SUPPRESSING BLACK CORING IN SINGLE-FIRE CERAMIC TILES BY CONTROLLING KILN ATMOSPHERE

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Ceramic tiles produced by single firing using ever-faster schedules are more susceptible to the appearance of black core. This defect in the body occurs when not all the oxidisable matter contained in the clays has oxidised. A dark core thus appears in the tile. This impairs quality, and affects dimensional characteristics and porosity. However the oxidation rate can be raised by introducing into the kiln a highly oxidising atmosphere based on oxygen.

To do this an industrial composition was studied, produced for fast single firing in a roller kiln. It was found industrially that the composition exhibited black coring in the form of a dark core when one of the clays in the composition was replaced by another. As the use of this other clay was more feasible economically, it was decided to study the cause of black core formation, and attempt to solve the problem by adjusting the kiln atmosphere.

The samples were characterised by thermodifferential analysis (TDA), thermogravimetric analysis (TGA), X-ray diffraction (XRD), X-ray fluorescence, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and mercury porosimetry. The TDA and TGA run on the sample allowed analysing the temperature ranges and atmospheres in which the main oxidation reactions arose. The results showed that all the mass loss took place in the range 500-900°C. This was therefore to be the temperature interval in which the kiln atmosphere needed to be controlled to suppress black coring.

The phases present in the sample were identified by XRD before and after firing, revealing which phases were responsible for the black core.

Chemical analysis by X-ray fluorescence showed the difference between the two compositions with regard to the iron oxide and organic matter content, which were present in greater proportions in the trial composition.

SEM and EDX indicated the microstructure of the sample affected by the defect. The region containing black core was observed to be more porous.

Heat treatments were run on the basis of these data, involving different atmospheres for eliminating the black core in the trial composition. An electric MAITEC kiln of the closed chamber type (80 x 150 x 240 mm) was used, with controlled atmosphere and temperature, in which test bodies 50x100x10mm of the two compositions being studied were treated, after undergoing industrial pressing and glazing, under various firing conditions. Controlled flows of a mix of oxygen and nitrogen of constant composition were continuously injected into the kiln for each series of experiments. The gas flow rate was controlled by a rotameter.

The test bodies were placed in the kiln, with atmosphere injection via an aluminium tube as shown in the schematic of Figure 1.

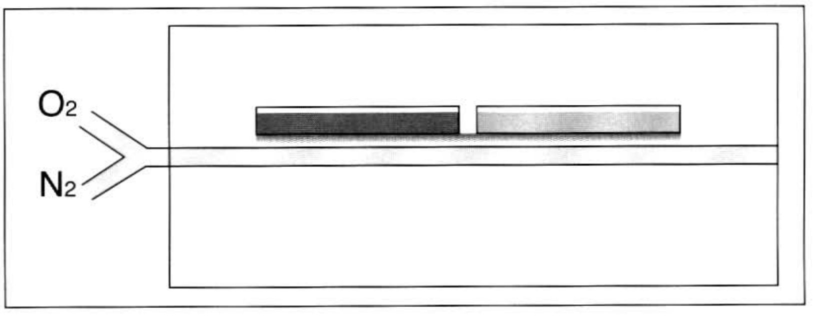

Figure 1. *Experimental set-up of the samples in the kiln.*

It was not possible to totally reproduce the firing conditions found in industry owing to factors such as: kiln volume, number of fired tiles, and mainly the short firing cycle. The results obtained may therefore differ from industrial findings.

Different flows of the N_2-O_2 mix were used to determine the minimum oxygen pressure required for eliminating the defect (see Figure 1).

The results found under the conditions indicated for the trial composition, since the reference composition did not exhibit this defect, can be visually observed in the test bodies or in the plot shown in Figure 2.

The experiment was started as a result of a critical condition in which the region affected by black coring was about 36% of the sample. By adding oxygen, the oxygen pressure can be optimised to wholly suppress black coring, when the oxygen is suitably distributed inside the kiln.

Thus, the total oxygen volume injected into the kiln can be calculated, which corresponds to the exposure time to kiln atmosphere for a given volume of fired samples.

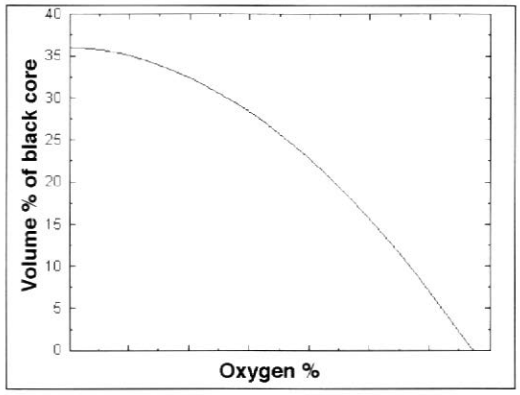

Figure 2. *Evolution of the elimination of black core as a function of atmosphere for the trial composition.*

As a result of these characterisation data, and verification in the laboratory simulation kiln of the effect of oxygen atmosphere on eliminating black core, implementation was started in a roller kiln on an industrial scale.