STUDY OF CALCITE DECOMPOSITION DURING WALL TILE FIRING

A. Escardino, J. García-Ten, M. Soriano

Instituto de Tecnología Cerámica (ITC)
Asociación de Investigación de las Industrias Cerámicas
Universitat Jaume I. Castellón. Spain

ABSTRACT

During the firing stage, in the manufacture of white-firing wall tiles, the decomposition of the calcite particles contained initially in the body needs to be completed before the glaze fuses and seals the body. The assessment of the time needed for this reaction to end is generally based on purely empirical information.

This paper sets out the results obtained when applying, under the conditions in which the industrial firing cycles in this manufacturing process occur, the mathematical expressions representing the variation of calcite particle degree of conversion as a function of time and operating temperature, obtained by studying the kinetics of this decomposition process under isothermal conditions.

The method used is based on breaking down the firing cycle into several stretches of constant-rate heating, applying to each stretch the expressions indicated, adapted to the development of the thermal cycles under constant heating conditions.

Based on the kinetic model indicated, the methodology used has allowed quantifying the influence of the variables studied (dry bulk density, piece thickness, initial calcite content and firing cycle) on the time required for the calcite particles contained initially in the green wall tile body to decompose completely during firing.

1. INTRODUCTION

Wall tiles are glazed ceramic tiles typically used for cladding internal walls[1]. The bodies of these tiles are characterised by high porosity, low expansion by moisture adsorption, and high dimensional stability. These properties are acquired through the formation of certain crystalline phases during the firing stage, such as calcium silicates and aluminosilicates (gehlenite, anorthite, wollastonite), as a result of the reaction between decomposition products of the clays and calcium oxide, introduced normally as calcite[2].

In white-firing wall tiles, the calcite particles contained in the initial body composition decompose during firing at temperatures above 700°C[3], providing the necessary CaO to form the above-mentioned crystalline phases and releasing CO_2.

If the calcite particles are small and the firing cycle is appropriately designed, decomposition is completed at temperatures below the glaze melting temperature. When this is not the case, the CO_2 that is released in the body can be trapped in the molten glaze layer, forming small bubbles which may reach the glaze surface and produce defects such as *dimples* or *pinholes*[4].

The calcite particle decomposition process needs to be completed, therefore, before the glaze fuses and seals the body during wall tile firing.

The study of the thermal decomposition, at constant temperature, of the calcite particles contained in the white-firing wall tile bodies[5] has allowed deducing a mathematical expression, based on the kinetic unreacted core model[6], which relates calcite degree of conversion to the main operating variables (temperature, porosity, calcite content and body thickness). The calcite particles used and the composition of the body were representative of those used in industrial practice in the manufacture of this type of ceramic tile. The differential equation obtained has enabled reproducing the experimental results with satisfactory accuracy.

The present paper studies the application of this equation to non-isothermal thermal cycles, analogous to the firing cycles used for the manufacture of wall tiles in industry. The methodology used allows quantifying the influence of some of the most important operating variables on the degree of advance of the calcite particle decomposition process, in the course of these firing cycles.

2. KINETIC MODEL

2.1. FIRING UNDER ISOTHERMAL CONDITIONS

In the study indicated it was observed that, at low degrees of calcite conversion, the velocity at which the decomposition process unfolded was controlled by the chemical decomposition reaction rate. However, at the highest degrees of conversion, the overall process rate was concurrently influenced by the chemical reaction step and CO_2 diffusion through the piece.

The differential equations proposed for each of the two ranges of degree of conversion were:

$$\frac{dX_L}{dt} = \left(\frac{1}{L \cdot c_B^{L0}}\right) \cdot \left[\frac{K_C \cdot c_B^{L0\,1/3} \cdot (1 - X_L)^{1/3} - c_Q^{G}}{\dfrac{K_C \cdot S_S}{k \cdot S^L_i}}\right] \qquad (1)$$

applicable to the period during which the chemical decomposition reaction is step-controlling and

$$\frac{dX_L}{dt} = \left(\frac{1}{L \cdot c_B^{L0}}\right) \cdot \left[\frac{K_C \cdot c_B^{L0\,1/3} \cdot (1 - X_L)^{1/3} - c_Q^{G}}{\dfrac{K_C \cdot S_S}{k \cdot S^L_i} + \dfrac{L \cdot X_L}{4 \cdot D^L}}\right] \qquad (2)$$

applicable to the second period during which the chemical decomposition reaction and carbon dioxide diffusion both influence the overall process rate.

In these equations:

X_L: degree of conversion of the $CaCO_3$ contained in the piece.

c_B^{L0}: initial molar concentration of calcite in the body test specimens (kmol of calcite/m^3).

c^G_Q: molar concentration of CO_2 in the gas phase (kmol/m^3).

D^L: effective diffusivity of carbon dioxide through the porous structure of the test specimens (m^2/min).

K_C: equilibrium constant of the calcium carbonate chemical decomposition reaction (kmol/m^3).

k: velocity constant of the direct decomposition reaction (kmol$^{2/3}$/(m·min)).

L: thickness of the test specimens (m).

S_S: cross-section area of the test specimen (m^2).

S^L_i: reaction interface area (m^2).

t : time elapsed from the start of the decomposition process (min).

In these equations, variables K_C, k and D^L depend exponentially on operation temperature (K).

The calcite degree of conversion in the piece at which the diffusion step began to be of influence, a circumstance conditioning the equation to be used, depended on the temperature at which heat treatment occurred and on the characteristics of the piece (calcite content, thickness, etc.).

2.2. FIRING UNDER CONSTANT-RATE HEATING CONDITIONS

When heat treatment takes place under non-isothermal conditions, at constant-rate heating, this variable (α) is defined from the expression:

$$\alpha = \frac{dT}{dt} \tag{3}$$

Multiplying the first member of Equations (1) and (2) by *dt/dT* and the second by α^{-1}, in accordance with the inverse of Equation (3), gives Equations (4) and (5).

$$\frac{dX_L}{dT} = \left(\frac{1}{L \cdot c_B^{L0}}\right) \cdot \left[\frac{K_C \cdot c_B^{L0^{1/3}} \cdot (1 - X_L)^{1/3} - c_Q^G}{\dfrac{K_C \cdot S_S}{k \cdot S^L{}_i}}\right] \cdot \alpha^{-1} \tag{4}$$

$$\frac{dX_L}{dT} = \left(\frac{1}{L \cdot c_B{}^{L0}}\right) \cdot \left[\frac{K_C \cdot c_B{}^{L0^{1/3}} \cdot (1 - X_L)^{1/3} - c_Q^G}{\dfrac{K_C \cdot S_S}{k \cdot S^L{}_i} + \dfrac{L \cdot X_L}{4 \cdot D^L}}\right] \cdot \alpha^{-1} \tag{5}$$

The integration of either of these two equations by a numerical method enables establishing the evolution of the degree of conversion with temperature when heat treatment takes place at a constant heating rate.

In order to integrate these it is necessary to know the dependence of variables K_C, $(k \cdot S_i^L)$ and D^L on temperature and the value of c_Q^G. These correlations, available in the study mentioned above[5], need to be substituted in Equations (4) and (5) before integrating them sequentially. Equation (4) needs to be integrated from the initial conditions of the firing cycle (T_0, $X_{L0}=0$) up to the value of X_L at which the curve resulting from the plot of the corresponding pairs of values X_L-T from the integration, on rectangular coordinates, cuts the straight line representing the pairs of values X_L-T (obtained in the study mentioned[5]), for which the equation needs to be changed, which must be plotted in the same graph. The coordinates of the intersection point are the initial conditions from which Equation (5) will be integrated, until a calcite degree of conversion equal to unity is reached.

From the pairs of values X_L-T resulting from the integration, the respective values of *t* can be calculated (time of heat treatment at constant-rate heating). For this, Equation (3) needs to be integrated for the boundary conditions t_0,T_0, which yields:

$$t = t_0 + \frac{T - T_0}{\alpha} \tag{6}$$

where:

T_0: initial temperature of the heat-treatment period at heating rate α (K).

t_0: value of the time at which this treatment commences (min).

2.3. APPLICATION OF THE MODEL TO AN INDUSTRIAL WALL TILE FIRING CYCLE

The thermal cycles typically used in firing wall tiles in industrial practice can be broken down into several stretches of constant-rate heating. This enables applying the equations proposed in section 2.2 for calculating the evolution of the calcite degree of conversion throughout each stretch of the industrial firing cycle breakdown.

For this, the operation described in section 2.2 is performed in each constant-rate heating stretch (α_i). The first stretch is integrated for the initial conditions (T_0, $X_{L0} = 0$), with the heating rate α_1, and each of the remaining stretches for the respective initial conditions (T_{0i}, X_{L0i}), which coincide with the corresponding X_L and T values at the end of the previous stretch, substituting in Equations (4) or (5) the value of α_i corresponding to the stretch considered, switching from one equation to another when the curve representing the sequential integration process cuts the straight line representing the change in mechanism.

The corresponding values of reaction time can be calculated, for each stretch, from the equation:

$$t = t_{0i} + \frac{T - T_{0i}}{\alpha_i} \tag{7}$$

obtained from applying Equation (6) to each constant-rate heating stretch (α_i), where t_{0i} is the time elapsing from the beginning of the thermal cycle that corresponds to the beginning of each constant-rate heating stretch α_i and which coincides with the time at which the foregoing stretch ends.

3. INFLUENCE OF PROCESS VARIABLES

In the following, Equations (4) and (5) will be applied using the procedure described in section 2.3 to quantify the influence of the major process variables on the time needed to complete the decomposition of the calcite particles initially contained in white-firing wall tile bodies.

In sections 3.1 to 3.4 this study will be conducted in relation to the same firing cycle, which is representative of most of the cycles used in wall tile manufacture. The heating stage of the selected cycle consists of two parts, as shown in Figure 1 and detailed in Table 1. The first is characterised by a high heating rate (50 °C/min), and ends at 880°C (1153K). The second, with a low heating rate (7 °C/min), during which most of the calcite decomposition process takes place, usually ends at 950°C (1223K), the temperature at which the glaze layer usually seals. When this stretch ends, calcite decomposition also needs to have ended, to avoid the appearance of the surface defects mentioned before. A third stretch then follows with a high heating rate up to the peak firing temperature.

STRETCH	T_0 (K) – (°C)	T_f (K) – (°C)	α (K/min)
1	1013 - 740	1153 - 880	48.5
2	1153 - 800	variable	6.9

Table 1. Initial temperature (T_0) and final temperature (T_f) of each stretch and heating rate.

Since the decomposition reaction must end before the third firing cycle stretch begins, only the first two stretches have been considered for the performance of the calculations, extending the second stretch as long as needed for calcite decomposition to be complete. Table 1 details the conditions under which the two stretches considered have developed.

In the performance of the calculations it has been assumed that the temperature of the reaction interface, in the ceramic piece, practically coincides with the temperature of the kiln shown in Figure 1.

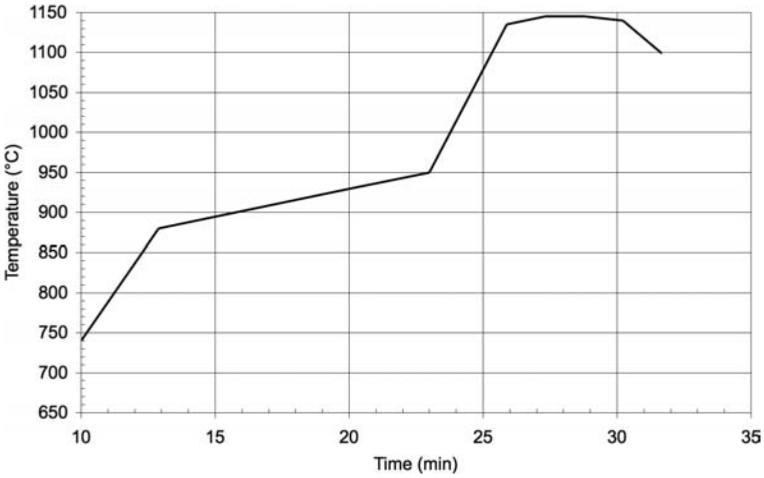

Figure 1. Scheme of the test firing cycle, broken down into constant-rate heating stretches.

3.1. INFLUENCE OF CALCITE CONTENT

The calcium carbonate content usually found in the compositions used in manufacturing white-firing wall tiles is about 13% by weight. For this reason, in this section the evolution of the calcite particle degree of conversion has been studied for contents of this mineral of 11, 13, 15 and 17%, by weight. This characteristic of the piece influences the value of parameter c_B^{L0} of Equations (4) and (5), representing the initial molar concentration of calcite in the piece. In this section the pieces are assumed to have the following characteristics:

Dry bulk density: 1950 kg/m^3
Thickness of the body: 0.007 m

Figure 2 displays the values of the conversion degree versus temperature, expressed in Kelvin, for pieces with different calcite contents in the course of the firing cycle depicted in Figure 1. Broken lines representing the pairs of values X_L-T [5] are also plotted, for which the equation must be changed in the integration. These lines depend on temperature and initial calcite content in the piece, as shown in Figure 2.

It can be observed in the figure that calcite decomposition begins around 1000K (727ºC) in the first stretch of the firing cycle, at the end of which it reaches a value of X_L around 0.2. The change from the first to the second stretch of the firing cycle is accompanied by a pronounced increase in the slope of curves X_L-T. In this second stretch, the curves representing the evolution of the degree of conversion with temperature tend to cut the straight lines, indicating a change of equation. After this point the slope of the curves decreases, and decomposition ends at temperatures between 1200 and 1220K, depending on the calcite content.

Knowing the values of X_L-T and the heating rate in each stretch (α_i), from Equation (7), we calculated the dwell time of the pieces inside the kiln. Figure 3 plots the evolution of the degree of conversion versus dwell time in the kiln, for each calcite content considered, together with the lines representing the evolution of temperature in the two firing cycle stretches involved.

Table 2 details, together with the initial calcite content in the pieces, the value of c_B^{L0}, the time needed to complete decomposition ($t_{X=1}$) and the temperature at which this ends in the second stretch. It can be observed that for each 2% increase in calcite content, the decomposition period needs to be prolonged by 0.7 minutes, which involves an 8% increase in residence time in the kiln.

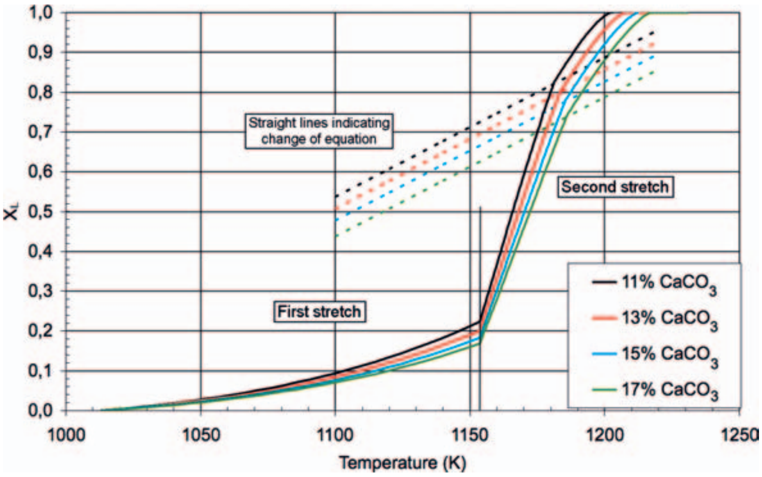

Figure 2. Evolution of degree of conversion with tile temperature throughout the kiln.

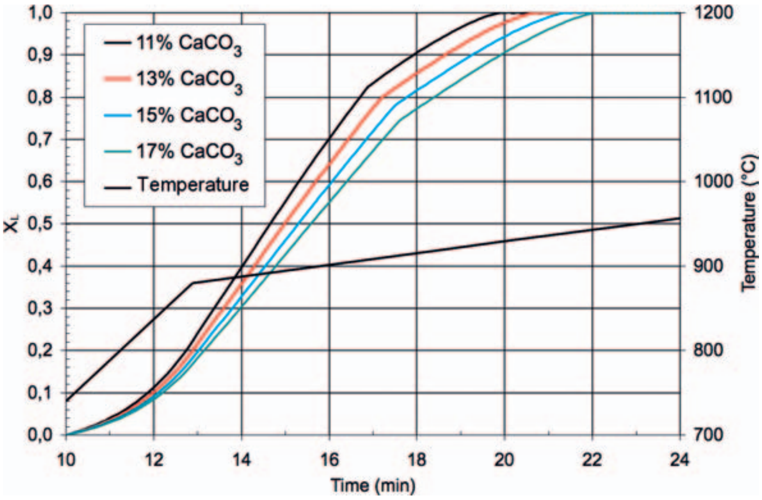

Figure 3. Evolution of degree of conversion with tile dwell time in the kiln.

CALCITE CONTENT (% BY WEIGHT)	c_B^{L0} (kmol $CaCO_3/m^3$)	$t_{X=1}$ (min)	T (K)-(°C)	$\Delta t_{X=1}$ (%)
11.0	2.145	9.9	1203-930	-
13.0	2.535	10.7	1208-935	8.1
15.0	2.925	11.4	1212-939	15.2
17.0	3.315	12.1	1217-944	22.2

Table 2. Time needed for calcite to decompose completely and temperature reached.

Since the evolution of the degree of conversion with temperature, for the variables studied in sections 3.2 to 3.4 follows qualitatively a trajectory similar to that observed in Figure 2, the corresponding graphs will not be shown hereafter, in order not to extend the present paper excessively.

3.2. INFLUENCE OF TILE BULK DENSITY

The bulk density or compactness of the green pieces also influences parameter c_B^{L0} and must affect the value of the effective diffusion coefficient (D^L) of carbon dioxide through the structure of the piece, in Equation (5). In this section the pieces are assumed to have the following characteristics:

Thickness of the body: 0.007 m
Calcite content: 15 % by weight

varying bulk density between 1850 and 2000 kg/m^3

Figure 4 depicts the evolution of the degree of conversion with dwell time in the kiln for pieces with different bulk densities. Although the bulk density values vary appreciably from the point of view of industrial practice, the X_L-T curves for low and medium values of the degree of conversion, where the chemical reaction is the sole controlling step, practically coincide, owing to the scarce variation of the value of c_B^{L0}. However, in the region of high degree-of-conversion values, where the process is also influenced by the rate at which CO_2 transport through the reacted piece layer takes place, the X_L-T curves begin to diverge, and their slope diminishes as dry bulk density increases. This is because the value of the effective diffusion coefficient decreases when the pieces are more compact.

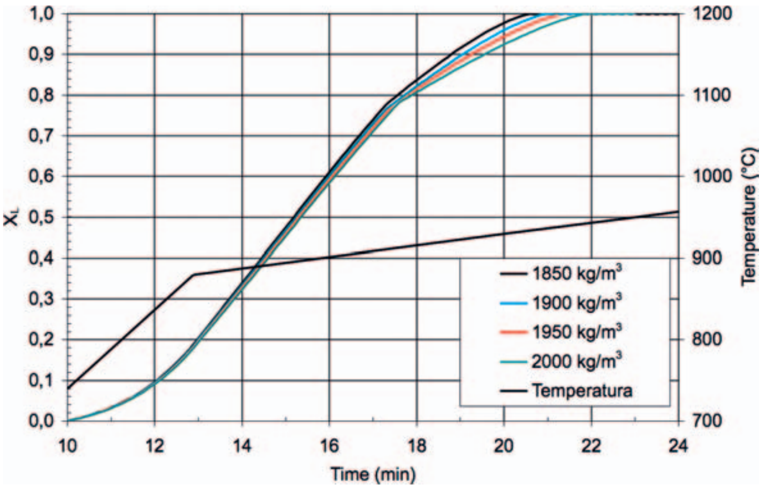

Figure 4. Evolution of degree of conversion with tile dwell time in the kiln.

Table 3 details, for each considered dry bulk density value, the value of parameter c_B^{L0}, the time needed for complete calcite decomposition and the temperature at which this ends in the second firing stretch. It can be observed that for each 0.050 g/cm^3 increase in bulk density, the decomposition period needs to be prolonged by 0.4 minutes, which entails an increase in tile residence time of about 4%, in the studied range of operating conditions.

DRY BULK DENSITY (kg/m³)	c_B^{L0} (kmol $CaCO_3/m^3$)	$t_{X=1}$ (min)	T (K)-(°C)	$\Delta t_{X=1}$ (%)
1850	2.775	10.6	1207-934	
1900	2.850	11.0	1210-937	3.8
1950	2.925	11.4	1212-939	7.5
2000	3.000	11.9	1217-944	12.3

Table 3. Time needed for calcite to decompose completely and temperature reached.

3.3. INFLUENCE OF BODY THICKNESS

Wall tile body thickness (parameter *L* in Equations 4 and 5) varies significantly, depending on tile size. The usual range of values lies between 7 mm for the smallest sizes and 12 mm for the largest sizes. In this section the pieces are assumed to have the following characteristics:

Dry bulk density: 1950 kg/m³
Calcite content: 15 % by weight

The values of the time needed to complete calcite decomposition and the temperature at which this ends in the second stretch for tiles with the thicknesses considered are set out in Table 4. They show that each millimetre increase in thickness requires prolonging the decomposition period for a little over one minute, involving an increase in tile dwell time of about 10% in the studied range of operating conditions.

The influence of tile thickness on the evolution of calcite degree of conversion during tile dwell inside the kiln is shown in Figure 5. It shows that the X_L-T curves diverge, as tile dwell time in the kiln increases: as tile thickness increases, the slope of the curves diminishes, both in the range of X_L values in which the chemical step is controlling, and in that in which the chemical step and the CO_2 transport step concurrently influence the overall process rate.

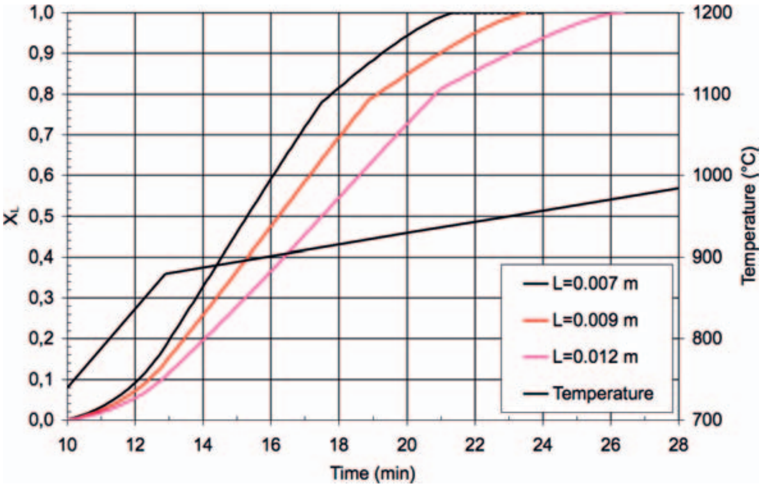

Figure 5. Evolution of degree of conversion with tile dwell time in the kiln.

THICKNESS (m)	$t_{X=1}$ (min)	T (K)-(°C)	$\Delta t_{X=1}$ (%)
0.007	11.4	1212-939	-
0.009	13.5	1227-954	18.4
0.012	16.2	1246-973	42.1

Table 4. Time needed for calcite to decompose completely and temperature reached.

3.4. INFLUENCE OF CO_2 CONCENTRATION IN THE KILN ATMOSPHERE

In this section the influence has been studied of the CO_2 concentration in the kiln atmosphere (c^G_Q) on the rate at which the calcite decomposition process develops, since this reaction is reversible. The CO_2 concentration in the preheating stage of the industrial kilns is relatively low, about 2.5 % in volume. This is why, in this section, three compositions of the gaseous phase have been considered, corresponding to CO_2 concentrations of 2.5, 5 and 10% in volume. In this section the pieces are assumed to have the following characteristics:

Dry bulk density: 1950 kg/m^3
Thickness of the body: 0.007 m.
Calcite content: 15 % by weight.

The results obtained are displayed in Figure 6. It shows that the CO_2 content in the atmosphere influences the X_L-T curves, such that as CO_2 concentration increases the X_L-T curves shift towards the right. Note that this influence is more important in the initial phases of the decomposition process, in which it is exclusively controlled by the rate at which the chemical reaction step unfolds.

Table 5 details the CO_2 concentration in the kiln atmosphere, the time required to complete calcite decomposition and the temperature at which this ends in the second stretch. It can be observed that for each 5% increase in CO_2 concentration, the decomposition period needs to be prolonged by 0.4 minutes, which involves an increase in tile dwell time of 3.5 %, under the studied operating conditions.

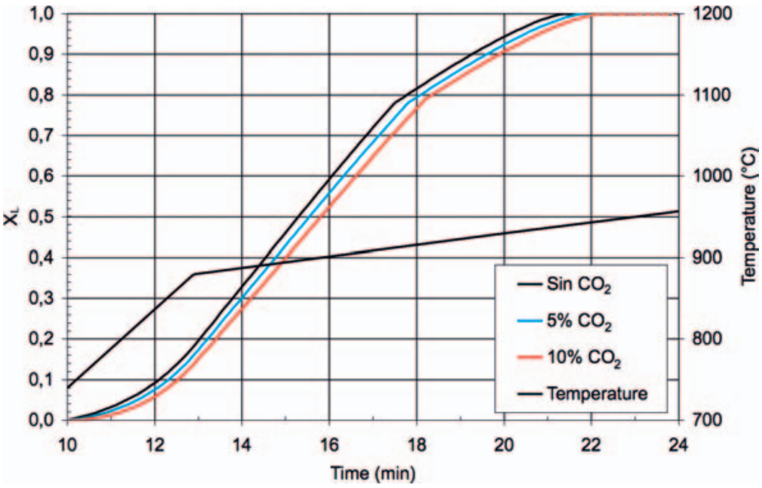

Figure 6. Evolution of degree of conversion with tile dwell time in the kiln.

CO_2 CONCENTRATION (%)	$t_{X=1}$ (min)	T (K)-(°C)	$\Delta t_{X=1}$ (%)
Without CO_2	11.4	1212-939	-
2.5	11.6	1213-940	1.8
5.0	11.8	1215-942	3.5
10.0	12.2	1218-945	7.0

Table 5. Time needed for calcite to decompose completely and temperature reached.

3.5. COMPARISON OF THE RELATIVE INFLUENCE OF EACH STUDIED VARIABLE

With a view to comparing the effect of each studied variable on the time required to complete the decomposition of the calcite particles contained in the body, the relative variation of each variable has been calculated in relation to the standard conditions and the relative variation of the time needed to complete the decomposition, with respect to the time calculated under standard conditions. Figure 7 plots these values, which it has been attempted to visualise by means of the equations given in Table 6. This figure is to be interpreted as follows: in the case of body thickness, an increase of 10% (from 7 mm to 7.7 mm) leads to a 6% increase in the decomposition period (from 11.4 min to 12.1 min).

This figure and table show that the variable that most affects the calcite particle decomposition process is dry bulk density, with a value of the slope of the corresponding straight line of 1.425. The following most important variables are tile thickness and calcite content, with slope values of 0.597 and 0.483, respectively. Finally the process variable that appears of least influence, in the range of concentrations in which the operation is usually conducted, is the CO_2 concentration in the kiln atmosphere, with a much lower value for the slope of the straight line, of 0.017.

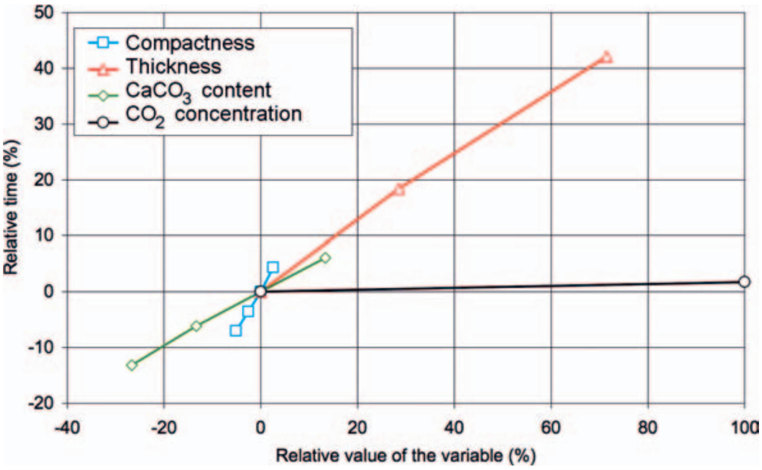

Figure 7. Comparison of the influence of each studied variable.

VARIABLE	EQUATION
Compactness	$Y=1.425 \cdot X$
Thickness	$Y= 0.597 \cdot X$
$CaCO_3$ content	$Y=0.483 \cdot X$
CO_2 concentration	$Y=0.017 \cdot X$

Table 6. Equations of fit of the values plotted in Figure 7.

3.6. INFLUENCE OF THE FIRING CYCLE

In this section the influence has been studied of the firing cycle when the temperature at which the second stretch begins (T_{02}) or the heating rate in this stretch (α_2) is modified. In the former case, a 25°C increase and decrease of this temperature has been considered in regard to the temperature of the reference thermal cycle tested up to this point (STD); in the latter, the heating rate has been halved. These firing cycles, as well as the evolution of the degree of conversion in these cycles, are depicted in Figures 8 and 9. Table 6 details the values of the time required to complete decomposition and the temperature at which this ends in the second firing stretch. In this stretch the tiles are assumed to have the characteristics indicated in section 3.4.

It can be observed that the increase in the temperature at which the second firing stretch begins raises the rate at which calcite decomposition occurs, as a result of the increase in the direct reaction rate constant (*k*). This involves a 14% decrease in the time needed to complete the decomposition, albeit with an increase in the temperature at which the process ends. In contrast, the reduction of the temperature at which the second stretch begins leads to a 17% increase in the time needed to complete the decomposition reaction, which then ends at a lower temperature.

In regard to the influence of the heating rate (STD* cycle), it is observed that when the average temperature of the second stretch is similar, the cycle with the lower rate heating simultaneously reduces the time and end temperature needed for complete decomposition.

In view of these results and, leaving aside other considerations (curvature control, energy consumption, thermal shock, etc.), it may be concluded that to accelerate the calcite decomposition process, the first stretch of the firing cycle should be run at the fastest possible heating rate, until reaching a sufficiently high temperature for the decomposition reaction to take place at great speed. During the second firing stretch it is advisable to operate at a relatively low heating rate, in order not to exceed the glaze sealing temperature before calcite decomposition is completed.

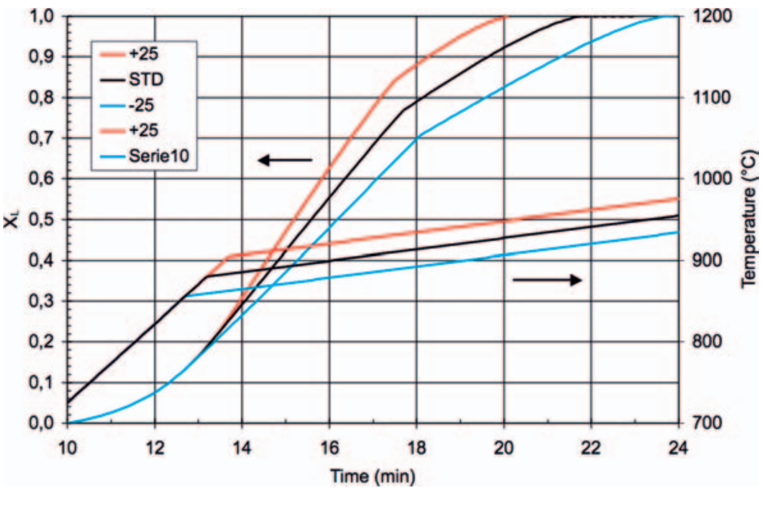

Figure 8. Evolution of degree of conversion with tile dwell time in the kiln.

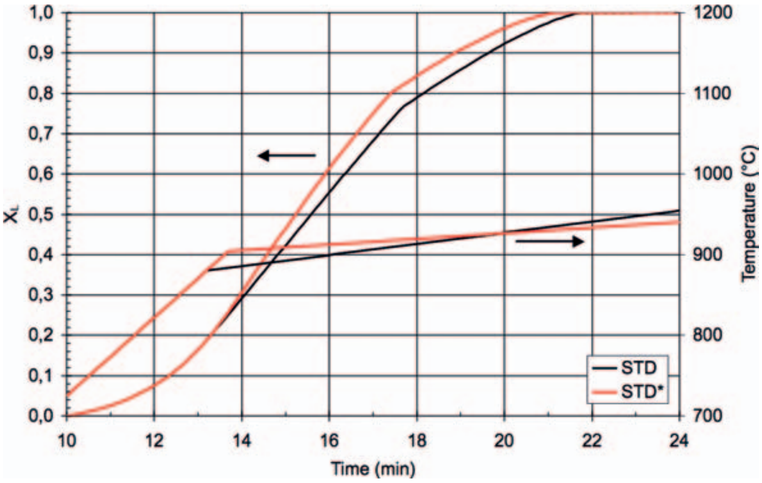

Figure 9. Evolution of degree of conversion with tile dwell time in the kiln.

CYCLE	T_{02} (°C)	α_2 (°C/min)	$t_{X=1}$ (min)	T (K)-(°C)	$\Delta t_{X=1}$ (%)
-25	855	6.9	13.7	1205-932	+17.1
STD	880	6.9	11.7	1212-939	-
+25	905	6.9	10.1	1222-949	-13.7
STD*	905	3.5	11.2	1204-931	-4.5

Table 7. Time needed for calcite to decompose completely and temperature reached.

4. CONCLUSIONS

The most important conclusions to be drawn from the study are as follows:

- The introduction of the concept of heating rate in the kinetic equations that describe the decomposition process of the calcite particles contained in wall tile bodies, under isothermal conditions, enables establishing the evolution of the degree of conversion of this reaction throughout the firing cycles used in industry to process wall tiles.

- By using the methodology proposed it is possible to quantify the effect of the main operating variables on the rate at which the calcite decomposition process takes place and the time needed to complete this. The results obtained practically coincide with those observed empirically in industrial practice.

- The variable that most influences the studied decomposition process appears to be tile compactness, followed by the thickness of the body and the calcite content of the composition used. The carbon dioxide concentration in the kiln atmosphere has little influence on the decomposition process under the usual industrial conditions.

- The proposed methodology enables explaining the way the wall tile preheating period is conducted in industrial firing cycles. It usually consists of two parts: the first has a high heating rate; the second has a high temperature and a low heating rate, and ends at temperatures slightly below the glaze sealing temperature.

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