositions

Tests were performed substituting the zircon in an engobe composition used in the production of wall tiles. The reference engobe composition (E-ZR) contained [mass-%]: 35 % opaque frit, 20 % sodium feldspar, 25 % white clay, 12 % quartz, and 8 % zircon. Two commercial alumina samples were used as zircon substitutes: AL_3 ($d_{50} = 45 \mu\text{m}$) and AL_4 ($d_{50} = 15 \mu\text{m}$).

The engobe compositions were characterised by determining their firing behaviour (pressed engobe compositions), firing range (variation of aesthetic characteristics of engobed tiles with temperature), and thermal expansion.

Microstructural characterisation was also performed, which consisted of identifying the arising crystalline structures (XRD) and observing the engobe layers by scanning electron microscopy (SEM).

The determination of the firing behaviour (Tab. 3) showed that replacing zircon with alumina led to increased engobe refracto-

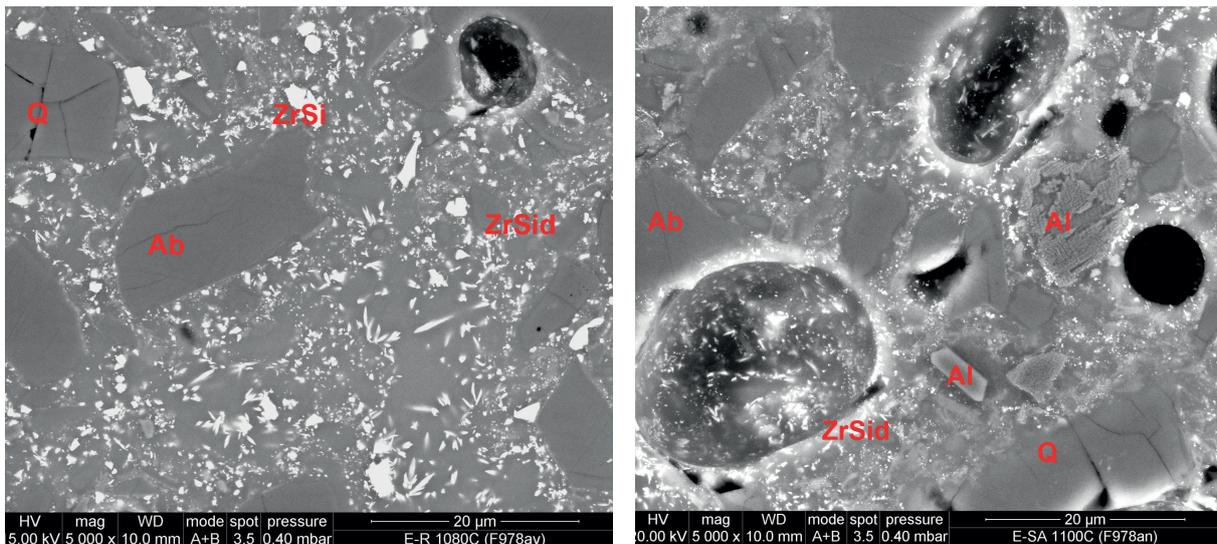


Fig. 5 Cross-sections of the pressed engobe compositions (Left: E-ZR 1080°C – Right: E-AL3 1100°C). Identified phases: Q) quartz; Ab) albite; ZrSi) micronised zircon; ZrSid) zircon devitrified from the opaque frit; and Al) alumina.

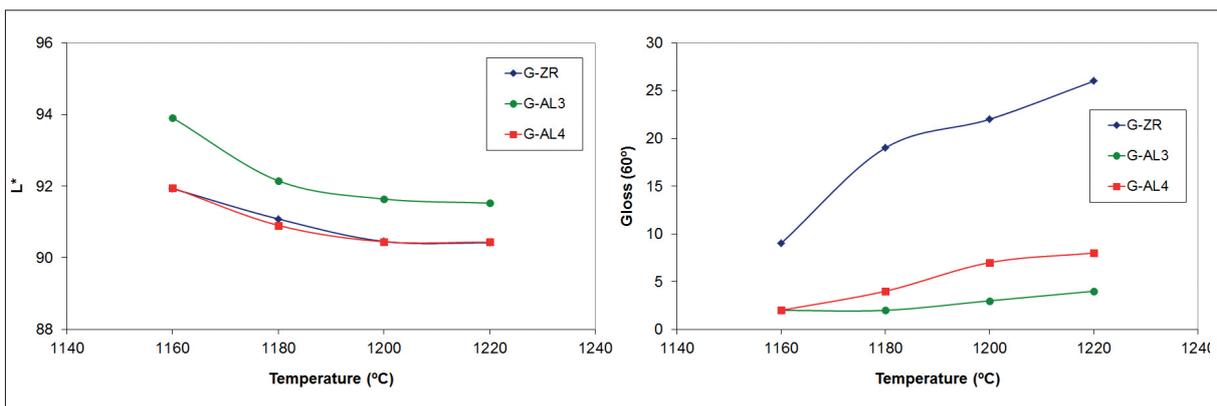


Fig. 6 Variation of the L* chromatic coordinate (l), and gloss (r) with temperature for glazed tiles

Tab. 4 Characteristic temperatures of the test glazes [°C]

Characteristic Temperature	G-ZR	G-AL3	G-AL4
Shrinkage start temperature	915	1090	925
Shrinkage end temperature	1170	1215	1200
Softening temperature	1185	1260	1225
Half-sphere temperature	1245	1300	1265
Melting temperature	1275	1315	1285

riness (i.e. a higher firing temperature was needed to reach the same water absorption). It would be possible to correct this by increasing the engobe flux content, in order thus to reduce the firing temperature to the appropriate level (this was not done in this study).

Engobed tiles (Fig. 4) with the zircon-containing engobe gave rise to higher L* coordinate values (i.e. higher opacity and whiteness) when zero water absorption was reached (1100 °C). Alumina produced whiter engobes at lower temperatures, when zero water absorption was not reached. This phenomenon is typically due to the higher opacity of the engobe layer with zircon. With respect to thermal expansion, no significant changes were observed when zircon was replaced with alumina.

The same was the case with microstructure: apart from the presence of alumina particles instead of zircon particles, no significant changes in microstructure (XRD and SEM) were observed (Fig. 5).

Glaze compositions

Tests were performed substituting zircon in a glaze composition used in the production of glazed porcelain tiles. The reference glaze composition (G-ZR) contained [mass-%]: 30 % matt frit, 20 % wollastonite, 26 % nepheline syenite, 5 % alumina, 5 % quartz, 8 % kaolin, and 6 % zircon. Two commercial alumina samples, the same ones as those used in the engobe compositions (AL₃ and AL₄), were used as zircon substitutes. The glaze compositions were referenced G-AL₃ and G-AL₄.

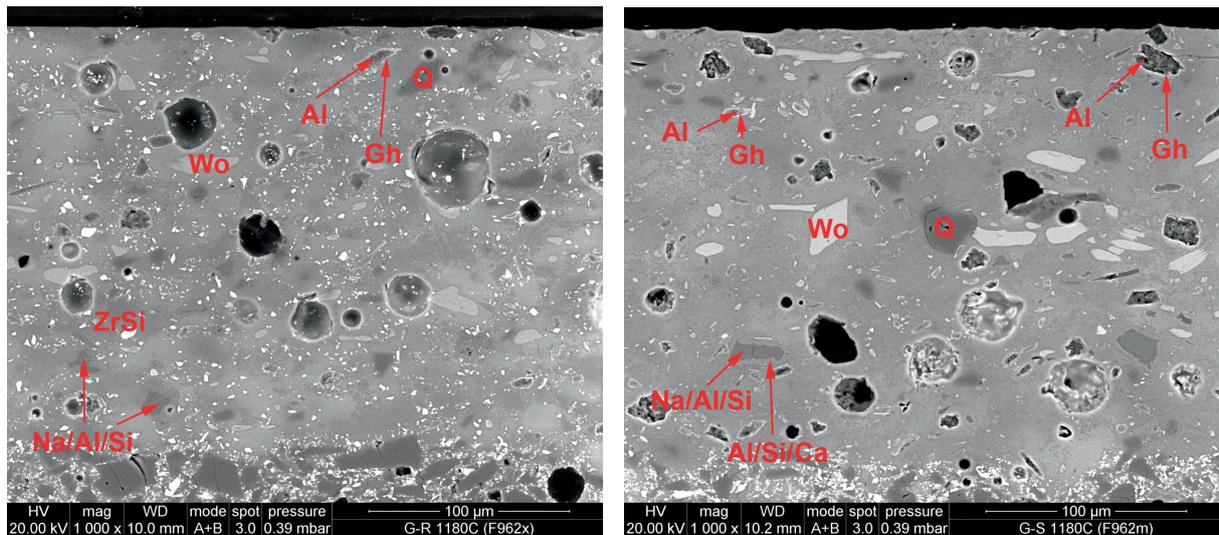


Fig. 7 Cross-sections of the glazes: G-ZR 1180 °C (l.), and G-AL4 1180 °C (r.); identified phases: Al) alumina; ZrSi) micronised zircon; Q) quartz; Wo) wollastonite; Gh) gahnite; Na/Al/Si) a phase rich in sodium, aluminium, and silicon; and Al/Si/Ca) a reaction layer richer in aluminium, silicon, and calcium

Tab. 5 Resistance to wear by pedestrian traffic [°C]

Glazed Tiles	Result	Abrasion Stage	Class
G-ZR	Change in visible appearance (*)	2500 revolutions	H4
G-AL3	Change in visible appearance (*)	>10 000 revolutions	H6
G-AL4	Change in visible appearance (*)	7500 revolutions	H5

(*) Change of appearance owing to surface staining

The glaze compositions were characterised by determining their fusion behaviour (hot stage microscope), firing range (variation of aesthetic characteristics of glazed tiles with temperature), and thermal expansion. Microstructural characterisation was also performed, consisting of the identification of crystalline structures (XRD) and the observation of the glaze layers by scanning electron microscopy (SEM). Finally, the glazed tiles were characterised by determining their chemical resistance and resistance to wear by pedestrian traffic. The replacement of zircon with alumina increased glaze refractoriness (Tab. 4); the glazes prepared with alumina displayed

higher characteristic temperature values. In general, the glazes prepared with alumina exhibited higher whiteness, but much lower gloss (Fig. 6). However, no change in thermal expansion was observed.

The use of alumina increased the formation of crystalline phases (Fig. 7).

Microstructural characterisation showed that, in this type of glaze, the use of alumina instead of zircon favoured the formation of new crystalline phases like anorthite, labradorite, and gahnite. As the quantity of such crystalline phases increased, the refractoriness and opacity of the glaze increased and glaze gloss decreased.

This contribution to opacity depended on the size and refractive index of the new crystals. Gahnite has a high refractive index (1,80), while the values for anorthite and labradorite are lower, namely 1,58 and 1,56, respectively. It should be taken into account that alumina, with a refractive index of 1,77, will also contribute to glaze opacity.

The presence of crystalline phases in a glaze increases wear resistance, so that the use of alumina will also increase wear resistance, as evidenced by the results of the determination of the resistance to wear by pedestrian traffic (UNE EN ISO 10545-7: 1999) shown in Tab. 5.

Conclusions

This paper reports on a study to compare the use of micronised zircon and calcined

alumina as opacifiers in porcelain tile bodies, engobes, and glazes.

In porcelain tile bodies it was necessary to increase the alumina loading rate by 50–70 mass-% to obtain the same degree of whiteness. These results allow a proper economic comparison to be made. The use of alumina impaired the rheology of the body suspension, increased the firing temperature, and reduced final tile size. For polished products, alumina increased the closed porosity slightly; as a result, the zircon-containing composition provided slightly better stain resistance.

The results obtained as a function of particle size in porcelain tile body showed that, for zircon, there was a significant benefit in performance when the opacifier was milled to a smaller size. For alumina the benefit of finer milling was much smaller.

The replacement of zircon in engobe and glaze compositions led mainly to increased refractoriness.

In the case of engobe compositions, in order to use alumina as opacifier, reformulation of the composition would be necessary. In the case of the glazes, the use of alumina gave rise to a significant decrease in glaze gloss because it favoured the formation of crystalline phases that made it difficult to obtain glazes with a non-matt finish.

This study equips ceramic tile producers with performance data for zircon and its alternatives, making possible value-in-use comparisons.

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