CARBONATE BREAKDOWN ON FIRING GLAZED WALL TILE. RELATION TO ARISING PINHOLES

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INTRODUCTION

The raw materials mixture used in manufacturing ceramic wall tile body contains calcite, a mineral that provides the calcium oxide needed to produce the crystalline phases in firing, which give such tiles their characteristic properties (high porosity, mechanical strength, low moisture expansion, etc.)[1].

Calcium carbonate breaks down in firing, releasing carbon dioxide according to the following reaction[2]:

$$CaCO_3 \Rightarrow CaO + CO_2 \uparrow$$

When the calcium carbonate particles are small and body permeability sufficiently high, the reaction usual ends at temperatures below glaze sealing temperature. However, as carbonate particle size increases, longer times are required to complete the decomposition. If the firing cycle is not suitably designed, such breakdown can occur at temperatures close to glaze sealing temperature. When this happens, the carbon dioxide that is released remains trapped in the glaze layer as small bubbles. These bubbles can, depending on glaze viscosity, reach the glaze surface and produce a series of defects, among which pinholes particularly stand out[3].

[1]. Sánchez, E.; García, J.; Sanz, V., et al. *Raw materials selection criteria for ceramic floor and wall tile manufacture*. In: Ist World Congress on Ceramic Tile Quality (QUALICER). Castellón, 1990.
[2]. Kingery, W.D.; Bowen, H.K.; Uhlmann, D.R. *Introduction to ceramics*. 2nd ed. New York: John Wiley, 1976.
[3]. Amorós Álbaro, J.L. ; Beltrán Porcar, V. ; Blasco Fuentes, A., et al. *Defectos de fabricación de pavimentos y revestimientos*. Castellón: AICE, 1991.

In this study, carbonate breakdown has been correlated with the appearance of pinholing, and the minimum degree of carbonate breakdown has been determined which needs to be achieved before the glaze seals in order to keep such defects from arising.

EXPERIMENTAL

The calcium carbonate breakdown reaction on firing ceramic tile can be monitored by measuring tile weight loss during heat treatment in a laboratory electric furnace. The resulting measurements allow defining the degree of conversion (X) of the arising decomposition reactions, from the equation:

$$X = \frac{\Delta M}{\Delta M_{\infty}}$$

where DM is mass loss at a given moment, and ΔM_{∞} mass loss at infinite time. Besides carbonate breakdown, the degree-of-conversion concept also includes other transformations such as the physical loss of absorbed water and clay mineral dehydroxylation reactions.

In order to determine the minimum percentage of non-decomposed carbonates that could give rise to pinholing, prism-shaped test specimens were formed by pressing from a typical industrial spray-dried powder used for wall tile bodies. The test specimens were sized 70mm x 50mm and were of varying thickness. Pressing moisture content was 0.055 kg water/kg dry solid, and pressing pressure was 250 kg/cm^2. First, the curves of the degree of conversion versus time were determined for these specimens at 850 and 950 °C. The specimens were subsequently fired at 850 and 950°C with different dwell times in the kiln, followed by fast cooling on withdrawing the specimens from the kiln to freeze the calcium carbonate breakdown reaction and obtain specimens with different calcium carbonate contents. A glaze with a low sealing temperature was then applied to these test specimens, which were subsequently heat treated at 950°C for 6 min, to complete the carbonate decomposition. This second heat treatment had to be short in order to have some non-decomposed calcium carbonate left when the glaze started fusing.

RESULTS

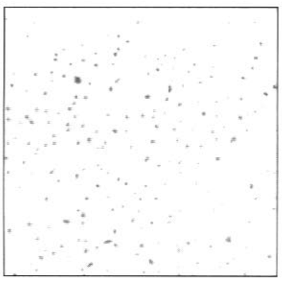
The Table details the required dwell time (t_p) in the kiln for test specimens of a given thickness (e) to reach a specific degree of conversion (X). It can be observed that as heat-treatment temperature rose and test specimen thickness decreased, shorter dwell times (t_p) were required.

The images show the appearance of 7 mm thick test specimens, in which a preliminary heat treatment at 950°C had eliminated 95 to 100% of the carbonates and constituents susceptible of decomposing at lower temperatures. It can be observed that pinholing appeared in every case in which X<1.0. The same result was found for the other tested specimens. The magnitude of the defect therefore depended on the non-reacted calcium carbonate (residual) proportion, which was related to the thickness of the specimen, carbonate particle-size distribution and specimen preliminary heat treatment.

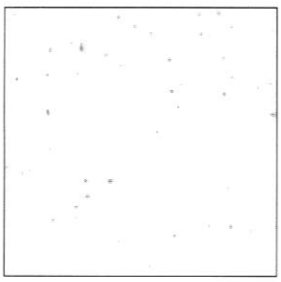
X	e (mm)	T=850 °C	T=950 °C
		t_p (min)	t_p (min)
0.95	5.5	13.54	4.11
0.97		14.77	4.39
0.99		16.31	4.83
0.95	7.0	16.77	5.22
0.97		18.46	5.55
0.99		20.77	6.11
0.95	8.5	20.92	6.14
0.97		22.90	6.56
0.99		25.84	7.44

These results indicate that the appearance of pinholes is due to the presence of even very small amounts of residual carbonates. Thus, to obtain wall tiles free of pinholes, it is essential that all the calcium carbonate particles present should decompose prior to glaze sealing

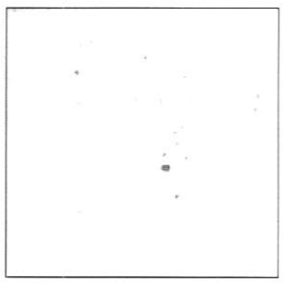
X=0.95



X=0.95



X=0.99



X=1.00