EFFECT OF THE KAOLIN PROPORTION CONTAINED IN THE GLAZE LAYER ON GLAZE BEHAVIOUR IN FIRING

A. Belda(*); J. Marco(*); R. Gimeno(*);
A. Escardino(**); E. Sánchez(**); J.L. Amorós(**); E. Bou(**)

(*)FRITTA S.L
(**)Instituto de Tecnología Cerámica.
Asociación de Investigación de las Industrias Cerámicas.
Universitat Jaume I. Castellón Spain.

ABSTRACT

The response to heat treatment was studied of blends of frit and kaolin of similar composition and particle-size distribution to those typically used in producing single-fire ceramic wall tile glazes, to determine why reducing the kaolin content of these mixtures below 6% by weight, tended to produce certain defects in the resulting fired glazes.

Dilatometry revealed that considerable differences existed in dimensional variation amongst the test specimens made from a standard wall tile composition and those formed from different blends of frit and kaolin in the 500-800°C temperature range, which might be the cause of the arising defects

On raising the kaolin proportion, the cohesive force rose between the particles of the frit-kaolin mixture making up the glaze layer, thus increasing its consistency in firing. This rise in cohesion appears to be due to a rise in the compactness of the layer in the temperature domain below 350°C. In the 350-800°C temperature range, the changes arising with kaolin dehydroxylation in the glaze layer also considerably affected this enhanced cohesion.

1. INTRODUCTION

A key objective in glazed tile manufacture is obtaining glaze coatings with continuously improved technical characteristics (resistance to abrasion, stain resistance,

resistance to chemical attack, etc.), as well as enhanced aesthetic characteristics (whiteness, gloss, texture, etc.)[1], [2].

In glossy, opaque wall tile glazes, whiteness is a key aesthetic property. The mixtures used as raw materials for producing such glazes typically consist of a frit in a 90-95 wt% plus kaolin. To date, attempts to optimise the whiteness of the resulting glaze have involved acting upon the composition of the frit, so that heat treatment will produce devitrification of crystalline phases with suitable refractive indices and appropriate crystal sizes[3], [4].

Kaolin is mainly added for its stabilising effect on the aqueous suspension of frit particles (slip) that is applied to the body to obtain the consolidated glaze layer that gives rise to the final glaze coating[5] on firing. Owing to its suitable particle-size distribution, kaolin also enhances the cohesion amongst the frit particles in the consolidated glaze layer and strengthens the layer's bond with the underlying engobe coating. Both factors are of great importance when screen-printing runs are to be made onto the glaze layer, whether by the traditional method (printing screens) or by rollers and rotogravure. However, as kaolin contains traces of chromophore oxides (Fe_2O_3 y TiO_2) and also dilutes the frit concentration, having kaolin in the mixture making up the consolidated layer of unfired glaze slightly decreases the degree of whiteness that the glaze might achieve if the frit were just used by itself.

It was attempted in laboratory and pilot scale tests to lower the kaolin proportion in the frit-kaolin blends with a view to raising the whiteness index of the resulting heterogeneous fired glaze. It had been observed that when the kaolin proportion was lowered below a given limit, usually around 6% (depending on the characteristics of the kaolin used), the texture of the resulting fired wall tile glaze deteriorated, and defects such as small cracks, depressions, etc. appeared. The findings of these studies remain as yet unpublished. A literature survey found no studies on the effect of the reduction or complete elimination of kaolin in such glaze blends on the degree of whiteness or characteristics of the resulting glaze or on possible defect formation.

It was therefore decided to examine how the kaolin content in the consolidated glaze layer affected glaze behaviour in firing and the characteristics of the resulting fired glaze coating. This was to attempt to reduce the kaolin proportion in frit-kaolin blends and slightly raise the degree of whiteness of the resulting heterogeneous, single-fire, wall tile glazes.

2. EXPERIMENTAL

2.1. MATERIALS

A standard industrial zirconium frit used to produce glossy, white, glazes for single-fire wall tiles was employed in the study. Kaolins D'Arvor (Kaoliner 1C) supplied the

---

[1]. AMORÓS, J.L. *Glazes for ceramic wall and floor tiles: evolution and perspectives*. Tile Brick Int. 9 (5), 273-278, 1993.

[2]. BOU, E.; JARQUE, J.C.; SÁNCHEZ, E., et al. *Optimizing glaze transparency by design*. Am. Ceram. Soc. Bull., 75(10), 71-75, 1996.

[3]. ESCARDINO, A. *Crystalline glazes*. In: IV World Congress on Ceramic Tile (QUALICER). Castellón, 1996, p. 87-110.

[4]. CABALLER, V.; MARCO, J.; NEGRE, F., et al. *Mejora de la blancura de un vidriado mediante la aplicación de un diseño factorial de experimentos*. Cerám. Información, 196, 2-10, 1994.

[5]. RODRIGO, J.L.; VIVES, M.; MORENO, A., et al. *Comportamiento del engobe durante la operación de esmaltado. Técnica Cerámica*, 204, 404-416 (1992).

kaolin employed in the study, a widely used type in the preparation of frit-kaolin blends for producing ceramic glazes.

2.2. EXPERIMENTAL PROCEDURE

2.2.1. GLAZE SUSPENSION PREPARATION

Aqueous glaze suspensions were prepared from blends of frit and kaolin of different composition. The tested kaolin proportions in wt% (calculated on a dry base) were: 0, 2, 4, 6, 8, 10, 16 and 20% (hereinafter referenced compositions C0, C2, C4, C6, C8, C10, C16 and C20 respectively). The mixtures of frit particles and kaolin together with 0.3% CMC (relative to the dry solid) and the distilled water needed to obtain a suspension with a solids content of 70% by weight, were milled in fast laboratory mills using alumina ball grinding media, until a reject of around 1% was obtained on a 40 µm mesh screen.

2.2.2. PREPARATION OF THE UNFIRED, GLAZED TEST SPECIMENS

The prepared glaze suspensions were applied by an automatic, variable-speed applicator[6] to hot, green bodies, formed from a pressing powder of a standard porous wall tile body composition. The applied glaze layer was approximately 0.4 mm thick. The resulting glazed specimens were then dried in an electric oven at 110°C.

2.2.3. CHARACTERISATION OF THE CONSOLIDATED GLAZE LAYER

i) Measurement of glaze layer cohesion and bonding.

To determine the cohesion of the consolidated glaze layer obtained from compositions C0 to C20, and their bonding to the body, a method developed at the Instituto de Tecnología Cerámica[7] was used. This procedure, described elsewhere[8], is based on the use of a blade, fitted to a rod that is connected to the loading cell of an INSTRON universal testing machine. The cell continuously measures the force needed to make the blade cut into the layer. The test ends when the layer peels or fractures, and the maximum force registered by the loading cell up to that point is recorded.

ii) Dry bulk density measurement.

Dry bulk density of the consolidated layer was measured with a porosimeter (Micromeritics Porosizer 9310). The measurement was run on a test specimen consisting of a previously fired body to which the frit-kaolin blend was applied, whose characteristics are set out in Section 2.2.1. This was subsequently dried and the resulting dry consolidated layer was separated from the body. A fired body was used to ensure that no parts of the body would come away on separating the layer.

iii) Dilatometer tests.

The dilatometric tests were carried out on specimens formed by casting,

---

[6]. Asociación de Investigación de las Industrias Cerámicas (AICE). *Dispositivo para la aplicación de suspensiones sobre soportes cerámicos*. F. Negre, M. Monzó, S. Giménez. Spain. Utility Model, 1036515 U, 1997.

[7]. Asociación de Investigación de las Industrias Cerámicas (AICE) *Sistema de evaluación del comportamiento mecánico de recubrimientos aplicados sobre soporte*. A. Moreno, S. Giménez, C. Feliu, V. Beltrán. Spain Patent. P9400338, 1994.

[8]. Bort, J.; Fenollosa, J.L. *Study of the bonding of unfired glazes*. In: III World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1994, p. 89-104.

analogously to those prepared at Point 2.2.3 (ii), producing 5 mm thick layers. After drying the cast layers in an electric oven, these were separated from the body and test specimens were formed sized approximately 30mm x 5mm x 5mm.

The measurements were performed at a heating rate of 25°C/min in an absolute dilatometer (Netzsch Model 420 E\7).

iv) Heat treatment in an electric kiln.

The test specimens formed as set out in Section 2.2.2, to which frit-kaolin blends of different composition had been applied, were fired in a laboratory electric oven (Pirometrol) at various peak temperatures. The following thermal schedule was used.

I) Fast heat-treatment (a_I=50°C/min.), from room temperature to 500°C.
II) Slower heat-treatment, at a heating rate of a_{II}=25°C/min, from 500°C to the peak temperature set for each thermal cycle.

III) Constant heat-treatment at set peak temperature (6-min dwell).

IV) Cooling by forced convection from peak temperature to 590°C.

V) Cooling by natural convection from 590°C to 540°C.

VI) Cooling by forced convection from 540°C to room temperature.

The peak temperatures studied ranged from 900°C to 1100°C. This latter temperature was very close to standard industrial peak firing temperature for glazed porous wall tile manufacture.

v) Detection of defects in the fired glazed specimen.

A stereoscopic magnifying glass at a magnification of 35x was used to visually inspect the glazed specimens fired at different peak temperatures. Photographs were taken with this instrument of some test specimens.

vi) Measurement of the Hunter whiteness index (60).

The Hunter whiteness indices were determined with a MACBETH COLOR EYE 7000 diffuse reflectance spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF THE KAOLIN PROPORTION IN THE UNFIRED CONSOLIDATED GLAZE LAYER

As set out above, it had been observed in industrial practice that reducing the kaolin proportion below 6 wt% in the frit-kaolin blends that are typically used to produce heterogeneous, single-fire, wall tile glazes, gave rise to surface defects in the final product. For this reason, the kaolin content in such compositions tends to range between 5 and 9%, a compositional proportion that has been found empirically.

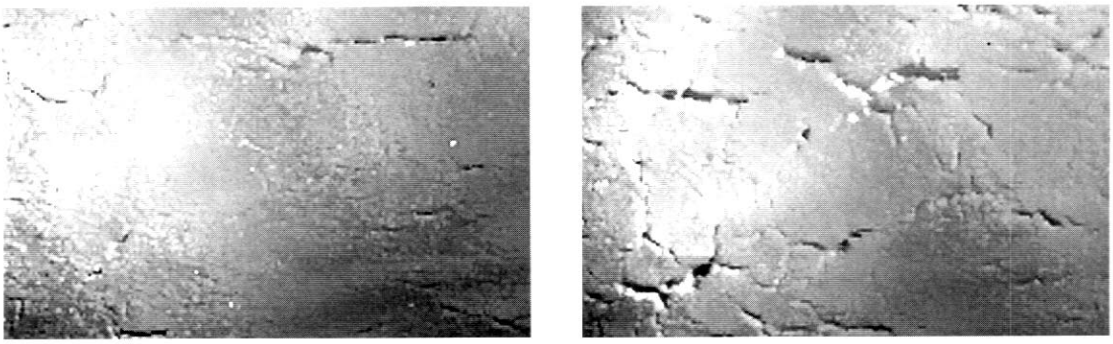
In order to study the influence of the kaolin content in these blends on the characteristics of the resulting single-fire glaze, two types of test specimens were prepared by applying composition C2 (2% kaolin) and C8 (8% kaolin) respectively (Section 2.2.1) to the selected body. The latter composition was chosen as a reference composition as this is a widely used blend in industry.

These test specimens were fired using the thermal schedule set out at Point 2.2.3 (iv), at peak temperatures of 900, 940, 980, 1040 and 1100°C.

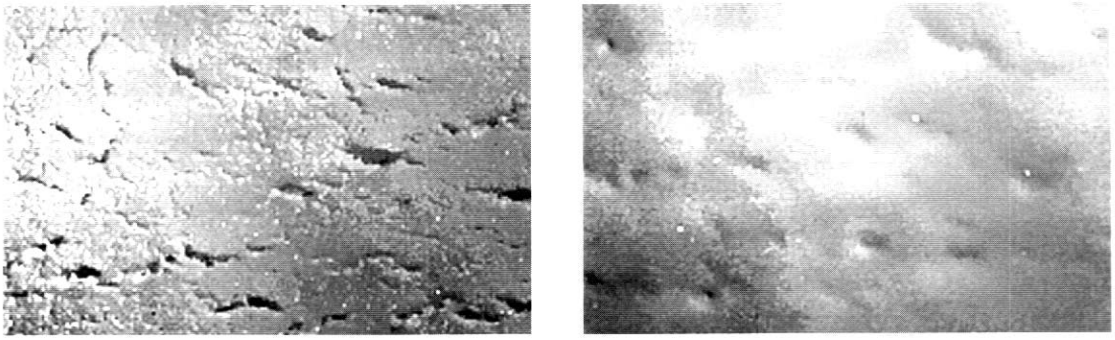
Figs. 1 and 2 show the surface appearance of the resulting fired glaze coatings. The photographs were taken with a stereoscopic magnifying glass, magnifying at 35x.

Small surface cracks can be observed in the test specimens obtained from composition C8 (Fig. 2), fired at T_{max}=940°C. The number of cracks rose in the pieces fired at T_{max}=980°C. On raising the temperature, the cracks diminished (Fig. 2.d), subsequently fully disappearing at 1100°C.

In the case of the test specimens obtained from composition C2 (Fig. 1), larger cracks started appearing in the specimen fired at T_{max}=900°C and their proportion rose on raising T_{max} to 980°C. After 1040°C, the fusing glaze layer progressively closed the cracks. However, at 1100°C they were still visible, forming small depressions, which represent a defect in the glaze surface. Pictures of the specimens fired at 1100°C cannot be shown. Photographs could not be taken of these glaze surfaces, as the specimen had to be set at a specific angle to be able to visualise the depressions.

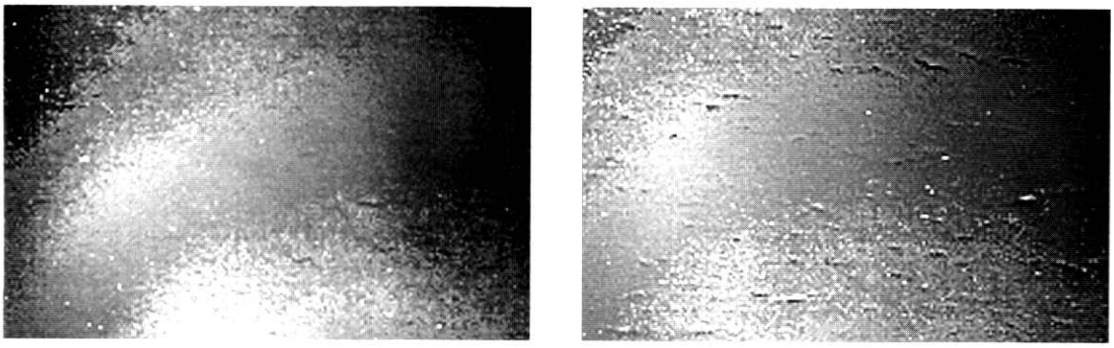


a) T_{max}= 900°C b) T_{max}= 940°C

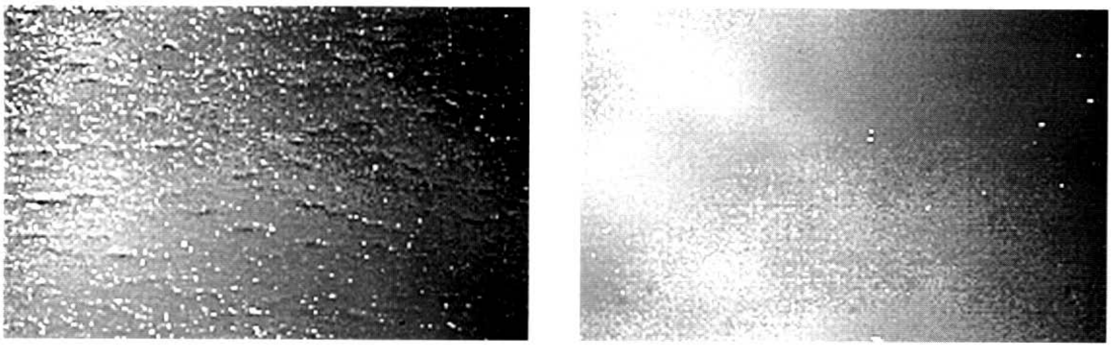


c) T_{max}= 980°C d) T_{max}= 1040°C

Figure 1. *Crack formation in fired specimen glaze surfaces at different T_{max} (composition C2).*



a) T_{max}= 900°C b) T_{max}= 940°C



c) T_{max}= 980°C d) T_{max}= 1040°C

Figure 2. *Crack formation in fired specimen glaze surfaces at different T_{max} (composition C8).*

3.2. POSSIBLE CAUSES OF CRACK FORMATION IN FIRED SPECIMEN GLAZE COATINGS

A series of tests was carried out, which are described below, to try and explain the differing behaviour of compositions C2 and C8 observed in Section 3.1 (Figs. 1 and 2), on firing these at different peak temperatures.

3.2.1. EXPANSION-SHRINKAGE CURVES OF THE BODY AND CONSOLIDATED GLAZE LAYER

The dimensional variation was assessed in a dilatometer of the test specimens formed from compositions C8 and C2, as well as the dimensional variation arising in specimens made from the wall tile body composition used in the tests set out in Section 3.1, on raising temperature.

The results have been plotted in Fig. 3 in the form $\Delta L/L_0$ versus T(°C), where $\Delta L = L - L_0$. It can be observed that the body expanded much more than the specimens made from the frit-kaolin blends on raising temperature. This difference in behaviour, which increased after 500°C (temperature at which the body continued expanding while the glaze specimen started shrinking), explained why cracks could form in the consolidated glaze layer, as the greater expansion of the body subjected the glaze to tensile stress that can produce cracking.

As the difference between the body's expansion curve and that of the C2 composition specimen was smaller than the difference between the body's curve and that of composition C8, according to the above hypothesis the arising cracks could be expected to be just as large or larger in the glaze layer formed from composition C8. However, an important difference, in the opposite sense can be observed (Figs. 1 and 2), which might be explained if the cohesive force between the particles in the consolidated layer were for some reason greater than that of the layer produced on applying composition C2, throughout the whole firing cycle. This would practically manage to neutralise the tendency for cracks to develop in these layers as a result of tensile stresses produced by the body (opposing cohesion), on raising the temperature of the piece in the temperature range between room temperature and 850°C.

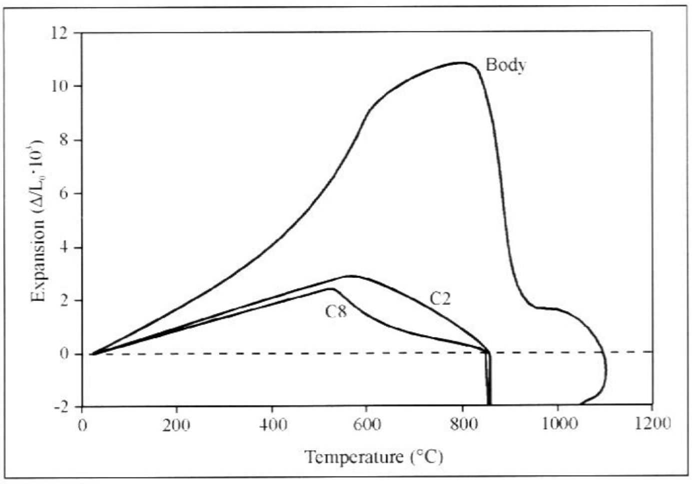


Figure 3. Expansion-shrinkage curves of the tested body and glaze compositions C2 and C8.

3.2.2. VARIATION IN CONSOLIDATED LAYER COHESION AND BONDING

Using test specimens prepared by applying blends C2 and C8, fired as set out at point 2.2.3 (iv) at peak temperatures of 200, 300, 400, 500, 600, 700 and 800°C, the maximum penetration force was determined in each case, using the set-up and procedure described at point 2.2.3 (i). Fig. 4 depicts the plots of the results in the form variation of maximum penetration force F_m, expressed in Newtons, versus peak firing temperature for each consolidated layer obtained from the two tested glaze compositions (C2 and C8).

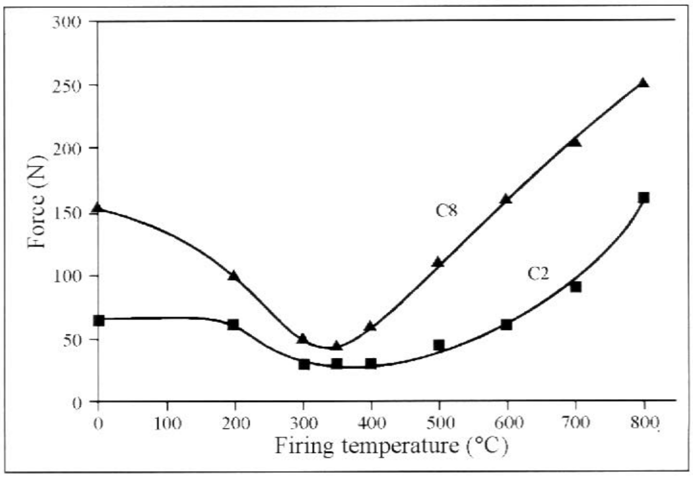


Figure 4. Variation of maximum force (measured with the test assembly employed) with peak firing cycle temperature. Coatings obtained with glaze blends C2 and C8.

As can be observed, both curves exhibited minimum values around 350°C. The fact that the curves exhibited a falling stretch at the start may be due to the progressive removal (by combustion) of CMC, which acts as particle binder in the unfired layer. On the other hand, the fact that both starting forces were different could be because of better particle packing in composition C8 than in C2, which would yield greater cohesion, a circumstance considered in Section 3.3. This assumption is based on the fact that dry bulk density of the layer formed from composition C8 was 1.72 g/cm^3, while that of C2 was 1.67 g/cm^3.

The greater and more rapidly growing interparticle cohesion in the C8 glaze layer (directly related to maximum penetration force recorded in the test assembly used), compared to that of C2 above 350°C, might explain the smaller degree of cracking in the C8 glaze layer (Fig. 2, Section 3.1), as suggested at the end of point 3.2.1.

3.2.3. ADDITIONAL TESTS TO VERIFY THE EFFECT OF KAOLIN PROPORTION IN THE GLAZE LAYER ON GLAZE BEHAVIOUR IN FIRING

The tests described in Sections 3.2.1 and 3.2.2 were repeated using specimens made with compositions C0, C4, C6, C10, C16 and C20 to verify the results obtained above.

i) Expansion-shrinkage curves

Fig. 5 plots the data obtained with the specimens made using blends C0, C4, C8 and C16 for comparative purposes. It can be observed that the composition C0 (kaolin-free frit) curve lay closest to the body's curve. As the kaolin proportion increased in the applied blends (C0 → C16), the expansion-shrinkage curves deviated further and further from the body's curve, as had been observed in Fig. 3 (Section 3.2.1), while concurrently lowering the temperature at which specimen shrinkage commenced. The curves practically coincided for all the tested compositions after 850°C.

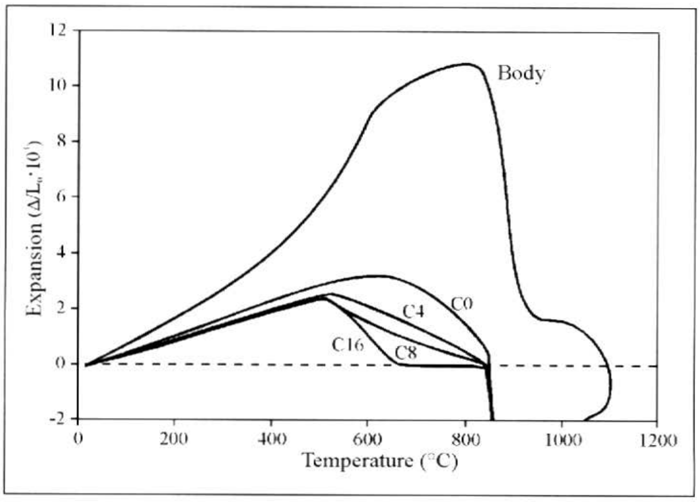


Figure 5. *Expansion-shrinkage curves of glaze compositions C0, C4, C8 and C16 and the tested body.*

ii) Variation of cohesion (measured by F_{max}) of the consolidated layer with starting kaolin proportion in the glaze layer and peak firing temperature

Using the specimens prepared by applying compositions C0, C4, C6, C10, C16 and

C20, fired as set out at point 2.2.3 (iv), at peak temperatures of 200, 300, 400, 500, 600, 700 and 800°C, the maximum penetration force required to separate the resulting consolidated layer was determined, as described at 2.2.3 (i).

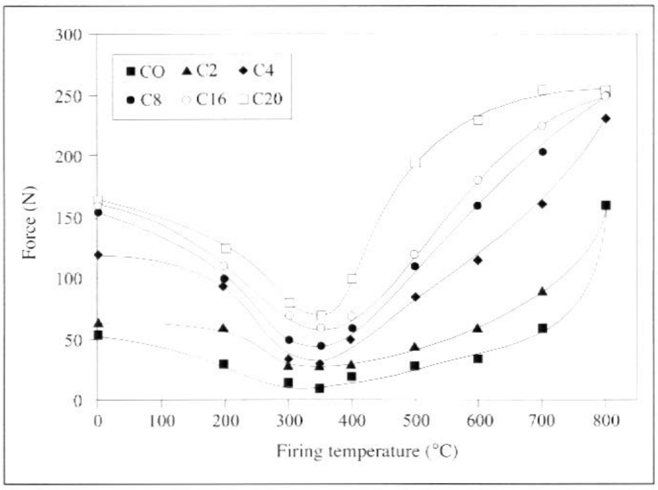


Figure 6. *Variation in maximum penetration force of the blade with peak heat-treatment temperature. Consolidated layers obtained with glaze compositions C0, C2, C4, C8, C16 and C20.*

The maximum penetration force of the blade versus peak heat-treatment temperature has been plotted in Fig. 6 for blends with different kaolin proportions. The resulting curves qualitatively resembled the ones found for compositions C8 and C2 (Fig. 4). Thus all exhibited a minimum value around 350°C, beyond which on raising the quantity of kaolin, the maximum penetration force and hence consolidated layer cohesion increased at all temperatures.

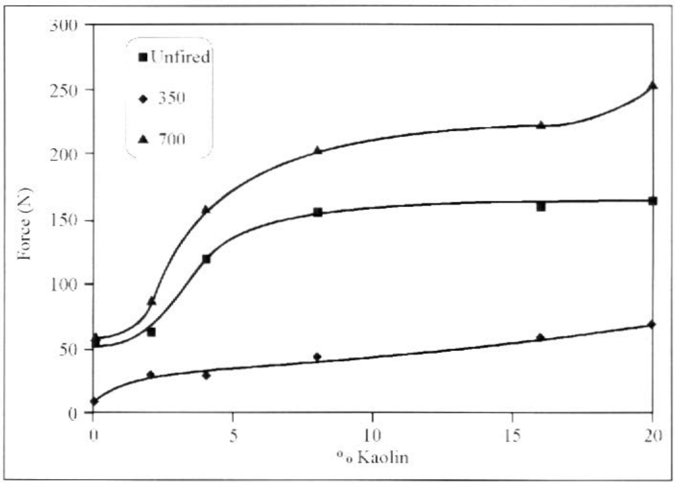


Figure 7. *Variation of consolidated glaze layer cohesion with starting glaze kaolin content in the unfired layer and in the layer fired at different peak temperatures.*

This conclusion can be better appreciated in Fig. 7, which plots the variation of "maximum penetration force" with the composition's kaolin proportion (%) for the unfired glaze layer and the heat-treated consolidated layer at 350°C (minimum cohesion region), and at 700°C. Maximum penetration force is observed to tend asymptotically to a constant value for kaolin proportions exceeding 16% in the unfired layer. However, maximum penetration force in the layers heat-treated at 350 and 700°C continued to rise with kaolin contents above 16%.

iii) Consolidated layer surface appearance (crack formation)

Test specimens prepared by applying compositions C0, C4, C6, C10, C16 and C20 were fired using heat-treatment cycles setting T_{max} at 900, 940, 980, 1040 and 1100°C. Inspection of the consolidated layer coating these test specimens and those of the specimens obtained in the series of tests described in Section 3.1 allow highlighting the following:

a) In all the studied test specimens, cracks appeared at peak firing temperatures ranging from 900 to 980°C.

b) The greatest crack number and size corresponded to the specimens produced on applying the CO composition, with cracks progressively decreasing in size and number until almost becoming imperceptible in the specimens obtained on applying blends C16 and C20.

c) The specimens to which a kaolin content of less than 6% was applied (C0, C2 and C4), fired at T_{max}=1100°C, continued to exhibit cracks though they were smaller or had become depressions. No cracks were observed in the specimens made with blend C6, fired at T_{max}=1100°C. However the glaze surface texture was not smooth.

d) The specimens to which blends were applied containing more than 6% kaolin (C8, C10, C16 and C20, fired at T_{max}=1100°C, exhibited a smooth glossy surface.

3.3. REASONS FOR INCREASED CONSOLIDATED GLAZE LAYER COHESION IN FIRING AS A RESULT OF THE KAOLIN PROPORTION

The foregoing sections have described kaolin's part in enhancing consolidated glaze layer cohesion throughout the firing process.

The tests described below were designed to attempt to explain the above results.

3.3.1. DILATOMETRIC CURVE OF THE STUDIED KAOLIN

In Fig. 8 a plot is depicted of the expansion-shrinkage curve corresponding to a test specimen formed from the kaolin used in the study. After initial expansion, sudden, fast shrinkage can be observed after 500°C, probably owing to the arising structural change (formation of metakaolin), as a result of dehydroxylation water loss, which starts at 470°C according to the literature[9], [10].

The shape of the figure explains the fact (observed in Figs. 3 and 5) that in the expansion-shrinkage curves corresponding to the test specimens made using different blends of frit and kaolin, specimen shrinkage starting temperature decreased with regard to the body's curve as glaze kaolin content rose.

---

[9]. Barba, A.; Feliu, C.; García, J., et al. *Materias primas para la fabricación de soportes de baldosas cerámicas.* Castellón: Instituto de Tecnología Cerámica-AICE, 1997. (in press)

[10]. Singer, F.; Singer, S.S. *Cerámica industrial,* vol. I. Bilbao: Urmo, 1971.

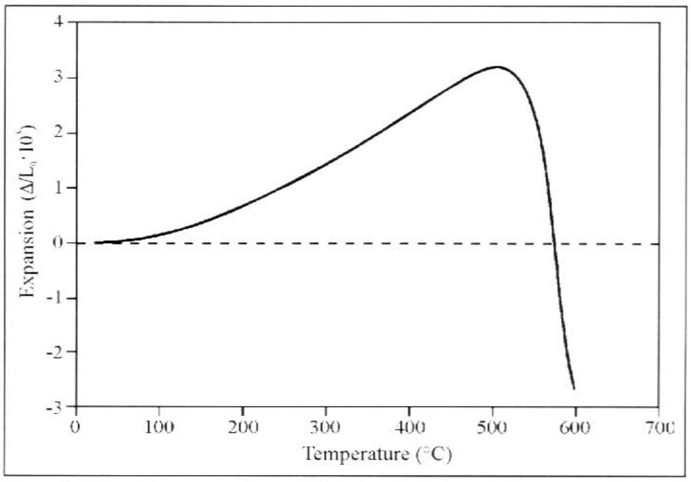


Figure 8. Expansion-shrinkage curve for the tested kaolin.

3.3.2. KAOLIN SHRINKAGE DURING DEHYDROXYLATION

To verify whether kaolin shrinkage during heating was related to dehydroxylation water loss, a series of firing tests were run using the firing schedule detailed at point 2.2.3 (iv) on kaolin test specimens formed by casting. Volume shrinkage and mass loss of these specimens were determined as a function of peak heat-treatment temperature. The resulting data have been plotted in Fig. 9, which shows that kaolin shrinkage in the 400-800°C temperature range coincided with its percentage mass loss relative to the specimen's starting dry kaolin mass content.

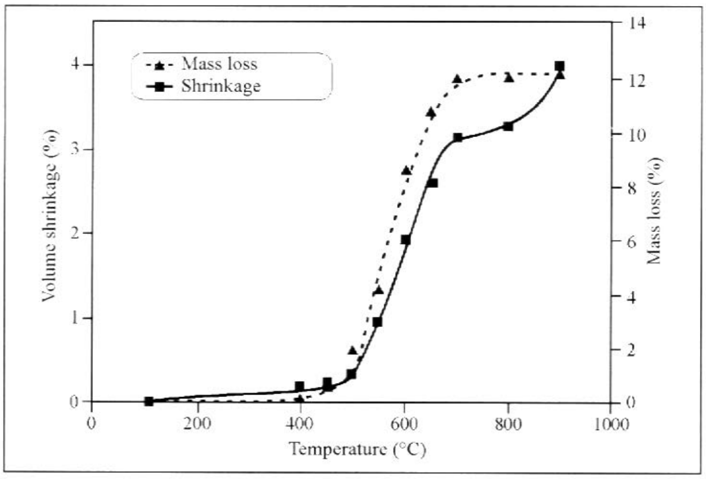


Figure 9. Variation of kaolin volume shrinkage and mass loss versus peak heat-treatment temperature.

3.3.3. RELATION BETWEEN MAXIMUM PENETRATION FORCE AT A CONSOLIDATED KAOLIN LAYER AND PEAK HEAT-TREATMENT TEMPERATURE

Fig. 10 plots the variation of the measured maximum penetration force [point 2.2.3 (i)] versus T_{max}, measured at a consolidated layer as set out in Section 2.2.2, using only kaolin, in order to study the eventual variation in interparticle cohesion with peak heat-treatment temperature.

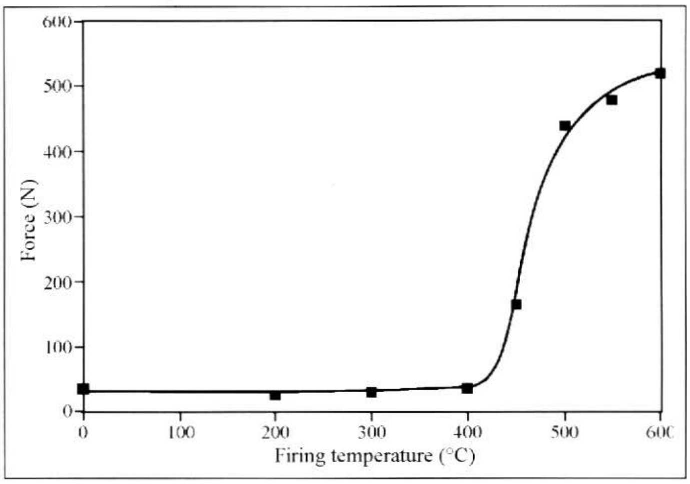


Figure 10. *Variation of maximum penetration force with peak heat-treatment temperature of a consolidated layer of kaolin.*

It can be observed that F_{max} remained virtually steady up to 400°C. However beyond this temperature, at which kaolin shrinkage started (Fig. 9), there was a sudden hike in penetration force up to 500°C, subsequently becoming less steep up to 600°C. After this temperature, the variation of F_{max} with T_{max} could not be quantified, as the body broke on attempting to force the blade into the consolidated layer. At this temperature the body did not yet have sufficient mechanical strength as sintering had not yet commenced, which impeded correctly performing the measurement.

3.3.4. ROLE OF KAOLIN IN THE CONSOLIDATED GLAZE LAYER DURING FIRING

i) Temperature stretch T<400°C

In this temperature range (Fig. 10), the maximum penetration force in the specimen made with kaolin remained practically invariable. The increase in F_{max} found in the frit-kaolin blends, on raising the kaolin proportion in the composition range of 0-20 wt% kaolin, was therefore thought to stem from the fact that this improved layer compactness and thus yielded raised interparticle cohesive force.

To verify this, bulk density was determined of the unfired consolidated glaze layer obtained from compositions C0 to C20, which allowed determining their compactness[11] The resulting data are plotted in Fig. 11 in the form layer compactness versus kaolin proportion (wt%) in the blend. They confirm that on raising the kaolin proportion compactness and hence interparticle cohesion increased in the consolidated glaze layer, though compactness grew more slowly as the kaolin content was progressively raised. This interpretation would appear to be further endorsed by the great resemblance between the shape of the curve plotted in Fig. 11 and that of the curve in Fig. 7 (F_{max} vs. kaolin %), corresponding to the unfired glaze layer. The parallelism found between both curves suggests that there is a direct relationship between unfired glaze layer compactness and F_{max} of the blade's penetration into the layer, which must be related to the cohesion between the particles making up the layer.

---

[11]. REED, J. S. *Principles of ceramics processing*. 2nd ed. New York: John Wiley, 1995, p. 215-230.

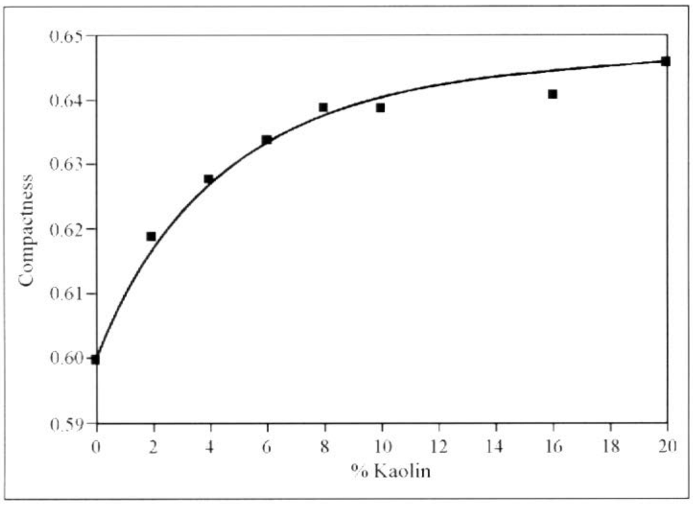


Figure 11. *Effect of kaolin proportion in the glaze composition on the compactness of the unfired glaze layer.*

ii) Curve minimum region in Figs. 4 and 6 (350-380° C)

In this region, in which the organic binder initially present in the glaze layer has already been removed (by oxidation), a difference was found in F_{max} amongst the consolidated layers obtained with the tested compositions for the reason set out in the foregoing section. Thus, the glaze layers exhibited enhanced compaction on raising the kaolin percentage, with the limitations mentioned, so that on exhibiting greater cohesion, a higher F_{max} was required to make the blade cut into the layers.

iii) Temperature stretch >400°C

In this region, the greater the kaolin proportion, the greater and faster (curve slope in Figs. 4 and 6) is the increase of F_{max} with heat-treatment T_{max}. This effect must stem from the same cause that produced the sharp rise in F_{max} in the last stretch of the curve in Fig. 10, which shows the results obtained with a consolidated layer just consisting of kaolin.

This cause must be related to kaolinite dehydroxylation, though it does not seem to be solely due to the shrinkage arising with dehydroxylation. When the kaolin particles in the consolidated layer contract, layer compactness is still necessarily limited by the presence of frit particles, which at T_{max}<700°C, have not yet undergone any shrinkage in the kaolin-free composition (C0 curve in Fig. 5).

The phenomenon observed could stem from presintering, caused by mass diffusion (encouraged by water release arising during dehydroxylation), or might be caused by the water released at T>400°C, which could react with the frit (glass) particles, decreasing their surface viscosity and producing premature softening, which might favour frit particles sticking together as well as to the dehydroxylated kaolin (metakaolin) particles dispersed between the frit particles

There is clearly a relation between the kaolin dehydroxylation phenomenon and the rise in cohesion amongst the particles in the consolidated frit-kaolin layer during heat treatment. Supporting these results, the mechanical strength of test specimens made from kaolin, fired at different heat-treatment T_{max} was shown to increase parallel to their volume shrinkage between 400 and 700°C, as a result of the same phenomenon (Fig. 12).

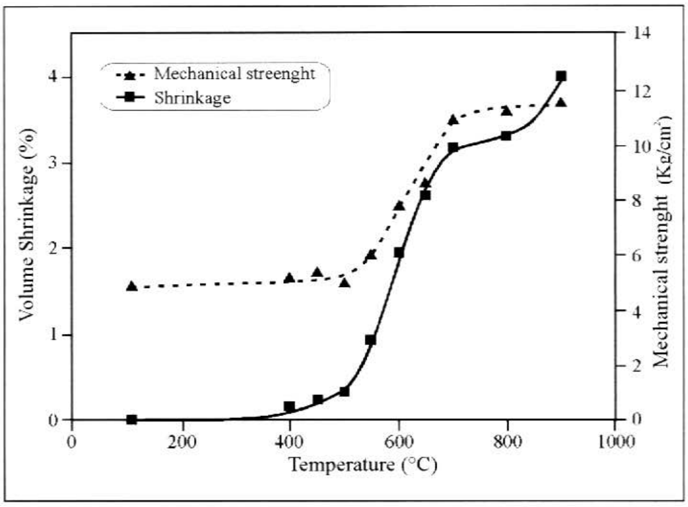


Figure 12. *Variation in mechanical strength and volume shrinkage of kaolin test specimens with peak heat-treatment temperature.*

3.4. EFFECT OF THE KAOLIN PROPORTION CONTAINED IN THE GLAZE LAYER ON THE WHITENESS INDEX OF THE RESULTING GLAZE

The results obtained in Section 3.2 indicate that the higher the kaolin content in the starting blend, within the range of values studied (0-20 wt% kaolin), the greater was interparticle cohesion in the consolidated glaze layer in the temperature range $T_{room}<T<800°C$. If it is taken into account that the kaolin used is generally cheaper than the frit with which it is mixed, the conclusion is warranted that the most suitable quantities of kaolin to be used in these glaze blends would then lie close to 20%.

It was mentioned in Section 1 that in the case of opaque white glazes, the presence of kaolin in the glaze blend detrimentally affected its whiteness, on the one hand owing to traces of Fe_2O_3 and TiO_2, which kaolin contains, and on the other because it dilutes the crystalline-phase content (responsible for whiteness) in the fired glaze. Both circumstances can constrain the advisable maximum kaolin content in the starting blend. To obtain experimental data in this regard, the Hunter whiteness index was determined of the glazes obtained on firing specimens glazed with blends C0, C2, C4, C6, C8, C10, C16 and C20, at $T_{max}=1100°C$, according to the schedule repeatedly used in this study. Table 1 details the findings.

Composition	C0	C2	C4	C6	C8	C10	C16	C20
Kaolin content (wt%)	0	2	4	6	8	10	16	20
Whiteness index	95.0	95.4	95.2	94.8	91.7	89.9	84.9	81.9

Table 1. *Variation of Hunter whiteness index in a zirconium glaze with the kaolin proportion (wt%) in the starting blend.*

It can be observed that on exceeding a kaolin content of around 4 % by weight, the whiteness index started dropping, slowly at first (up to 6%) and then faster (beyond 8%).

4. CONCLUSIONS

The following inferences were drawn from the results obtained on studying the behaviour in firing of a glaze layer consisting of a zirconium frit and kaolin:

i) On reducing the kaolin proportion in the blend below 6 wt%, glazes were obtained whose surfaces exhibited small cracks and depressions.

ii) Glaze surface cracks appeared to be due to considerable differences in dimensional change between the body and the glaze during firing.

iii) During glaze firing at T≤350-380°C, interparticle cohesion in the glaze layer rose with the glaze composition's kaolin content, owing to the rise in compaction as a result of improved packing.

In the 380-800°C temperature range, besides the foregoing factor, another factor related to kaolin dehydroxylation was also active, whose nature still remains to be determined, which extraordinarily enhanced glaze layer cohesion.

As a result, at kaolin contents exceeding 8 wt%, cracks were no longer found in the glaze layer at the standard firing temperature for glazed ceramic wall tile (1100-1120°C).

iv) The whiteness index of the resulting glazes remained virtually steady for kaolin contents below 6 wt% in the glaze blend. At higher kaolin contents, whiteness started dropping noticeably.

v) Considering the two opposing effects (rise in consolidated glaze layer cohesion and drop in final glaze whiteness) as a result of raising the kaolin content in frit-kaolin blends used for producing white glazes by crystalline-phase devitrification, the kaolin percentage that optimised both effects was concluded to lie between 6 and 8 wt%, which coincides with the empirical values being used in industry,

NOTE: The foregoing conclusions are valid for the frit and kaolin used in this study. However, it is assumed that analogous conclusions with very slight variations can also be established for similar frits.