# **GLAZE-SUPPORT ADHESION FACTORS ON WHICH IT IS DEPENDENT AND ITS INDUSTRIAL CONTROL**

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#### **1. INTRODUCTION**

The lack of adjustment between thermic dilation curves for glazes and supports causes concave or convex curves in fired pieces, and sets up stresses between the glaze and the support. These curves and stresses develop as the piece is cooling in the oven, when the glaze and support are already hard; this is due to both materials undergoing different contractions during this stage. (Fig. 1)

At temperatures higher than Ta, the two components (glaze and support) have the same dimensions, the glaze will tolerate any decrease in size that the support undergoes as it is still in a viscous phase. As the piece cools down, the glaze begins to solidify until the glaze becomes rigid and fixed to the support, at a temperature Ta (effective glaze adhesion temperature). If cooling of the piece continues below this temperature, the glaze and support may experience different contractions which will give rise to stresses between the two materials and to curves in the piece. Thus, during cooling from Ta to T1, the glaze contracts more than the support, this is translated as a concave curve in the piece and puts the glaze under a tensile force from the support. If cooling is continued from T1 to ambient temperature, the support contracts more than the glaze, this gives rise to a convex curve and a compressive force on the glaze which increase progressively.









Although the differential contraction (dC) that the glaze and support experience during cooling in the oven is the origin of curvature and glaze-support stresses, their magnitude depends on, amongst other factors, their moduli of elasticity (ES and EV) and the thickness (es and ev) of both materials. Using Timoshenko's equation for an elastic lamina composed of two different materials, and assuming some simplifications (the intermediate glaze-support reaction zone is not well developed, the glaze and the support are solid, isotropic and homogeneous, etc...), theoretical equations are obtained that relate the curvature of the piece and the stress which the support exerts on the glaze with the properties (1) (2) (3) mentioned above.

The degree of curvature (D) of the centre of a piece of thickness (h) and longitude (L) caused by a difference in contraction between the glaze and the support (dC) is given by the expression:

$$D = \frac{1}{8} \frac{L^2}{h} K_R \Delta C$$
(1)

$$K_{R} = \frac{6 (m + 1)^{2} mn}{m^{4}n^{2} + 4m^{3}n + 6m^{2}n + 4mn + 1}$$
(2)

The parameter KR is an adimensional modulus that takes into account the effect of the ratio of the moduli of elasticity of the glaze and support (n = EV/ES) and the ratio of the thickness (m = ev/es) on curvature. Thus KR will also indicate how m and n influence curvature in the piece, when the dimensions and the glaze-support differential contraction are kept constant (figure 2).

The difficulty in accurately estimating some of the parameters that appear in the above equation is the main cause for not using them to predict either the curvature of the piece or the force that the support exerts on the glaze (from similar equations). We therefore resort to experimental methods such as the optic method, which is only valid for transparent glazes (4) and the Steger method, which is described below.

Traditionally the procedure most commonly used in the ceramic paving and tiling industry is based on the comparison of dilation co-efficients for the glaze and support. This method predicts on many occasions the type of curvature that will appear in the glazed and fired piece or the force that the support exerts on the glaze. However, there are many other cases in which neither the type nor magnitude of curvature (or stress) can be explained using only dilation co-efficients for the two materials.

# 2. OBJECT AND RANGE OF THE REPORT

The objects of the report are as follows:

- i) To determine the influence that the nature of the glaze and support, and process variables, such as porosity of the unfired support, the thickness of the glaze layer and temperature of firing have on the magnitude of curvature in the piece.
- ii) To study the usefulness of the aforementioned theoretical relations in predicting the magnitude and type of curvature of the finished piece as a function of the properties and dimensions of the glaze and support. If the relations are valid, we can systematically analyse the effect of process variables on the glaze support adhesion, determining the relationship that exists between the properties of both materials and the process variables.
- iii) To propose an alternative method to the one which is presently used in the paving and tiling industry for estimating glaze-support adhesion.

# 3. MATERIALS AND EXPERIMENTAL PROCEDURE

#### 3.1 Material used.

The following materials were used in the study: - Glaze V-1; used in the production of single fired vitreous paving. - Glaze V-2; used in the production of single fired vitreous paving. - Glaze V-3; used in the production of single fired ceramic tiling. - Support S-1, used in the production of single fired vitreous paving. Pieces pressed industrially at a humidity of 0.055 kg water/kg dried solid and at pressures of 160 and 260 kg/cm2. - Support S-2; used in the production of single fired ceramic paving. Pieces pressed industrially of 0.055 kg of water/kg of dried solid at a pressure of 260 kg/cm2.

Table I shows the chemical analysis of the materials used and Table II the minerals which compose them.

	V-1	<b>V-2</b>	V-3	S-1	S-2
SiO2	48'50	37'70	58'70	62'67	55'65
Al2O3	8'20	6'20	5'93	17'02	15'50
B2O3	0'89	4'05	2'84	-	-
Fe2O3	0'24	0'10	0'11	6'50	5'30
CaO	6'42	3'91	13'66	1'54	7'20
MgO	1'52	0'53	0'15	1'10	1'60
Na2O	0'99	2'26	0'40	0'44	0'40
K2O	1'42	1'62	2'62	3'10	3'19
TiO2	0'08	0'21	0'06	0'79	0'70
ZrO2	23'85	13'30	0'21	-	-
MnO2	-	<b>-</b> ·	-	0'24	0'03
BaO	1'53	14'83	5'44	-	-
Li2O	<0'01	<0'01	0'01	-	-
PbO	0'48	4'59	0'01	-	-
ZnO	3'71	9'05	8'64	o -	-
Pcc	1'46	0'97	0'42	6'40	10'20
	99'29	99'32	<b>99'2</b> 0	99'80	<b>99'7</b> 0

#### **TABLE 1. CHEMICAL ANALYSIS OF MATERIALS USED**

# TABLE II. MINERALS IN MATERIALS USED

	<b>V-1</b>	V-2	V-3	<b>S-1</b>	S-2
Kaolinite	-	-	-	x	x
Illite	-	-	-	x	x
Quartz	x	-	-	XX	XX
Feldspar	XX	-	•	-	-
Zr Silicate	XX	XX	-	-	-
Dolomite	x	-	-	-	-
Frit	XXX	XXX	XXX	-	-
Calcite	-	-	-	-	x

# **3.2 Experimental Procedure**

# 3.2.1 Application of glaze and firing

The compositions of glazes V-1 and V-2 were prepared by damp industrial milling to a percentage residue of 2-3% on a 40 micra screen. The composition of glaze V-3 was prepared from a single fired porous frit, adding 5% of kaolin, 0.3% CMC and 0.2% deflocculant, then by damp grinding with an aluminium ball mill of 500cm3 capacity to a 2% residue in weight on a 40 micra screen. The prepared slips, with a density of 1.65g/cm3, were applied to supports 1 and 2 (only glazing the centre), using a spray gun at an air pressure of 5kg/cm2. The quantity of glaze applied to each piece was 0.094 gr/ cm2.

All the firings were done in an electric laboratory oven with a rapid cycle, controlled temperature and low thermic inertia, obtaining a good uniformity of temperature throughout the chamber. The maximum temperatures tested were 1000, 1050, and 1100°C. Samples were also prepared with glaze V-3 and the biscuited support S-2 at 1130°C.

#### **3.2.2 Dilatometric Analysis**

The thermic expansion curves were obtained from an absolute dilatometry. The support samples were prepared from cutting an industrial piece (or laboratory piece) to 30 x 4 x 4 mm3.

The procedure used to prepare the glazed samples involved the calcination of the samples in a crucible, followed by a firing cycle similar to industrial cycles. Afterwards the glaze was damp ground in a ball mill to a residue of 2-3% on a 40 micra screen, the resulting slip was dried by infra-red lamps. The resulting powder was moistened and pressed to give pieces of the aforementioned dimensions. The sample obtained was fired at 30oC above the melting point of the glaze and subsequently cooled, following an analogous industrial cycle. Finally, the ends of the piece were polished with emery, until the planes were parallel and even. Rate of heating in the dilatometric oven was 5°C/min.

# 3.2.3 Determination of the moduli of elasticity of the fired support.

The moduli of elasticity were calculated by continuously measuring the deformation that the 80 x 40 x 8 mm3 rectangular samples, supported at two points, underwent when a flexible load was applied. (5)

# 3.2.4 Determination of the development of curvature in the glazed and fired piece with temperature (STEGER METHOD).

This method assumes that the variation in curvature that the glazed and fired piece undergoes when it is reheated to the effective adhesion temperature (Ta) of the glaze, corresponds to the variation the piece experienced during firing from Ta to ambient temperature.



Figure 3. Diagram of apparatus.

The samples used in the test were prepared from industrially pressed pieces (biscuited and crude) that were only glazed in the centre (an 8cm band). These pieces, once fired following an analogous cycle to that used in industry, were cut to suitable dimensions ( $260 \times 15 \times 6mm$  approx.). The rate of heating in the test was 5C/min. As the curvature developed in the piece, during heating on the equipment, is registered at the free end of the sample (4 in fig. 3), by measuring its displacement we can attempt to relate the curvature the piece undergoes, as a result of a lack of adhesion between the glaze and support, to the properties of both materials and with the thickness of the glaze layer, using the expression:

 $D = AK_R dC$ 

In this equation, A depends on the dimensions of the sample, the width of the glazed band and the apparatus used. All these factors were kept constant in the experiments performed in the study.

#### 4. RESULTS AND DISCUSSION

4.1 Influence of process variables on the glaze-support adhesion. Relationship between curvature and some of the factors on which it is dependent

#### 4.1.1. Influence of the thickness of glaze layer

To determine the influence of this variable on the curvature of the fired piece, a set of experiments altering glaze layer thickness and maintaining the remaining factors constant was performed.

In these experiments glaze V-3 was applied to support S-2, which was fired beforehand at 1130°C. Once the pieces were glazed, they were fired at a constant temperature of 1100°C. In this way the reaction zone generated between the glaze and support is considerably more reduced than the zone which would have been produced if the glaze and support had been fired at the same temperature. The moduli of elasticity of the glaze and support were also maintained constant in this case.

Figure 4 shows the variation in the curvature of the piece with temperature for different glaze thicknesses. As was expected, the magnitude of curvature increased considerably as the glaze thickness increased.



Fig. 4.- Variation of curvature in the piece (D) with temperature for different glaze thicknesses.



Fig. 5.- Variation of curvature in the piece (d) with the product KR. dC

With a view to proving the validity of equation - 3- for estimating the magnitude of curvature at ambient temperature, fig. 5 shows the values of curvature of the piece, experimentally obtained, plotted against the corresponding values of KR. dC.

The values of dC was obtained from superimposing one of the expansion curves for the glaze and support on the other (fig. 4). The value n = EV/ES needed to calculate KR (eq. 2) was obtained from the modulus of elasticity of the support, determined experimentally, and the modulus of elasticity of the glaze, determined theoretically (6). As can be seen, the experimental results correspond well to the straight line predicted by equation 3.

# 4.1.2 Influence of firing temperature and the nature of glaze and support

Altering the firing temperature of the piece can, in principle, alter the thermic expansion curves and moduli of elasticity of both materials. Also, as the firing temperature increases, the thickness of the zone of reaction between the glaze and support increases. All these factors can affect, to a greater or lesser extent, the curvature of the resulting piece and the stress which is exerted on the glaze by the support. To try to individualize the effect of the firing temperature on each one of the aforementioned factors, a set of experiments were performed altering the process conditions (single and double firing, temperature of glaze and support), and the nature of the glaze and support. In all these experiments the thickness of the glaze layer and the pressing conditions for the pieces were maintained constant, using similar values to those used industrially.

# 4.1.2.1 Study of a tiling support and glaze

#### i) Rapid double-firing experiments

In these tests the firing temperature of the support S-2 was maintained constant at 1130°C.

The firing temperature of the V-3 glaze applied was 1000, 1050 and 1100°C. As the firing temperature of the support (1130°C) is above the firing temperature of the glaze, the modulus of elasticity and the thermic expansion curve of the fired piece can be considered constant in all the experiments. Consequently, these experiments should show the effect of firing temperature on

curvature, almost exclusively due to the variation of the modulus of elasticity and of the thermic expansion curve of the fired glaze.

Figure 6 shows the thermic expansion curves for glaze V-3, obtained from the samples fired at 1000 and 1100oC. The curve corresponding to 1050oC is omitted to simplify the graph, since it falls between the other two. A small increase in thermic dilation is noticed with the increase of firing temperature, probably due to greater sintering in the glaze. Figure 7 shows the variation of curvature with temperature in the fired piece and the variation in differential contraction between the glaze and support (dC), for different firing temperatures tested.

Examining this, it is seen that the curvature of the piece at ambient temperature is convex and decreases as the firing temperature of the piece increases. If the two pieces are compared, a strong similarity can be seen between them; at low temperatures there is a parallel increase in curvature and dC, as the glaze firing temperature decreases.



Figure 6. - The thermic expansion curves of the glaze



Figure 7. - Variation of curvature in the piece and of AC with temperature, for different firing temperatures.

If the module of elasticity of the glaze is assumed not to vary -or vary very little- with firing temperature, the value of KR (equation -2-), will remain practically constant, since the thickness of the glaze layer can only be altered very slightly. Figure 6. Thermic Expansion curves of glaze V-3. As a result the value of n for the calculation of KR will be the same as in the previous section.

Consequently, if this hypothesis is correct, a straight line passing through the origin should be obtained by plotting the experimental values of curvature against the calculated values of KR. dC (figure 8). It can be seen that the results correspond quite well to the predicted straight line, which verifies the validity of the model and the simplifications used. In this case, the decrease that the curvature of the piece, at ambient temperature, undergoes when the temperature is increased again to firing temperature is due to the reduction of differential contraction (dC).

#### ii) Rapid single firing experiments

Glaze V-3 and support S-2 were simultaneously fired at temperatures of 1000, 1050 and 1100°C. In these experiments the dilation co-efficients and the moduli of elasticity of both materials can, in principle, vary, when the firing temperature is altered.



Figure 8 - Variation of curvature in the piece (D) with the product KR . dC.



Figure 9. - Thermic expansion curves of support S-2 and variation of dilation co-efficients with temperature.

Figure 9 shows the thermic expansion curves for the fired support S-2 at different temperatures. The variation of the dilation co-efficient with temperature is also included on this graph. An increase in the thermic expansion of the curve with firing temperature is seen up to temperatures around 1050°C. This is due to the progressive increase of sintering in the support and to the formation of silicates and calcium silicoaluminates (anortite, gelenite,...) with high dilation co-efficients. At higher temperatures, thermic expansion decreases as this operation variable increases, due to the progressive dissolution of quartz.

The variation that the modulus of elasticity of the support (ES) undergoes with firing temperature, is given in Table III. In the same table, values for n = EV/ES needed to calculate the curvature of the piece are included. To calculate n, the module of elasticity of the glaze was estimated theoretically and it was assumed that this didn't vary with firing temperature. As can be seen, the modulus of elasticity of the support increases with its firing temperature due to progressive sintering.

Variation of curvature in the fired piece with temperature and variation of dC with the same variable are shown in figure 10, for the different firing temperatures test



Figure 10. - Variation of curvature in the piece (D) and of dC with temperature, for different firing temperatures.





#### TABLE III

Firing Temp. (oC)	Es*10-5(kg/cm2)	n
1000	1.44	5.3
1050	1.55	4.9
1100	1.85	4.1

Comparing the graphs in figure 10, it is seen that, as in the previous section, they are very similar to each other, with a parallel, at ambient temperature, between the values of curvature of the pieces and their corresponding dC values.

If the calculated values of n (Table III) are correct and if the effect of the glaze-support reaction zone is negligible, the experimental results should correlate to equation 3. So, when the experimentally obtained values of curvature are plotted against the corresponding calculated values of KR. dC, the result should be straight lines that pass through the origin (figure 11). Although there is a certain dispersion of points, basically due to experimental error, the results correspond well to a straight line. In this case, the decrease that the curvature of the piece, at room temperature, experiences when the temperature is increased again to firing temperature is due to an increase in the modulus of elasticity of the support (decrease in KR) and a reduction in dC.

#### 4.1.2.2 - Study of a support and two glazes for paving

To study the influence that the nature of the glaze exerts on curvature in singled fired paving pieces, two very different glazes were chosen: one composed of a frit and zirconium silicate (V-2) and the other formulated with a lesser proportion of frit and different additives (V-1). The co-efficient of dilation and the modulus of elasticity of the first glaze (V-2) will probably vary very little with firing temperature, as a result the study of curvature will be very similar to that in section 4.3.2.1. On the other hand, the significant physical and chemical changes that take place during the firing of V-1 will probably be translated as important alterations in the modulus of elasticity and dilation co-efficient of the glaze when the firing temperature is altered; this will complicate the interpretation of curvature.

Figure 12 shows thermic expansion curves and dilation co- efficients for support S-1 fired at different temperatures. It can be seen that the thermic expansion curve of the fired support increases with firing temperature until 1100°C. This is probably due to an increase in the vitreous phase, with a high alkaline content and a reduction in the porosity of the piece. Above this firing temperature, thermic expansion and dilation co-efficients () increase, due to the progressive dissolution of quartz in the vitreous phase. This interpretation agrees with the marked decrease in the co-efficient of dilation at 573°C, that the piece undergoes passing from 1100 to 1150°C.



Figure 12. - Thermic expansion curves for support S-1 and variation of the co-efficients of dilation with temperature..





The variation that the module of elasticity of the support S-1 (ES) undergoes with firing temperature is given in table IV. It is seen that when firing temperature increases the module of elasticity increases, due to a progressive decrease in the porosity () of the piece.

#### **TABLE IV**

Firing Temp	E_*10 <sup>-5</sup>	е
oC	(kg/cm2)	%
1000	1.54	25.2
1050	2.37	20.9
1100	3.22	15.7

## i) Glaze V-2

Figure 13 shows thermic expansion curves for the fired glaze at 1000 and 1100oC. As can be seen, the expansion curves for temperatures below melting point (700oC) are very similar.

Figure 14 shows, for each temperature tested, the variation of curvature in the piece and of dC with temperature. Examining both graphs, it is seen that, contrary to expectation, the curvature of the piece, at ambient temperature, decreases, while the difference in contraction between the glaze and support (dC) increases. These results show, as indicated previously, that in some cases the difference in thermic expansion between the glaze and support is not enough to estimate the curvature of the fired piece.



Figure 14 - Variation of curvature of the piece (D) and dC with temperature, for different firing temperatures.



Figure 15 - Variation of curvature of the piece (D) with  $K\!R$  .  $d\!C.$ 

With a view to checking the validity of equation -3- for interpreting these results, the values of n = EV/ES were first calculated from the values of Es in table IV and from a theoretically estimated values of EV for each firing temperature. Afterwards, as in previous cases, the experimental values of curvature were plotted against the corresponding values of KR. dC (figure 15). As can be seen, the results correspond well to a straight line, which verifies the validity of the equation and the hypotheses assumed previously. In this case, the decrease that the curvature of the piece, at ambient temperature, undergoes when the temperature is increased again to firing temperature is due to an increase in the module of elasticity of the fired piece.

#### ii) Glaze V - 1

As i have already mentioned, this glaze, as different from the others, sufferes big transformations during firing which must result in considerable modifications their own propieties.

In table VI, you can see the evolution of the crystalline phases present at the glaze with its firing temperature (obtained through diffraction of x rays). You can also see the apparent density of the glaze for each firing temperature tested.

#### TABLE VI

#### **INTENSITY OF X-RAY PEAKS Firing**

Apparent Temp (℃)	quartz	zircon	dolomite	feldspar	diopside	Density gr/cm <sup>3</sup>
Unfired	25	70	10	15	-	-
1000	17	70	_	15	5	2.24
1050	15	70	_		5	2.71
1100	10	65	_		5	2.86

A large variation in the content of the phases present and a marked decrease in the glaze's porosity are noted on increasing firing temperature.

Obviously the thermic expansion curves for the glaze are also greatly affected by alteration in firing temperature (figure 16). Indeed, as the firing temperature increases the thermic expansion of the glaze progressively decreases due to the progressive dissolution of the crystalline phases present. It can also be seen that for low firing temperatures(1000 and 1050°C) the glaze starts to sinter at high temperatures (900-1000°C), which indicates a low proportion of vitreous phase in the glaze.

Although experimental values for the modulus of elasticity (EV) are not available for this glaze fired at different temperatures, it can be assumed that the modulus will increase considerably as firing temperature increases, due to the marked decrease in porosity.

Figure 17 shows the variation of curvature with temperature, experimentally measured, and the variation of dC obtained by superimposing one of the expansion curves for the glaze and support on the other. At ambient temperature, an increase in the values of curvature and dC are noted as firing temperature increases. However, the considerable increase of curvature in the fired piece between 1000 to 1050oC, does not correspond to a parallel increase in dC (figure 18). This is probably due to the module of elasticity of the glaze, fired at various temperatures, being considerably lower than that for higher firing temperatures.



Figure 16 - Thermic expansion curves for glaze V-1.



Figure 17 - Variation of curvature (D) in the piece with temperature, for different firing temperatures.

In this case, given the low fusibility of this glaze, the increase that its modulus of elasticity (EV) undergoes is probably greater than the corresponding value for the support. As a result, not knowing the relationship of Ev with temperature, it is neither possible to calculate KR nor apply equation -3-

#### 4.1.4 Influence of porosity of unfired support.

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To study the influence that the porosity of the unfired piece has on the curvature of the fired piece, a set of experiments were performed altering the pressing pressure of s-1. Glaze V-2 was applied to the pieces, which were subsequently fired and tested in the same way as in section 4.1.2.i.

In figure 19 the corresponding thermic expansion curves for the samples pressed at two different pressures and fired at 1000 and 1100°C are shown. As can be seen, the effect of pressure on the thermic expansion curves is very small at the lowest firing temperature and negligible at 1100°C.



Figure 18.- Variation of temperature of the piece (D) with KR. dC.



Figure 19.- Thermic expansion curves for support S-1.

The influence of the porosity of the unfired piece on the module of elasticity (ES) and on the porosity of the fired piece () is shown in table VII.

# TABLE VII

Firing temp (oC)	Pressing pressure (kg/cm2)	Es*105 (kg/cm2)	e (%)
1000	160	1.35	26.9
1000	260	1.55	25.2
1050	160	2.05	22.3
1050	260	2.40	20.9
1100	160	3.00	16.9
1100	260	3.25	15.7

It can be seen that increasing the pressing pressure and the firing temperature reduces the porosity of the fired piece, which is translated as an increase in the modulus of elasticity.

Figure 20 shows values of curvature at ambient temperature for the fired piece at various firing temperatures and for the two test pressures. It is seen that for all firing temperatures tested, the fired piece pressed at a higher pressure has a lesser curvature; this is due to the fact that its modulus of elasticity is higher.



Figure 20.-Variation of curvature of the piece (D) with firing temperature and pressing pressure.



Figure 21.- Variation of the curvature of the piece (D) with KR. dC.

With a view to checking the validity of equation -3- for interpreting the variation that the curvature of the fired piece undergoes when the modulus of elasticity of the support is altered by altering the compactness of the unfired support and/or firing temperature, the values of curvature experimentally obtained are plotted against the corresponding values of KR.dC in figure 21. As was expected, the results correspond well to a straight line.

#### 4.2 Verification of equations used

When all values of curvature (D) obtained experimentally were plotted against the corresponding values of KR. dC, altering operation variables and the nature of support and glaze, a straight line was obtained.

These results confirm the validity of the proposed equations and the hypotheses used to predict the curvature of the glazed and fired piece due to glaze-support adhesion.

# 4.3 Recommended experimental procedure for estimating glaze-support adhesion.

The Steger method (described in section 3.2.4.), is the most suitable procedure for experimentally determining the curvature of the glazed piece (directly related to the force which the support exerts on the glaze). Also, due to the fact that the validity of the equations relating the curvature of the glazed piece to some of the factors on which it is dependent has been proven, an appropriate estimation for the glaze-support adhesion can be obtained from the thermic expansion curves, the moduli of elasticity and the thicknesses of the two components.





It is essential, if the estimation is to be correct, that the samples used for determining thermic expansion curves for the glaze and support are produced using a similar procedure to that used in industry. In this way, dC, the most influential factor for determining magnitude and type of curvature (and tension), can be easily obtained by superimposing one of the thermic expansion curves of the two materials at Ta (Ta = (TT=TR)/2) on the other.

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