VARIABLES THAT DETERMINE THE MATT APPEARANCE OF SOME CERAMIC FLOOR AND WALL TILE GLAZES

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ABSTRACT

The present study was carried out as a result of the increase in recent years of ceramic tile models with a matt surface finish and the lack of information in the literature on glazes that yield this finish.

The study consisted of both a macroscopic and microscopic characterisation of three glazes that give rise to a matt surface in tile production by fast twice-fire, single-fire, and porcelain tile manufacturing processes. The glaze used in fast twice fire corresponded to a calcium matt, and the other two glazes to a barium matt.

The matt appearance of these glazes is due to the surface roughness they present, caused by the formation, during firing, of crystalline species, wollastonite and cristobalite in the case of the calcium matt glaze and celsian (or barium orthoclase) in the barium matt glazes. It was verified that these crystalline species appear during heating, partly dissolving at peak temperature and forming again during cooling.

The influence of different variables (particle size and firing cycle) was determined on the properties of the three glazes; it was observed that the calcium matt glaze was less stable with regard to changes in particle size and peak firing temperature than the barium matt glazes. The increased firing temperature in the calcium matt glaze encouraged the formation of the double silicate of zirconium and calcium, which hinders the crystallisation of wollastonite and cristobalite during cooling, thus increasing gloss and reducing opacity. This decrease in opacity was due to a reduction in the quantity of the zircon found in the glaze.

1. INTRODUCTION

In recent years, the production of ceramic tile models with a matt finish has risen considerably. However, few studies have addressed the causes that produce these finishes and the variables on which these causes depend. In general texts on ceramic glazes [1-8] some information was found on matt glazes but no specific studies on this type of glaze.

Matt glazes present a higher surface roughness than that found in glossy glazes [9]. This surface roughness causes multiple reflections of incident light, reducing the amount of light reflected in the specular direction and therefore producing a loss of gloss. The quantity of light reflected depends, not only on the surface roughness but also on the refractive index of the material and angle of incident light.

Normally, surface roughness of the matt glazes is produced by the presence of crystals in the glaze, although it has not been verified whether the roughness is due to the presence of crystals near or on the surface, or to a rise in glaze viscosity in the molten state, because of the presence of these crystals, which hinder optimum surface stretching. It should be taken into account that any glaze with very high viscosity, even without crystals, yields a matt surface due to the fact that it impedes adequate smoothness of the surface [9-10]. The crystals found in a matt glaze may come from:

a) addition of raw materials to the glaze composition, which remain undissolved in the glassy phase formed during firing.

b) crystallisation, during firing of the glaze composition, of crystalline phases from the glassy matrix that forms during firing.

The glaze compositions used for producing matt glazes in tile manufacturing are generally made up of frits and other raw materials (alumina, quartz, feldspar, etc), so that the glaze appearance could be due to the presence of crystals by the two causes mentioned above.

Until a few years ago, the most widely used matt glazes were the so-called calcium matts and zinc matts, which were characterised by being composed of frits, which during tile firing devitrified wollastonite ($CaSiO_3$) in the case of the calcium matt, and willemite ($ZnSiO_3$) in the zinc matt. At present the use of so-called barium matts in producing matt glaze surfaces has spread in glazed ceramic tile manufacture. These glazes are made up of frits with a high BaO content, which according to the literature surveyed [1,3,8], give rise to celsian crystallisation ($BaAl_2Si_2O_8$).

The industrial experience in the use of these glazes suggests that calcium matts are less stable with regard to changes in particle size and firing cycle than the zinc and barium matt glazes.

3. OBJECTIVE AND SCOPE

The objective of the present study has been to acquire more knowledge on the causes of the appearance produced by the matt glazes currently used in manufacturing, as well as to determine the principal variables that influence this appearance.

To carry out the study three glazes employed industrially were used, which yield matt glazes in different tile manufacturing processes. One of the glazes was a calcium matt and the other two barium matts. It was thus attempted to establish the causes that bring about the differences in the behaviour of the two types of glazes.

3. MATERIALS AND EXPERIMENTAL PROCEDURE

3.1.MATERIALS

The study was carried out using three glazes that produced matt glaze finishes in different tile manufacturing processes. The three glaze compositions are principally made up of a frit, which by itself produces a matt glaze, with a different composition in each case, and also of different crystalline raw materials (zircon, feldspar and nepheline). The following gives a brief description of each glaze:

- **ER:** glaze composition used in fast twice-fire tile manufacturing, mainly made up of one frit (FER) with a high CaO content (calcium matt).
- **EP:** glaze composition used in single-fire tile manufacturing, mainly made up of one frit (FEP) with a high BaO content (barium matt).
- **EG:** glaze composition employed in glazed porcelain tile manufacturing, mainly made up of one frit (FEG) with a high BaO content (barium matt).

3.2 GLAZE PREPARATION

To carry out the **glaze characterisation**, suspensions were prepared from the mixtures of raw materials corresponding to each glaze composition by milling the solids with the amount of water needed to obtain a 70% solids content by weight in an alumina ball mill. Milling was carried out as long as needed to obtain a reject of approximately 1% by weight on a 40 µm mesh screen.

The resulting glaze suspensions were applied to previously fired porous tile bodies, in the case of fast twice-fire and single-fire glaze compositions, and in the case of the porcelain glaze composition, the suspension was applied to a green porcelain tile body. For this, a layer of engobe was previously applied, which corresponded in each case to the type of glaze composition (twice fire, single fire and porcelain tile glaze). The applied unfired glaze and engobe layer was about 400 µm thick.

The glazed specimens were fired in an electric laboratory kiln at a heating rate of 25°C/min with a 6 minute dwell at peak temperature. Different peak temperatures were tested for each glaze composition: 1040°C (ER), 1100°C (EP) and 1200°C (EG).

To determine the **influence of particle size**, milling time of the reference glaze composition was modified with a view to obtaining glaze compositions with a reject on a 40 µm mesh screen of less than 1 wt% and more than 3 wt%. Subsequently, the glazed specimens were prepared as set out above.

The **influence of the firing cycle** was determined by using the prepared glazed test specimens in the same way as those used to carry out glaze characterisation. For each type of glaze composition, test specimens were fired modifying peak firing temperature, heating rate, cooling rate and residence time at peak firing temperature.

3.3 DETERMINATIONS PERFORMED

Colour was determined of the different glazes obtained using a spectrophotometer, performing the measurements according to the CIE Lab system, using a C light source and CIE 2° observer. The parameters determined were:

- Chromatic co-ordinates: L* (L*=0 black, L*=100 white), a* (a*<0 green, a*>0 red), b* (b*<0 blue, b*>0 yellow).
- Whiteness index, Ib, according to HUNTER 60.
- Yellowness index, Ia, according to ASTM D1925.

Of these parameters only the chromatic co-ordinate L* is indicated in the results, as this is related to glaze opacity. The higher the L* value, the more opaque is the glaze.

Glaze surface **gloss** was determined on a spectrophotometer, measuring at an angle of 85°, recommended for measuring the specular gloss of low gloss materials.

Glaze **surface roughness** was determined on a roughness meter with a pick-up fitted with a diamond tip of 90° curvature and 5 μm radius. A topography was made of each of the studied surfaces, consisting of 100 profiles, 10 mm long with a 100 μm spacing between each one, covering a surface of 10x10 mm. A 2.5 mm filter was used to calculate the parameters. From each of the profiles found, the parameter that best represented the mean surface roughness was calculated. This parameter, called Ra, is the arithmetic mean of the absolute values of the distance of the points that make up a profile to an average line.

The **crystalline structures** in the glazes were identified by X-ray diffraction (XRD) of a powdered glaze sample. To obtain the glaze sample, cylindrical test specimens were made from the glaze composition being tested by casting, and fired according to the cycle established for each test. The fired test specimen underwent milling in order to obtain the powdered glaze sample. The resulting diffractogram enabled identifying the mineralogical species present by means of the JPDS files for pure crystalline phases.

Observation and analysis was carried out by means of a scanning electron microscope (SEM), connected to an energy-dispersive X-ray analysis (EDXA) instrument on all the resulting fired glazes.

Behaviour of the glaze compositions with temperature in the sintering stage was determined on a hot-stage microscope, using samples of the glaze powder prepared by milling and drying.

4. RESULTS

4.1 GLAZE CHARACTERISATION

Glaze compositions ER, EP and EG yield matt white glazes (Table 1), presenting a higher surface roughness than that usually found in glossy glazes (Ra between 0.1 and 0.3 μm) [9].

Glaze	L*	Gloss (‰)	Ra (μm)
ER	92.0	47	0.8
EP	90.6	29	1.0
EG	90.8	31	1.0

Table 1. Chromatic co-ordinate L, gloss and surface roughness of the tested glazes.*

The results of the identification of the crystalline phases found in the glazes are indicated in Table 2. Zircon appears in all three glazes as it is added as a raw material to the three glaze compositions; the remaining phases are formed during firing. Barium feldspar or celsian ($BaAl_2Si_2O_8$) and barium orthoclase ($[K,Ba][Si,Al]_4O_8$) are two very similar species as regards their crystalline structure, belonging to the orthoclase part of the barium replaced by potassium. Given their similarity, both types of crystals will be referred to hereinafter as celsian.

Glaze	Identified crystalline phases
ER	Wollastonite ($CaSiO_3$), Zircon ($ZrSiO_4$) and Cristobalite (SiO_2)
EP	Celsian ($BaAl_2Si_2O_8$), Barium Orthoclase ($[K,Ba][Si,Al]_4O_8$) and Zircon ($ZrSiO_4$)
EG	Celsian ($BaAl_2Si_2O_8$), Barium Orthoclase ($[K,Ba][Si,Al]_4O_8$) and Zircon ($ZrSiO_4$)

Table 2. Crystalline phases identified by X-ray diffraction in each of the glazes.

In glaze ER (Figure 1) the existence of a great quantity of glassy phase can be observed in which four types of crystals are found immersed, corresponding to the three crystalline species identified:

- **A:** Approximately hexagonal-shaped, very dark crystals, occasionally surrounded by a crack, which correspond to cristobalite that has devitrified during firing.
- **B:** Crystals of an intermediate colour with a rod-like shape, which correspond to wollastonite that has devitrified during firing.
- **C:** Very light coloured crystals with an irregular shape, which are added zircon.
- **D:** Very light coloured acicular crystals, corresponding to devitrified zircon.

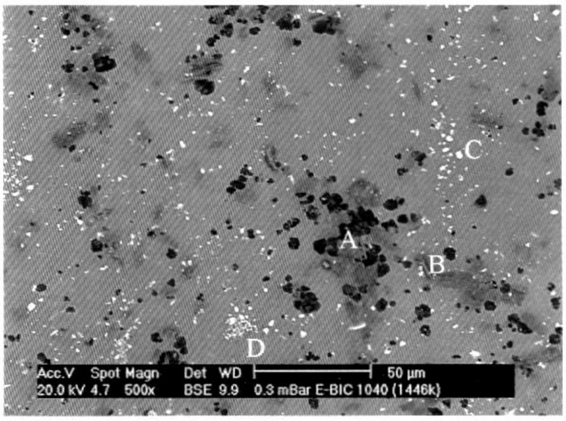


Figure 1. ER glaze surface (1040°C).

The existence of two types of areas and two types of particles can be observed in glaze EP (Figure 2):

- **1:** Area of glass without crystals
- **2:** Area with acicular celsian crystals (E) that devitrified during firing.
- **F:** Dark particles of added nepheline.
- Added zircon.

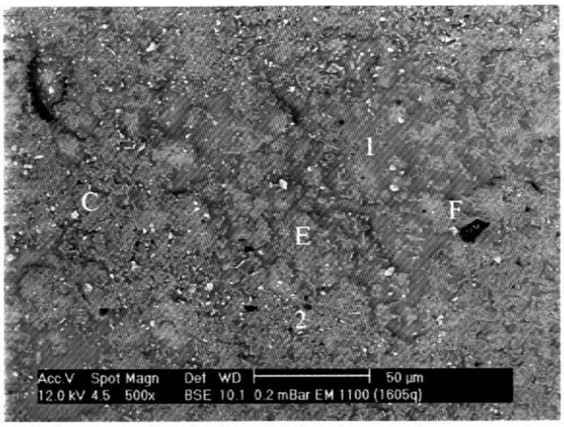


Figure 2. EP glaze surface (1100°C).

Figure 3 shows a detail of glaze EP where the glass, zircon particles and celsian crystals can be clearly observed. Figure 4 exhibits a cross section of this glaze where some of the type F particles can be observed to dissolve and react with the glass surrounding them, thus forming acicular crystals of a similar nature to that of the celsian crystals (possibly barium orthoclase). This seems to indicate that the presence of nepheline as a raw material favours the formation of crystals that provide a matt glaze appearance.

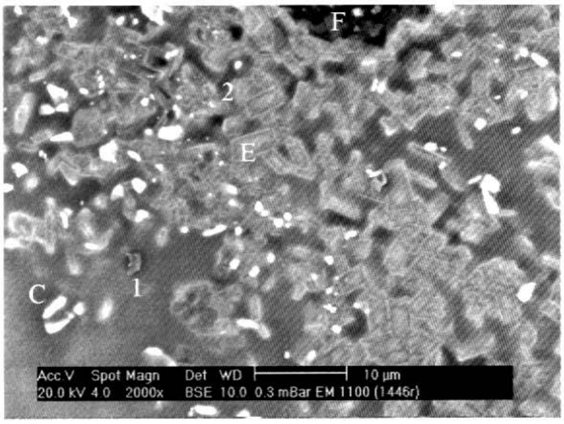


Figure 3. Detail of glaze EP (1100°C).

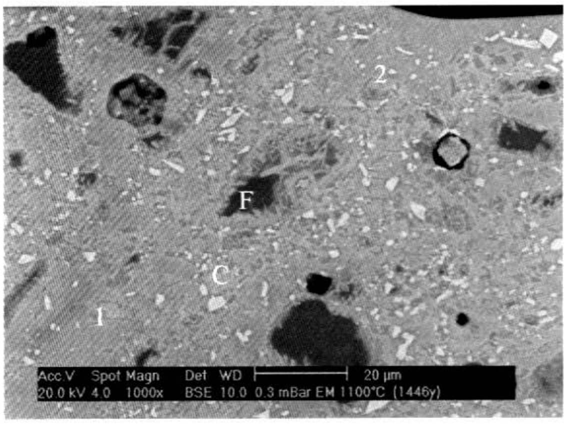


Figure 4. Cross section of glaze EP (1100°C).

In glaze EG (Figure 5) the existence of numerous celsian laminar crystals (E) can be observed, which because of their large number, have left only small gaps between each other, together with very little residual glassy phase. As occurred in the previous cases, added zircon particles (C) are found in clusters in specific areas. Figure 6 shows a detail of this glaze where both types of crystals can be seen more clearly.

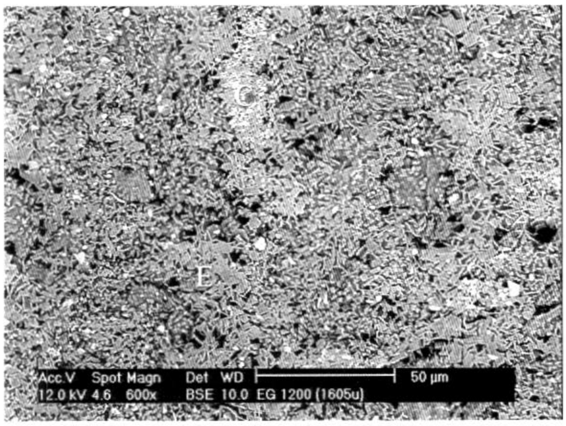


Figure 5. EG glaze surface (1200°C).

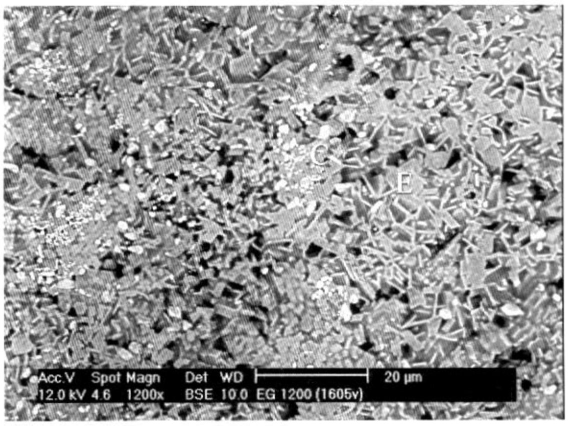


Figure 6. Detail of glaze EG (1200°C).

Figure 7 plots the results of the determination of the behaviour of the three tested glaze compositions with temperature in the sintering stage. Glazes EP and EG exhibit an area where shrinkage stops, due to the formation and growth of crystalline phases that form a skeleton and finally slow down or stop the sintering process [11]. This area is not found in glaze ER, as was observed in the micrographs, since the amount of crystalline phases that devitrify is considerably smaller.

With a view to determining the role of the frits that make up a major part of these glaze compositions, an XRD was carried out on each of the three frits, and no crystalline phase was found. Subsequently, these frits were used to make ceramic glazes, which presented a matt appearance owing to the crystalline phases that devitrified during firing, and that were identified by XRD (Table 3). Figures 8 to 10 exhibit the micrographs of the three glazes produced with the frits.

Glaze	Identified crystalline phases
FER	Wollastonite ($CaSiO_3$) and Cristobalite (SiO_2)
FEP	Celsian ($BaAl_2Si_2O_8$), Barium orthoclase ($[K,Ba][Si,Al]_4O_8$)
FEG	Celsian ($BaAl_2Si_2O_8$), Barium orthoclase ($[K,Ba][Si,Al]_4O_8$)

Table 3. Crystalline phases identified by XRD in the glazes made from the frits.

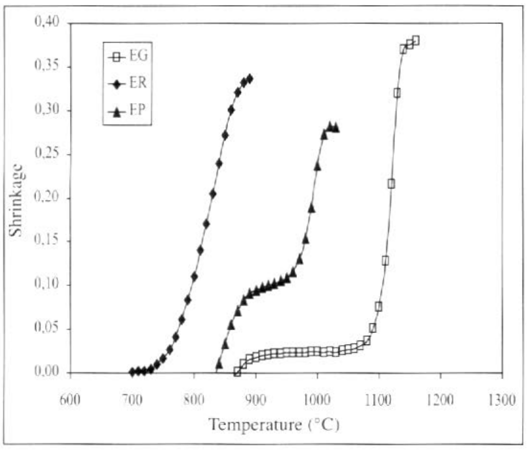


Figure 7. Behaviour of glazes ER, EP and EG with temperature in the sintering stage.

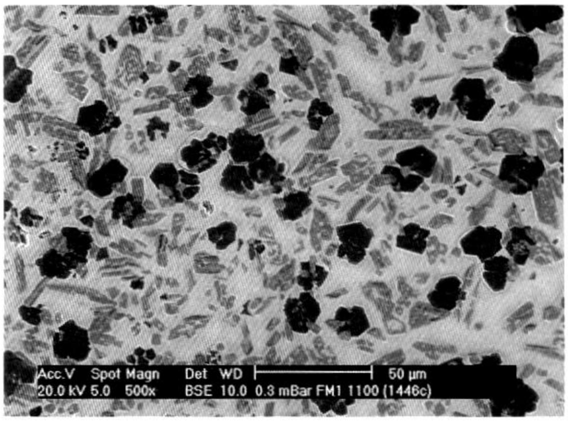


Figure 8. FER glaze surface.

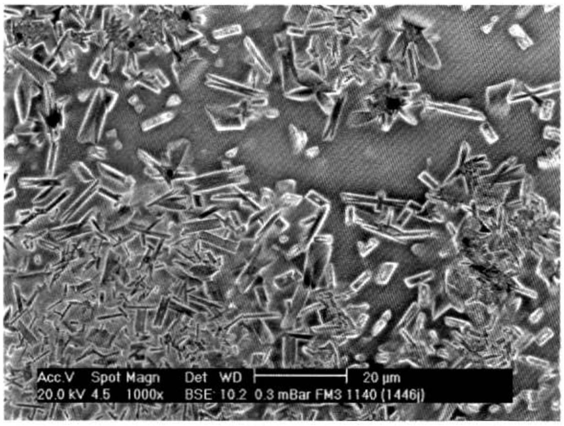


Figure 9. FEP glaze surface.

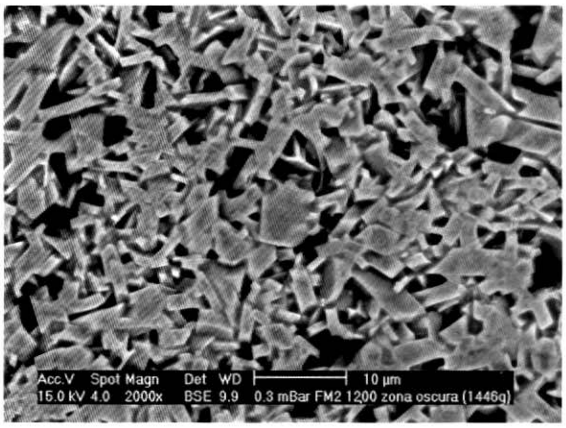


Figure 10. FEG glaze surface.

As can be observed, the devitrifying crystalline phases in the glazes made from the frits coincide with the devitrifying phases in the glazes produced from the glaze compositions. Therefore, it can be stated that in this type of glazes, devitrification of the crystalline phases in the frit contained in the glaze composition is the principal cause of the matt appearance.

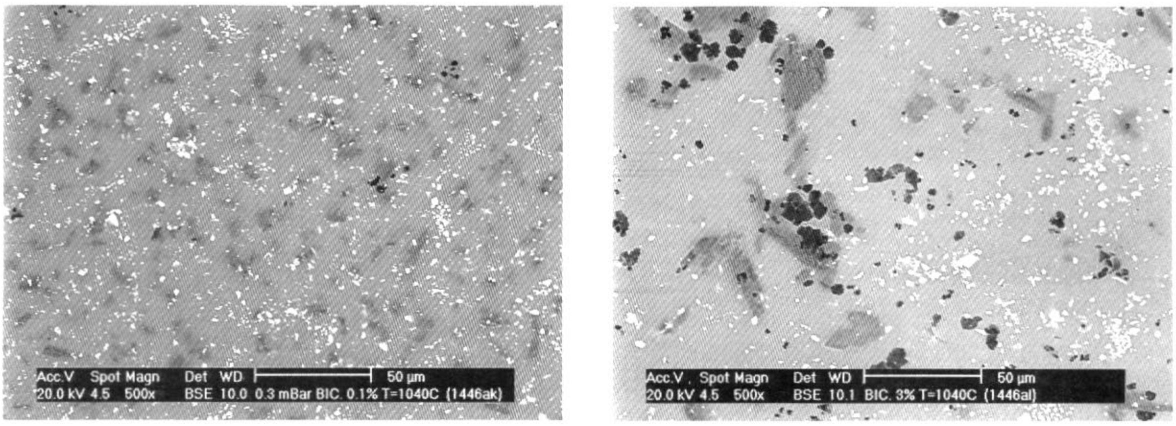
It can be concluded from the tests carried out that the presence of a larger quantity of crystals (glazes EP and EG) produces greater surface roughness, which yields more matt glazes (Table 1). The frit contained in the glaze composition is the main cause of devitrification, during glaze firing, of the crystalline species that give rise to the matt appearance, which are wollastonite and cristobalite in the calcium matt and celsian in the barium matts. However, it was also observed that in glaze composition EP, celsian formation is encouraged by the addition of nepheline as a raw material in the glaze composition.

4.2. .INFLUENCE OF PARTICLE SIZE

Table 4 sets out the results of the determination of colour, gloss and surface roughness of the glazes obtained from the three test glaze compositions, modifying particle size. As can be observed, the decrease in particle size of the three glaze compositions reduces surface roughness and increases gloss; this increase is considerably more pronounced in glaze composition ER than in the other two test compositions. Figures 11 to 13 show the micrographs of the resulting glaze surface on modifying glaze particle size.

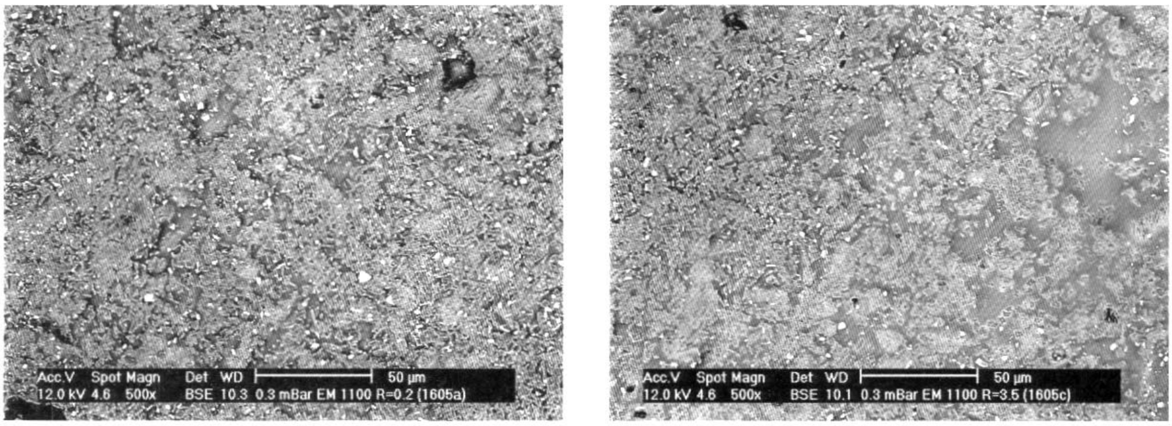
Glaze	Reject (% by weight)	L*	Gloss (‰)	Ra (µm)
ER	0.1	92.2	83	0.4
	1	92.0	47	0.8
	3.5	92.3	40	0.8
EP	0.2	90.7	38	0.7
	1	90.6	29	1.0
	3.5	90.5	23	1.2
EG	0.3	91.0	38	0.7
	1	90.8	31	1.0
	3.5	91.3	26	1.0

Table 4. Variation of the surface properties of glazes ER, EP and EG on modifying glaze particle size .



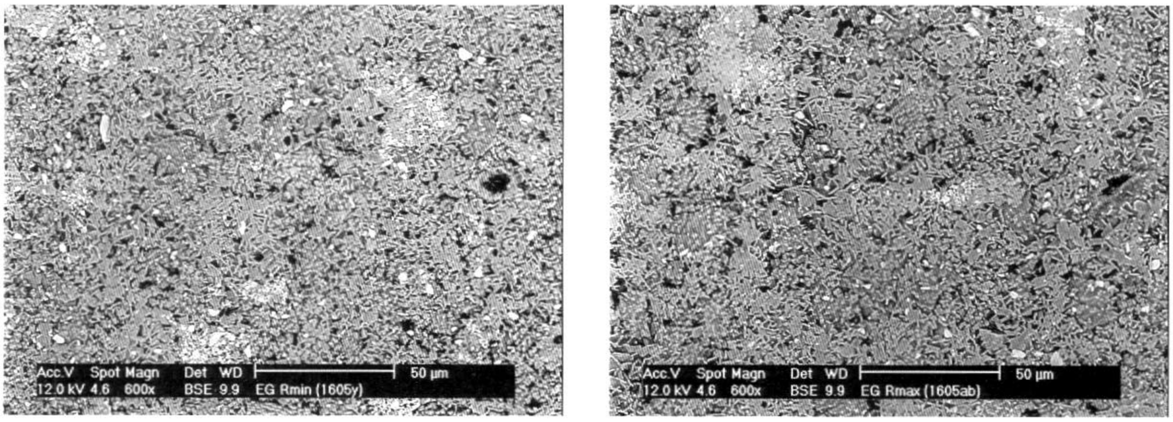
R=0.1% R=3.5%

Figure 11. Surface of the glazes obtained on modifying glaze ER particle size (1040°C).



R=0.2% R=3.5%

Figure 12. Surface of the glazes obtained on modifying glaze EP particle size (1100°C).



R=0.3% R=3.5%

Figure 13. Surface of the glazes obtained on modifying glaze EG particle size (1200°C).

The micrographs show that on reducing glaze particle size, the size of the devitrified phases decreases; this decrease is highly pronounced in glaze ER, in which a marked change in gloss can be observed. XRD confirmed that modifying the particle size did not produce any important change in the quantity of crystalline species present.

The changes observed in glaze ER gloss are therefore due to a variation in the size of the crystalline species. In glaze EP, the increase in particle size is reflected in the increase in glass area size and in crystal clusters, producing a greater difference between areas and, therefore, greater roughness. Glaze EG, due to its tendency to crystallise and absence of glassy areas, is least sensitive to the change in particle size.

4.3 INFLUENCE OF THE FIRING CYCLE

In order to determine the influence of the firing cycle the following variables were modified: peak temperature, cooling rate, heating rate and residence time at peak temperature. On obtaining the glazes it was observed that the first two variables produced a considerable variation in glaze gloss, so that only the results corresponding to those two variables are set out.

4.3.1 Peak temperature

Table 5 shows that raising peak firing temperature of glaze ER decreases surface roughness, increases gloss and reduces glaze opacity (decrease of chromatic co-ordinate L*). The greatest change observed in glaze appearance is produced on raising firing temperature from 1060 to 1080°.

Temperature (°C)	**L***	**Gloss (‰)**	**Ra (μm)**
1000	92.6	29	1.3
1020	92.8	31	1.3
1040	92.0	47	0.8
1060	91.4	66	0.6
1080	89.1	93	0.4

Table 5. Variation of colour, gloss and surface roughness of glaze ER with firing temperature.

The crystalline phases found in the glazes produced at peak firing temperatures of 1000 and 1080°C were determined, observed and analysed by SEM. The XRD results indicate that increasing temperature reduces the quantity of crystalline phases present (cristobalite, wollastonite and zircon) (Figure 14). On the other hand, at the peak temperature of 1080°C a new species appears, the double silicate of zirconium and calcium ($Ca_2ZrSi_4O_{12}$).

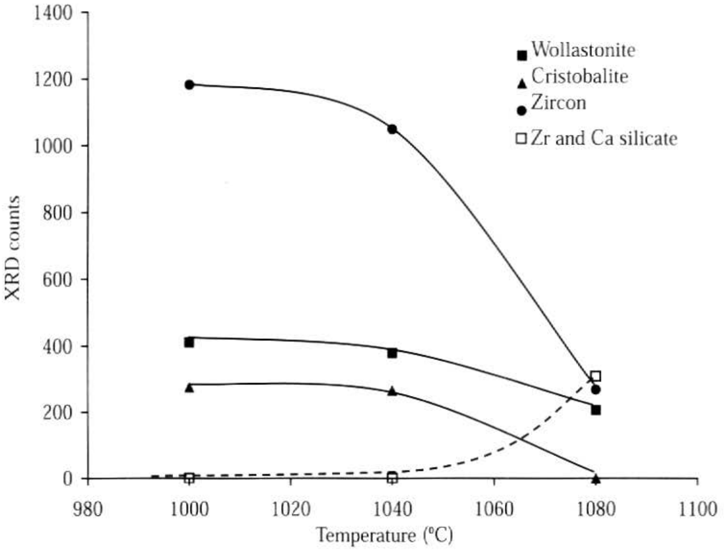
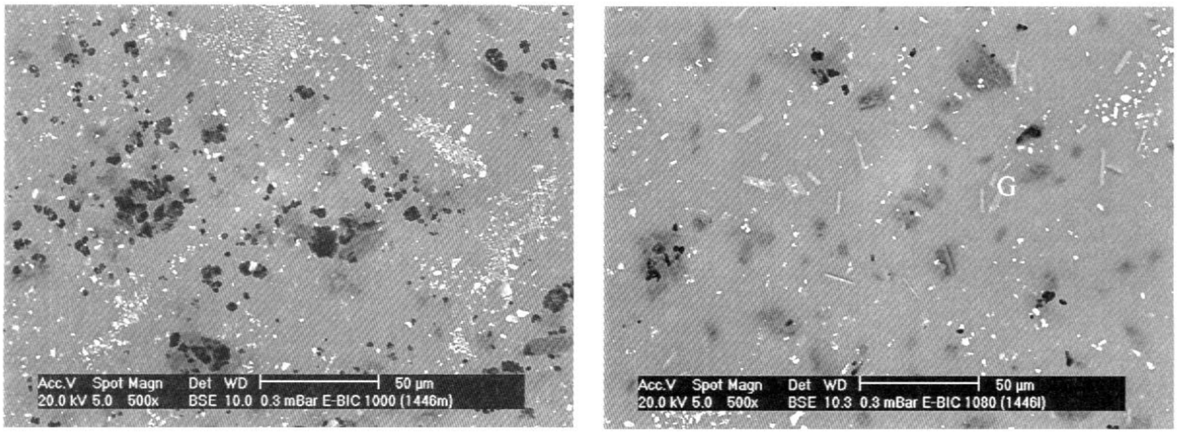


Figure 14. Variation of the quantity of crystalline species found in glaze ER with firing temperature.



1000°C 1080°C

Figure 15. Surface of the glazes obtained on modifying glaze ER firing temperature.

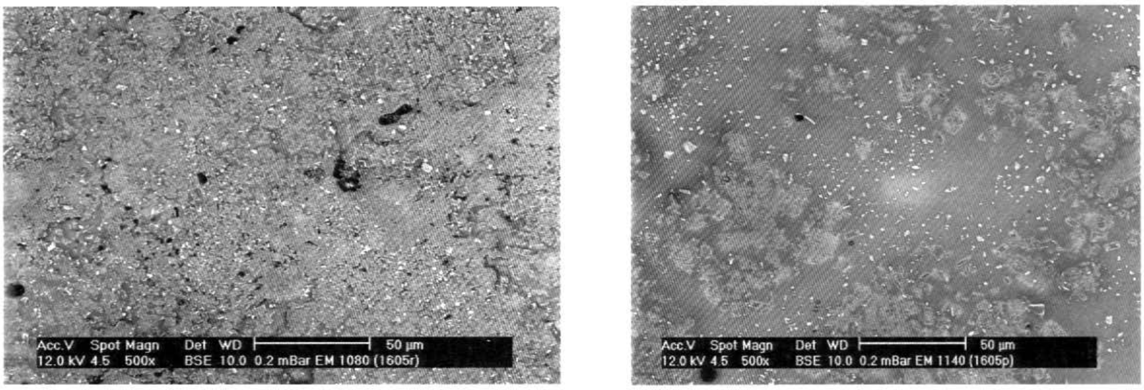
In view of the results, it can be stated that the reduction in the amount of zircon is responsible for the decrease in glaze opacity because of the difference of the refractive index between the zircon crystals (n=1.94) and the glassy phase (n≈1.6), and that, furthermore, the reduction in the quantity of wollastonite and cristobalite seems to be responsible for the rise in gloss, since these crystals contribute less to opacity, as their refractive indices are similar to those in the glassy phase.

The XRD results were verified on viewing the micrographs of the ER glaze surfaces produced at 1000 and 1080°C (Figure 15). At 1080°C almost all the wollastonite and cristobalite has dissolved, as also largely has the added zircon. Moreover, a new, rod-shaped crystalline phase has devitrified (type G species), corresponding to the Zr and Ca double silicate.

For glaze EP, the variation observed in gloss and opacity on increasing firing temperature (Table 6) is far less pronounced than for the ER. At 1080 and 1140°C the crystalline phases present were determined and observed by SEM. Figure 16 shows the micrographs of both glaze surfaces and Figure 17 depicts the micrographs of a cross section of both glazes.

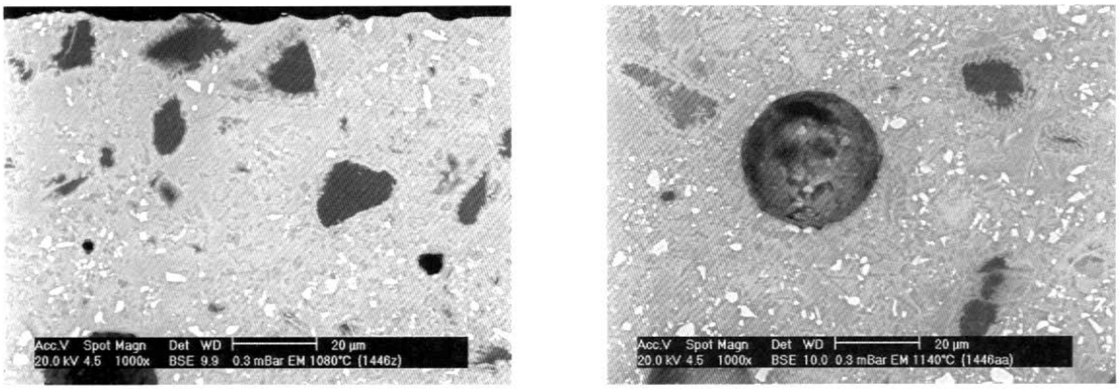
Temperature (°C)	L*	Gloss (‰)	Ra (µm)
1080	90.9	21	1.6
1100	90.6	29	1.0
1120	89.4	34	1.0
1140	89.1	30	1.2

Table 6. Variation of colour, gloss and surface roughness of glaze EP with firing temperature.



1080ªC **1140°C**

Figure 16. Surface of the glazes obtained on modifying glaze EP firing temperature.



1080°C **1140°C**

Figure 17. Cross section of the glazes obtained on modifying glaze EP firing temperature.

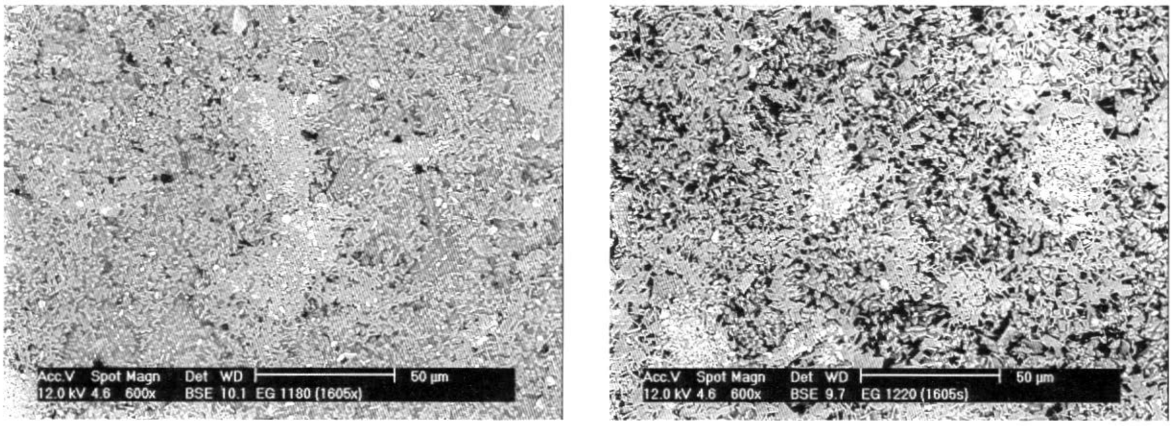
At 1140°C a rise in the quantity of glassy phase present and in the size of the devitrified celsian crystals can be observed at the surface. However, the XRD results do not show a considerable change in the amount of crystalline species when firing temperature is increased from 1080 to 1140°C. This could be due to the fact that although an increased amount of glassy phase is found at the surface, observation of the cross section of these glazes (Figure 17) indicates that, on raising temperature, the quantity of crystals rises. It can also be observed in this figure that, on increasing firing temperature, the nepheline particles dissolve and react with the glass surrounding them, forming celsian crystals.

The increase in roughness at 1140°C could be caused, as already indicated in section 4.2, by the existence of very different areas of glass and crystal clusters. In contrast to what occurred with glaze ER, in glaze EP there does not seem to be an important dissolution of the added zircon, so that in the tested range of temperatures, the opacity of these glazes varies less.

Table 7 sets out the variation of glaze EG surface characteristics on modifying peak firing temperature. The tested range of temperatures was smaller than that corresponding to the other two glazes, since although a glaze was obtained at 1160°C, it did not present a suitable texture, yielding a glaze with reduced gloss, and furthermore, the body used could not be subjected to temperatures over 1220°C, since it deformed. In the range of temperatures in which the glaze presented adequate smoothness (1180-1220°C), it can be observed that opacity and gloss vary very little with firing temperature. On subjecting the glazes obtained at 1180 and 1220°C to XRD analysis, it was found that the amount of crystalline species present hardly varied with peak firing temperature. On observing these same glazes by SEM, the only change produced on increasing the firing temperature was found to be an increase in size of the crystals contained.

Temperature (°C)	L*	Gloss (‰)	Ra (μm)
1160	91.5	15	--
1180	91,1	28	1.6
1200	90,8	31	1.0
1220	90,1	29	0.9

Table 7. Variation of colour, gloss and surface roughness of glaze EG with firing temperature.



1180ªC **1220°C**

Figure 18. Surface of the glazes obtained on modifying glaze EG firing temperature.

For glaze compositions EP and EG a rise in the crystal size is observed, associated with a decrease in roughness and increase in gloss, in contrast to what occurred when particle size was modified. This could be due because in this case, increasing peak firing temperature lowers glassy phase viscosity, producing better surface stretching, which leads to less surface roughness, and hence greater gloss.

The results obtained in this section indicate that glaze ER has the least stability, confirmed on an industrial scale, with regard to variations in peak firing temperature, because raising temperature inhibits the formation of crystalline phases that produce the matt appearance.

4.3.2 Cooling rate

With a view to determining the influence of the cooling rate, glazes ER, EP and EG were subjected to air quenching, which consisted of withdrawing the test specimens from the kiln after the hold at peak temperature. The resulting glazes presented the surface characteristics set out in Table 8. The three glazes exhibited a rise in gloss after quenching, related to a slight decrease in surface roughness. On subjecting these new glazes to XRD analysis, it was observed that the quantity of devitrifying crystalline species decreased in specimens obtained by quenching (Table 9).

Glaze	Cooling	L*	Gloss (‰)	Ra (μm)
ER	Quenching	92.0	65	0.5
	Standard	92.0	47	0.8
EP	Quenching	90.6	46	1.0
	Standard	90.6	29	1.0
EG	Quenching	91.2	47	0.9
	Standard	90.8	31	1.0

Table 8. Variation of the surface properties of glazes ER, EP and EG on modifying the cooling rate.

Cooling	ER		EP	EG
	Wollastonite (d=2.97 Å)	Cristobalite (d=4.04 Å)	Celsian (d=3.33 Å)	Celsian (d=3.33 Å)
Quenching	262	240	640	708
Standard	380	266	980	876

Table 9. Peak intensity (counts) of the devitrifying species in glazes ER, EP and EG according to type of cooling.

Figures 19 to 21 show the micrographs of the glaze surfaces obtained by quenching. The quantity of crystals present is found to be considerably less than that in the glazes subjected to standard cooling (Figure 1, 2 and 5).

These results indicate that the crystalline species in the glazes form during heating, partly dissolve at peak temperature, and subsequently recrystallise during cooling.

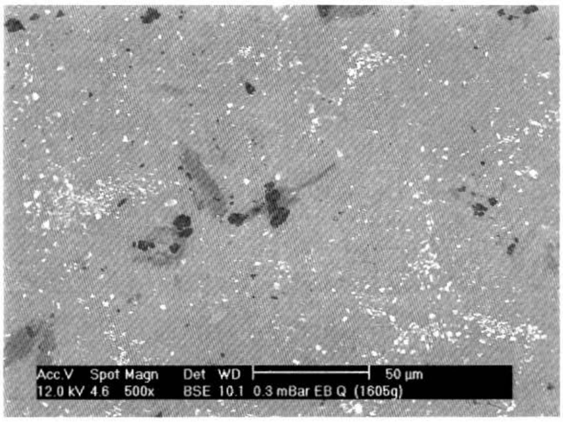


Figure 19. ER glaze surface (1040°C-quenching).

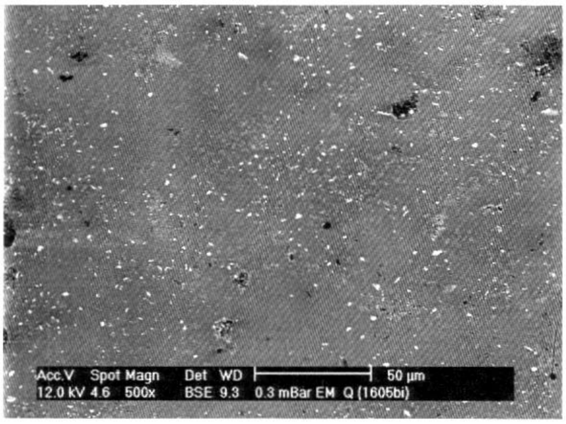


Figure 20. EP glaze surface (1100°C-quenching).

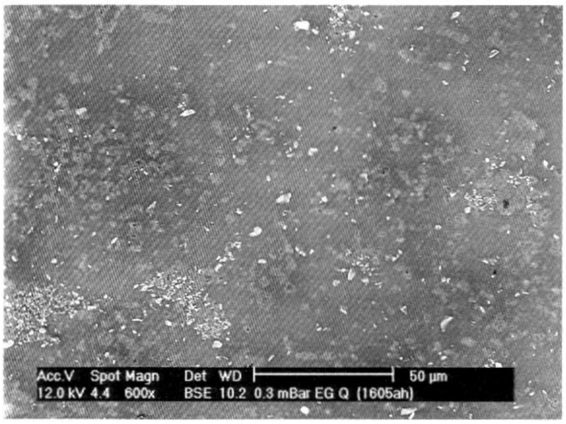


Figure 21. EG glaze surface (1200°C-quenching).

This phenomenon (sequence) explains why modifying the heating rate and dwelling time at peak temperature does not produce an important change in glaze gloss, since it is the cooling rate that actually controls the amount of crystals found in the glaze and hence final gloss. On the other hand, in the case of glaze ER, peak firing temperature is also important as high temperatures (1080°C) favour the formation of a crystalline species (double silicate of zirconium and calcium) that inhibits crystallisation during cooling of wollastonite and cristobalite, which are species responsible for the matt appearance of glaze ER.

5. CONCLUSIONS

The matt appearance of the studied glazes is produced by the formation, during firing of crystalline species wollastonite and cristobalite in the case of the calcium matt, and celsian or barium orthoclase in the case of the barium matts, which increase surface roughness compared with that of glossy glazes. The barium matt glazes studied, owing to the large quantity of crystals that form during firing, yield rougher surfaces with less gloss than the calcium matt glaze. It was observed in the three studied glazes that the main cause of the formation of crystalline species is the frit used in preparing the glaze composition. For the EP barium matt glaze, the presence of nepheline in the composition favours the formation of celsian or barium orthoclase.

The decrease in glaze particle size reduces the size of the crystalline species that form during firing, reducing surface roughness and raising gloss, this change being very pronounced in the calcium matt glaze.

For all three tested glazes, a noticeable change was produced in gloss on modifying the cooling rate. This fact demonstrates that the crystalline species found in the three glazes form during heating, partially dissolve at peak firing temperature and recrystallise during cooling.

The calcium glaze matt is the only glaze that presents a considerable variation in gloss when peak firing temperature is modified. High temperatures (>1040°C) encourage the formation of a new crystalline species (double silicate of zirconium and calcium) which inhibits the formation of wollastonite and cristobalite during cooling, thus increasing gloss and reducing opacity, the latter caused by the reduction in the quantity of zircon in the glaze.

On modifying the hold at peak temperature, no important change is produced in the gloss of the three glazes studied, since it is the cooling rate that controls the quantity of crystals present inside each glaze.

6. REFERENCES

[1] PARMELEE, W.C. *Ceramic Glazes.* 2nd ed. Chicago: Industrial publications, 1951

[2] TAYLOR, J.R.; BULL, A.C. *Ceramics glaze technology.* Oxford: Pergamon press, 1986

[3] SINGER, F.; SINGER, S.S. *Cerámica Industrial. Volumen I: Principios generales de la fabricación de cerámica.* Bilbao: Urmo, 1971.

[4] EPPLER, R.A.; EPPLER, R.D. *Glazes and glass coatings.* Westerville:ACERS,2000.

[5] MATTHES, W.F. *Vidriados Cerámicos: fundamentos, propiedades, recetas, métodos.* Barcelona: Omega, 1990

[6] SINGER, F.;GERMAN, W. *Vidriados Cerámicos.* Barcelona: Borax producer and A.Q.S.A., 1970

[7] SIMONIS, H. *Esperienze in ceramica. Gli smalti. Caratteristiche, diffeti, soluzioni e particolari effetti di superfici ceramiche.* Faenza: Faenza Editrice, 1994.

[8] TOZZI, N. *Smalti ceramici. Considerazioni teoriche e pratiche.* Faenza: Faenza Editrice, 1992.

[9] IBÁÑEZ, M.J. *Estudio de las propiedades mecánicas y superficiales de recubrimientos vidriados de piezas cerámicas. Puesta a punto de nuevas técnicas de medida.* Castellón: Universitat Jaume I, 1998. Doctoral dissertation.

[10] CAMPA, F.; GINÉS, F.; ROBLES, J. Matting of a transparent porous wall tile glaze by adding alumina. In: *Qualicer 2000: IV World Congress on Ceramic Tile Quality.* Castellón: Cámara Oficial de Comercio, Industria y Navegación. Vol III, 1996. p. 15-18.

[11] ESCARDINO, A. Crystalline glazes. In : *Qualicer 96: IV World Congress on Ceramic Tile Quality.* Castellón: Cámara Oficial de Comercio, Industria y Navegación. Vol I, 1996. p. 91-112.