INFLUENCE OF VARIATIONS IN KILN ATMOSPHERE ON FIRED TILE QUALITY IN CERAMIC PROCESSES IN GENERAL, AND IN POROUS SINGLE FIRING IN PARTICULAR

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ABSTRACT

A method was developed for the study of the composition of the kiln firing atmosphere during the industrial manufacturing process, and this was correlated to variations in the physico-chemical features of white and red, porous, single-fired ceramic tile bodies, and their glazed surfaces. Research was carried out on a laboratory scale, and to this end an electric tubular kiln was designed with an automated nitrogen/oxygen gas inlet assembly. Data were gathered, and an electroceramic sensor was used to analyze oxygen partial pressure (P/P_0) at each point on the firing schedule. The materials used were characterised both structurally and microstructurally using calorimetric analysis (DTA/TG), X-ray diffraction (XRD), and scanning electron microscopy and microanalysis (SEM/EDX). The calorimetric analysis method was also used on the ceramic bodies after their various treatments, and plots were thus obtained for ΔE versus oxygen partial pressure, P_{O2}. Lastly, this study was confirmed in quality control testing in the production cycle of an industrial porous, single-fire kiln, showing the validity of this method, which is relatively unknown in the ceramic industry.

1. INTRODUCTION

However small, an electric signal may be transmitted across any material in order for its features to be examined. Thus, using electrical measuring techniques, ceramic manufacturing processes and products may be controlled, induced and modified. This is what is known as the use of electrical and electrochemical techniques in industry, which has now begun to appear as a scientific branch in its own right, called Electroceramics. It starts with the assumption that «any ceramic material is electroceramic». There is much rigorous published evidence of its uses and potential. To quote a number of examples, electrical experiments allow characterisation of the materials, showing if it is an insulator, semiconductor, a semimetal, if it behaves like a metal conductor or if it is a solid electrolyte etc. They can follow a glass crystallisation curve, or a viscosity plot versus temperature, and are able to determine the glass transformation temperature, as well as also monitoring a cement hydration process. Likewise they may illustrate the densification and sintering mechanisms in ceramic materials. During ceramic processing information is gathered, for instance, in the drying processes of the gels and co-precipitates, slips, suspensions etc. Also, the systems are ideal for product quality control, and lastly they are excellent tools with which to analyze corrosion mechanisms in materials (1).

Generally speaking, it may be said that any ceramic material has mixed electronic-ionic conductivity. This statement is based on the electrical conductivity behaviour of these materials as a function of the oxygen partial pressure.

Fig. 1 shows the conductivity of a solid zirconia electrolyte as a function of the oxygen partial pressure at constant temperature. Basically, the figure shows three areas: one is the electrolytic domain, where conductivity is totally ionic, and there are two electronic domains, where electron conduction prevails at extremely low oxygen pressures, i.e. in reducing atmospheres, and at high oxygen pressure levels, the process is carried out by electronic drops. One result of this phenomenon may be of great importance to industry - most materials behave in a similar manner, manufacturing products in particular, since these are generally multi-stage products with given levels of impurities.

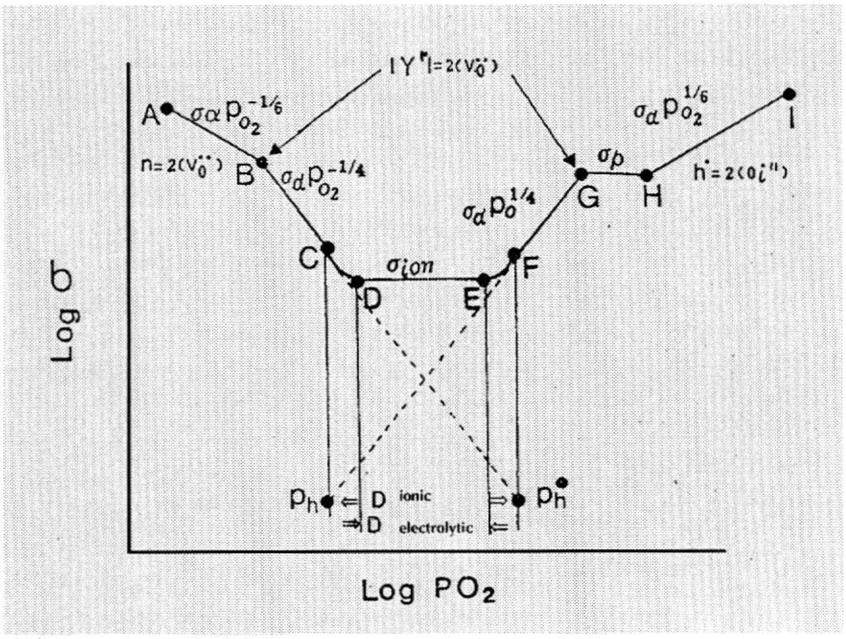

Figure 1. Electrical conductivity versus oxygen partial pressure of stabilised zirconia.

Both these features are a source of ionic and/or electronic defects in the product, and thus an auto-assessment of oxygen partial pressure in the ceramic product is possible at constant temperature during the manufacturing process. This process is carried out beforehand in the laboratory and the conductivity curve is plotted as a function of the product's oxygen partial pressure. Then an «in situ» configuration is set up consisting of two electrodes (although a three-electrode grouping may be used to make a pseudo voltamogram, i.e. intensity versus voltage, and observe the oxidation-reduction mechanisms that arise in the course of the manufacture of ceramic materials). Determining the relevant domains not only tells us the nature of the product's state of conductivity (at manufacturing temperatures most materials become fairly conducting), but can also show us the working atmosphere at any given time. Summing up, it turns the product being manufactured into an autosensor which can monitor the surrounding atmosphere.

Ceramic sensors are materials in which electrical changes may be observed as a function of variations in temperature, oxygen partial pressure and relative humidity of their surroundings. The electrical changes are interpreted as signals which may be analyzed using standard signal processing techniques. As has already been mentioned, ceramic gas sensors may involve stabilised zirconia as an oxygen sensor, titanium oxide doped with Nb and Ta, perovskites based on lanthanum, titanium and iron as nitrogen oxide sensors, while zinc chromate spinels make good humidity sensors (2-7).

The prime motivation behind this paper is the constant concern in the ceramic wall and floor tile manufacturing industry for enhancing the quality of the manufactured ware. This is because single- fire ceramic processing is carried out under certain extremely drastic conditions (8,9); extremely fast manufacturing cycles (from 35 minutes to less than an hour, from the time when the formed tile enters the kiln and leaves it); relatively high temperatures (1100 to 1160°C) and much compositional variation for the same heat-treatment process (glaze, screen prints and decoration, ceramic body); besides increasingly exacting demands on the quality of the manufactured ware, if companies are to maintain their competitiveness in the marketplace (current production requirements demand that 90% or more of tiles manufactured be flaw-free).

Faults in ceramic tiles may be due to many factors (10,11), the most common being the following: rheological problems with the glazes used, the presence of unmelted particles in starting frits, carbonate breakdown in the body, «black coring», pressing defects, colour changes etc.

At present, many of these defects are closely controlled as a result of research was carried out into body formulations, compaction level, improved frit manufacturing and increasingly advanced analysis techniques. Likewise, increased automation of the single-layer roller kiln and use of cleaner forms of energy have also contributed to higher manufacturing output with no drop in quality.

However, despite this technological progress, it is currently difficult to measure, and thus control the firing atmosphere at the exact spot where the glazed tile is located in the kiln. This is due to the fact that, although we may be able to control the gas flow to the kiln burners for optimum combustion, there is no doubt that within the combustion chamber a series of chemical transformations will take place as a result of various reactions that occur in the tile, altering kiln atmosphere and obviously having some effect on the quality of the resulting product. Fig. 2 schematically shows some typical reactions that arise, with subsequent release of gases, which will to a certain extent modify the atmosphere surrounding the tile being fired. Among other faults or structural changes that we may find directly caused by modifications in the atmosphere surrounding the glazed tile are changes in the colour of glazed tiles, the appearance of shades, variations in their refractive index, more or less gloss, «pinholing», «black coring» in the body, etc.

In view of this, our paper seeks to indicate, on the one hand, changes in the characteristics of the body and the glaze directly related to a modified atmosphere surrounding the white- and red-bodied wall tiles in a single-fire manufacturing process, and on the other hand to correlate electrical measurements with the industrial ceramic manufacturing processes, thus monitoring and controlling them, so that such defects may be suppressed.

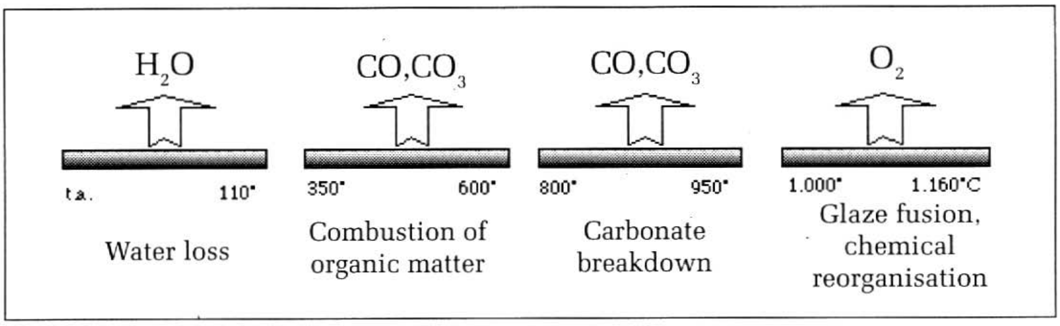

Figure 2. Diagram showing the various reactions taking place in glazed tile within the kiln combustion chamber

2. EXPERIMENTAL

The experimental process followed consisted of constructing an assembly that would allow exact measurement of the variations in atmosphere of an industrial kiln, particularly with regard to oxygen partial pressure, and so correlate this parameter with the physico-chemical changes arising in glazed tiles during the single-firing manufacturing process.

In order to carry out this task, it was found necessary to design an assembly in an electric tubular kiln allowing automatic regulation of kiln inlet gas, whose oxygen percentage composition was known, using a «Fuzzy Logic» control system based on temperature and gas sensors. Thus it was possible to work out the relationship between the composition of the kiln atmosphere and some parameters of the glazed tiles.

2.1. Materials and methods.

The samples selected for the test were 5 x 5 cm^2 white and red-firing pressed wall tile bodies, of the composition generally used in industrial manufacture. In a number of cases the company's own commercial engobe coating was used, referenced C1

The following instrumentation was used for materials characterisation:

- Philips scanning electron microscope (SEM), model XL20, with an energy-dispersive X-ray analysis system (EDAX), model DX4i.
- Siemens D5000 X-ray diffractometer, operating with a copper cathode and a nickel filter. The range of analysis was in all cases between 2° and 70°, at steps of 2Θ. Identification of crystalline phases was carried out automatically using the JCPDS files.

- Differential thermal analysis (DTA) and thermogravimetric analysis (TG) with Perkin Elmer instruments, models DTA 7 and TG 7. The treatment was carried out from 50°C to 1100°C, with a heating rate of 5°C/min in a nitrogen atmosphere in some cases, and in air atmosphere in others.
- Hunterlab COLORQUEST colorimeter
- TESTO 350 (ISO 9001) gas analyzer, duly calibrated.
- Carbolite tubular electric kiln, maximum temperature 1500°C with a tank-type chamber built from silicoaluminous material.
- Industrial single-firing kiln.

2.2. Description of the experimental measuring assembly.

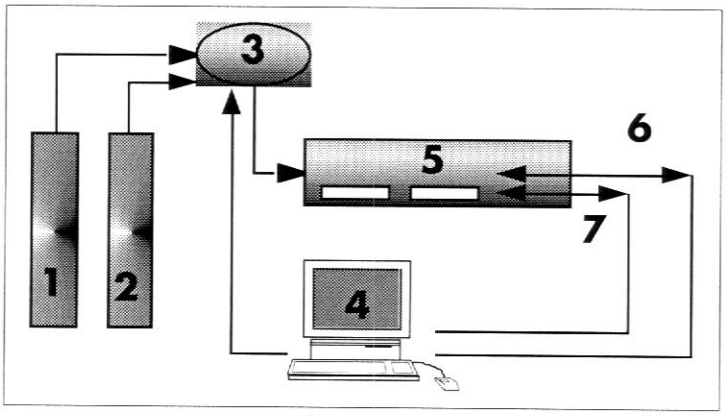

Figure 3. Schematic of the setup used to conduct the laboratory-scale experiments.

Fig. 3 shows a general scheme of the assembly used to conduct the laboratory-scale experiments.

The equipment consists of two gas tanks, one containing nitrogen [1], referenced C-45, and another with industrial oxygen [2]. Both have a purity of 99.999%. This mixture of gases forming the kiln gas inlet composition was regulated with a servovalve [3]. The exit flow rate measured with a pressure gauge varied in the case of N_2 between 1-10 bar and in the case of O_2 between 0.5-1 bar. Opening was controlled by an electrical signal from the computer [4] using an acquisition card (Keithley, DAS-8/AO), following a preset cycle. In the tubular kiln [5], with a tank-type chamber to keep the internal atmosphere saturated, a heat-treatment cycle was programmed with a heating rate of 10°C/min, from ambient temperature to 1125°C, with a dwell time of 5 min at this maximum temperature, followed by free cooling.

Two types of sensor were fitted: one to read temperature [6], consisting of a Pt-Rd alloy, and another for oxygen [7]. Both were connected to the computer via the signal acquisition card mentioned above. The oxygen sensor consisted of a tube of stabilised zirconia (solid electrolyte) closed at one end, and this was put into the kiln at the point where oxygen partial pressure was to be monitored. For the ionic conduction process to be possible, Pt electrodes had to be placed on the sensor's interior and exterior surfaces. In our case, the electrodes were placed with a process involving the painting and drying of conducting pastes. The assembly provided an electric voltage between terminals which was a function of the oxygen partial pressure and temperature inside the kiln. This relationship is called Nernst's equation:

$$V = \frac{RT}{4F} \ln \frac{P_{O2}^{r}}{P_{O2}} \qquad (1)$$

where R is the gas constant, F the Faraday constant, T the temperature, P_{O2}^{r} the oxygen partial pressure in the reference gas (usually the atmosphere outside the kiln), and P_{O2} the oxygen partial pressure inside the kiln. Given the values for oxygen partial pressure normally found for industrial ceramic kilns (10-21% O_2), the sensor will emit a signal in the interval between (0-100 mV) to more than 1% of accuracy. The biggest drawback with these types of devices is that they cannot be used at temperatures below 700°C, since ionic conduction processes are only completely activated above this temperature.

The information obtained from the oxygen and temperature sensors was transferred to a computer which, using suitable analysis, showed the evolution in time of the parameter in question: oxygen partial pressure inside the kiln (measuring was carried out just beside the problem samples). Moreover, thanks to the voltage analog output contained within the signal acquisition card and a software programme designed to this end, there was an automatic control system for the kiln gas feed. The control programme follows a «Fuzzy Logic» type algorithm, in common usage.

3. RESULTS AND DISCUSSION

3.1. Structural and microstructural characterisation of raw materials.

Figs. 4 and 5 show the results obtained from the differential thermal analysis (DTA) and thermogravimetric analysis (TG), carried out in a nitrogen atmosphere on samples of unfired white and red tile bodies. The DTA for the red-bodied sample (Fig. 4a) shows an endothermic peak between 680°C and 770°C, coinciding with a considerable weight loss in the TG (Fig. 4b) of 10%, possibly due to the presence and consequent thermal breakdown of carbonates. Losses noted below these temperatures were insignificant. Above these temperatures, the DTA registered a small exothermic shoulder at 960°, while the TG did not register any appreciable weight losses.

The DTA for the white body sample (Fig. 5a) showed exothermic peaks between 450°C and 600°C, and in this range the TG (Fig. 5b) registered 5% weight losses, doubtlessly caused by combustion of organic matter. The DTA also registered endothermic peaks between 700°C and 950°C, with TG losses of 10% due to carbonate decomposition.

Mineralogical analysis using X-ray diffraction (XRD) on the unfired specimens, Fig. 6, shows the presence of the following crystalline phases: in the white body (Fig. 6a) there were more intense diffraction peaks of quartz, SiO_2 (ASTM file no. 33-1161) and less intense peaks of nepheline, (Na,K) $AlSiO_4$ (ASTM file no. 9-0338), kaolinite, $Al_2Si_2O_5(OH)_4$ (ASTM file no. 14-0164), and calcite $CaCO_3$ (ASTM file no. 5-0586). For the red body (Fig. 6b), quartz peaks were also observed to be the most intense, along with diffractogram peaks for the illite phase -$KAl_2Si_3AlO_{10}(OH)_2$ (ASTM file no. 2-0056) and the nepheline phase (ASTM file no. 9-0338).

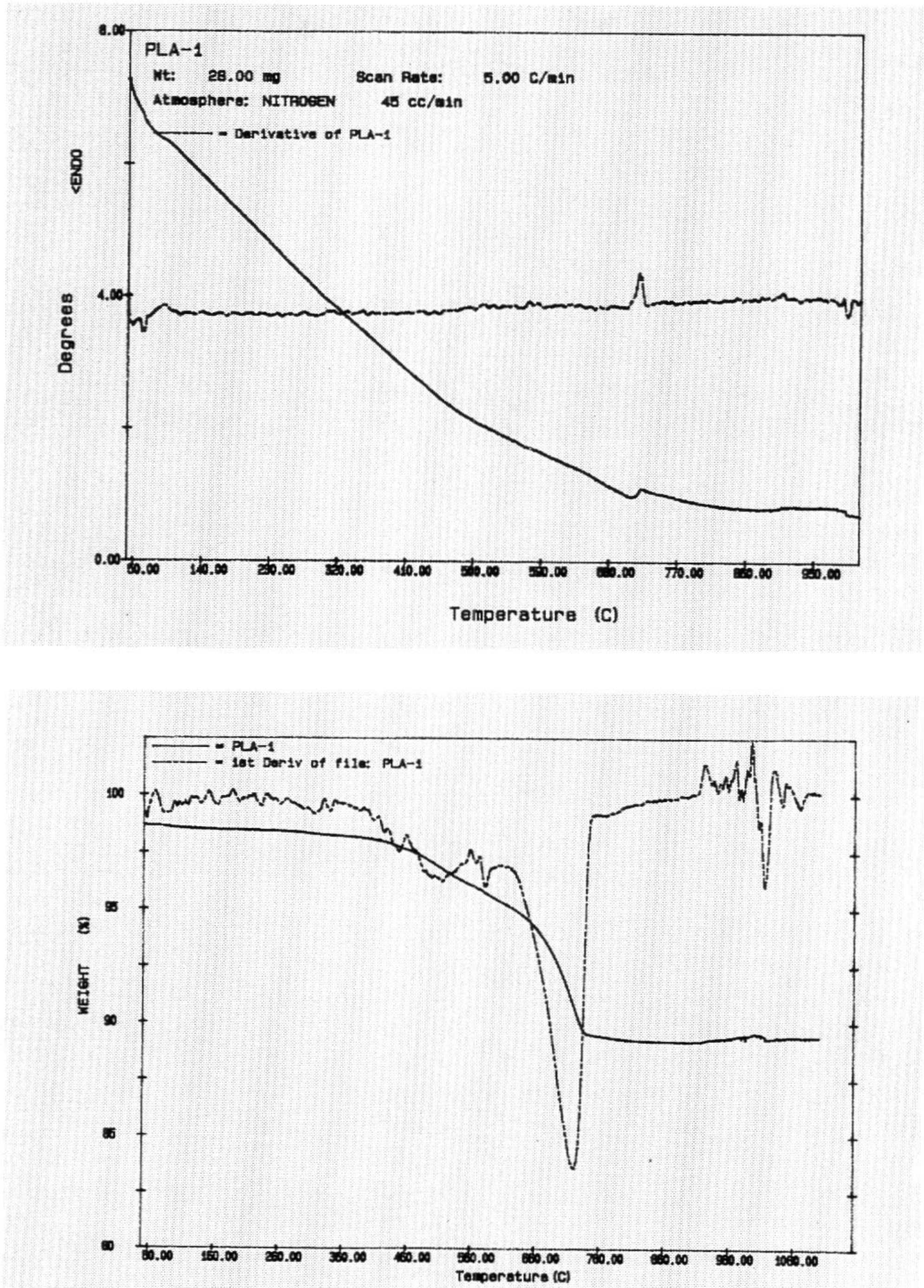

Figure 4. Differential thermal analysis of the red tile body sample (a) and thermogravimetric analysis (b).

Lastly, the red and white tile bodies were characterised microstructurally and microanalytically using electronic microscopy and energy-dispersive X-ray microanalysis (EDX). To this end it was necessary to coat the samples with a layer of gold using the sputtering technique to make them conducting and avoid discharges. Analytical conditions of the equipment were an acceleration voltage of 20 kV and a 37.5 mm sample/detector working distance. Fig. 7 shows the SEM micrograph of the red body to 952 magnifications, with EDAX microanalysis. In the micrograph obtained using the back-scattered e(BSE) detector which shows up compositions of heavier elements in brighter shades of colour

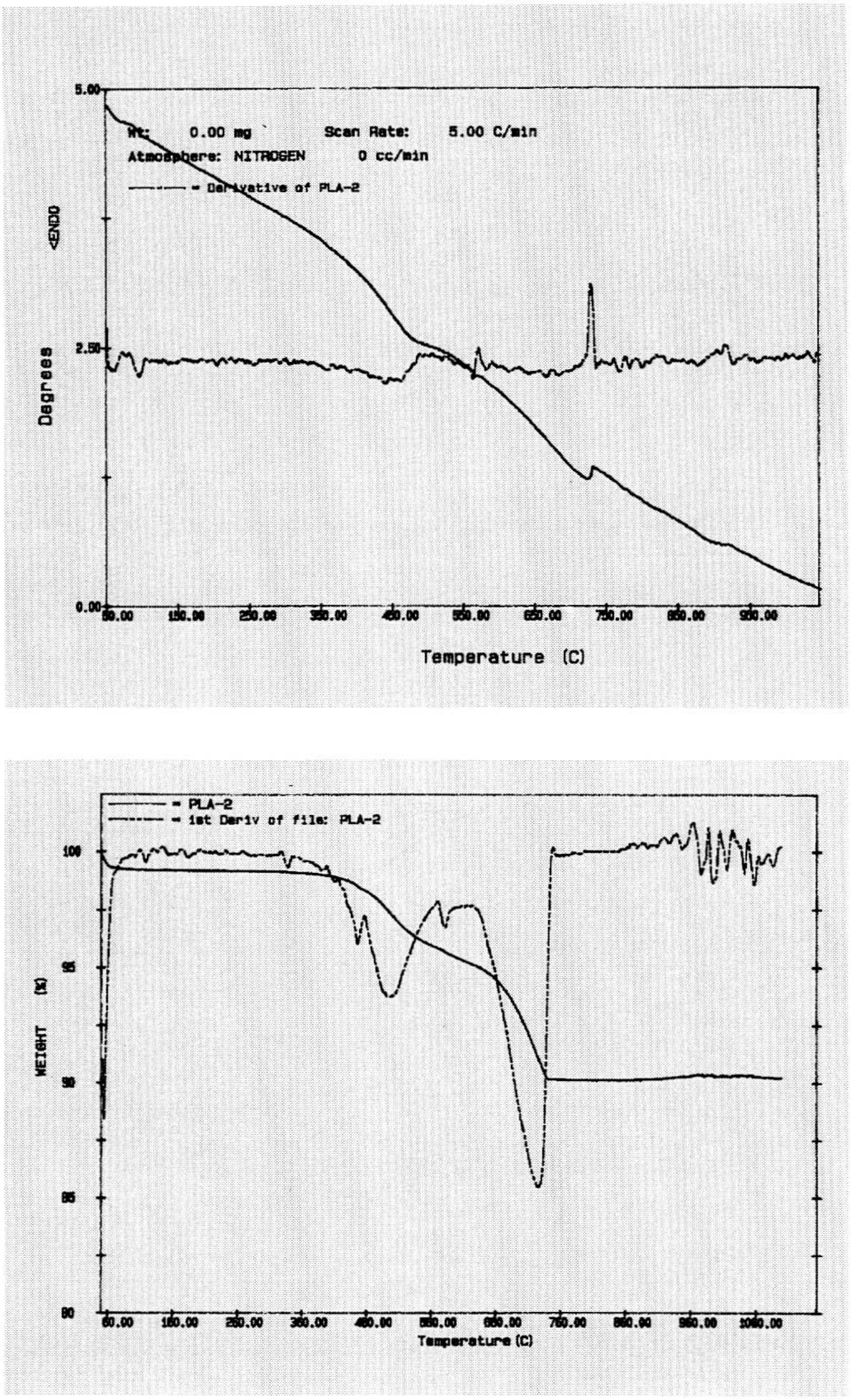

Figure 5. Differential thermal analysis of the white tile body sample (a) and thermogravimetric analysis (b).

and lighter elements in lighter shades, brighter particles were observed whose spot analysis showed Ti and Fe to be present in the composition. The greyest particulate shows Al-Si-K-Mg in some particles and Ca-Mg-Si-Al in others, and grains which contain only Si. This information matches data obtained from the XRD mineralogical analysis, where the mineral phases of illite, kaolinite, nepheline and quartz were identified.

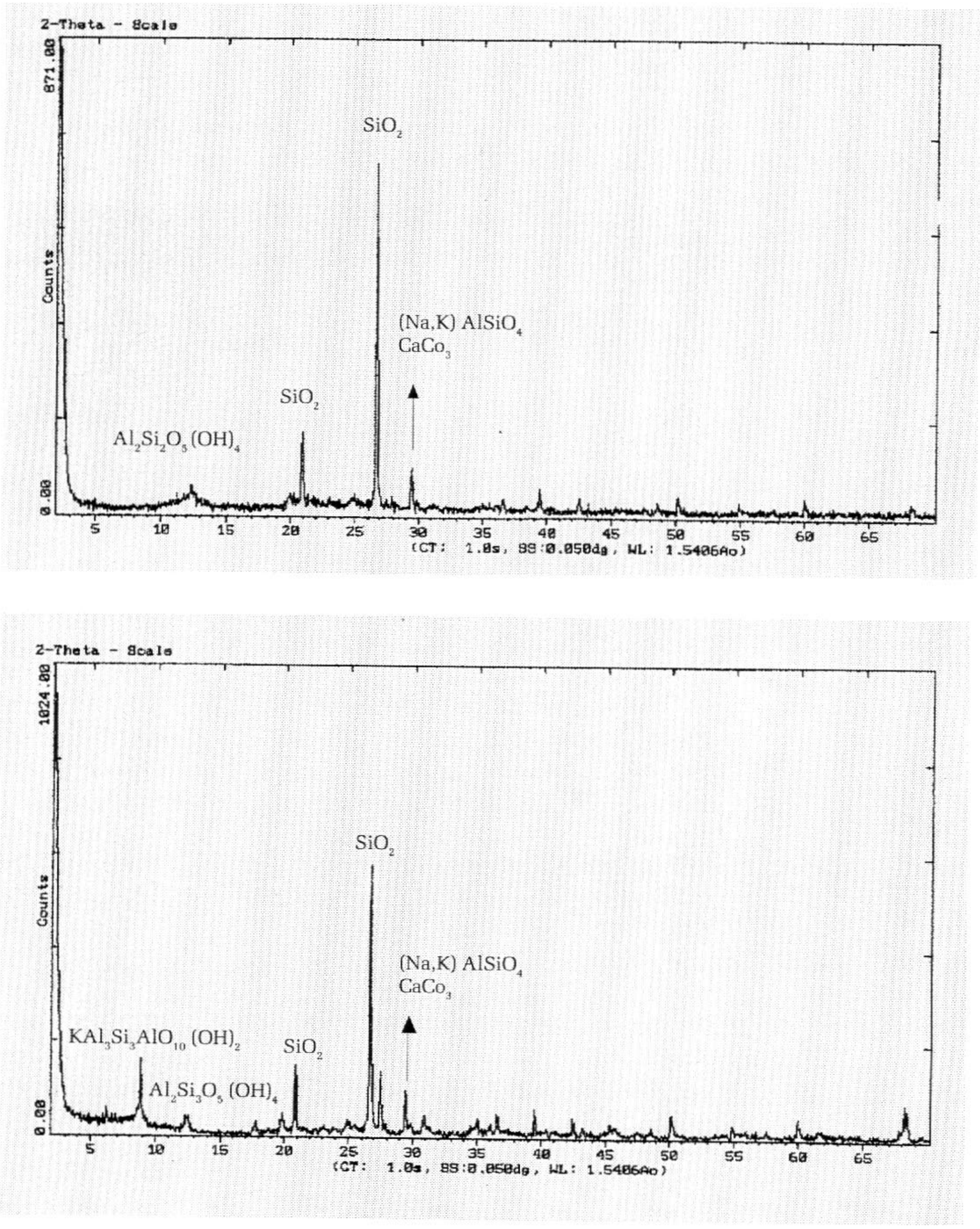

Figure 6. X-ray diffractogram of the white (a) and red body sample (b).

Average microanalysis carried out on the sample at low magnifications (46x, 306x and 612x) shows the presence of the following elements, which could affect the firing atmosphere:

- Carbon: between 0.65 and 3.28% by weight, expressed as CO_2 assignable to organic matter within the sample.
- Calcium: between 7.31 and 9.10% by weight, expressed as CaO, assignable to carbonates.
- Titanium: around 1% by weight, expressed as TiO_2 assignable to titanium oxide particles.
- Iron: between 10 and 27% by weight, expressed as Fe_2O_3, assignable tohematite
- Sodium: between 0.6 and 1.5% by weight, expressed as Na_2O
- Potassium: around 5% by weight, expressed as K_2O.

Moreover, the presence of Si as a major element whose percentage values as SiO_2 lay between 38 and 48% by weight, as well as Al as Al_2O_3, which ranged from 15 to 21% by weight.

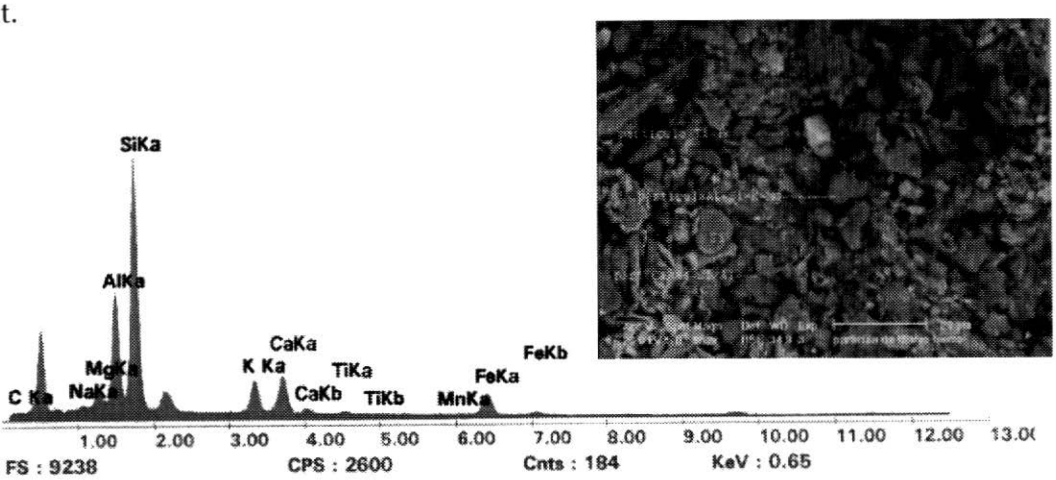

Figure 7. SEM micrograph of the red body sample and EDAX microanalysis.

It is useful to bear these analytical results in mind when analysing the values obtained for the firing atmosphere, since this atmosphere will be modified by them. Thus they show the presence of carbon in the sample due to a low content of organic matter within the sample, which will involve variation of the atmosphere during the heat treatment cycle by release of C, CO or CO_2 to create an atmosphere which is slightly reducing. The same phenomenon will occur with the presence of carbonates and sulphates, since these will give off CO_2 and SO_2. Also, Fe and Ti particles were observed, probably in the form of hematite, Fe_2O_3 and TiO_2, and which in the course of the process give off O_2 molecules due to local rearrangements or reductions.

Fig. 8 shows the SEM micrograph of an unfired sample of the white tile body. Its morphology exhibits larger particles (›20 μm), whose spot analysis shows only Si content, assignable to the quartz crystalline phase, SiO_2 analyzed with XRD. Surrounding this is a finer particulate (around 1mm), whose spot analysis shows the presence of Si-Al-Ca-K, comprising the kaolinite and nepheline phases, also recorded by XRD.

Average microanalysis carried out on the sample at low magnifications gave the following results:

- Carbon: present in 1.5-3.5% by weight, expressed as CO_2, assignable to organic matter within the sample.
- Calcium: present in 9-10% by weight, expressed as CaO, assignable principally to carbonates.
- Titanium: present in around 1% by weight, expressed as TiO_2 assignable to titanium oxide.

- Iron: present in 2-2.5% by weight, expressed as Fe_2O3, assignable to hematite particles.
- Sodium: present in around 1% by weight, expressed as Na_2O.
- Potassium: present in around 2.5% by weight, expressed as K_2O.

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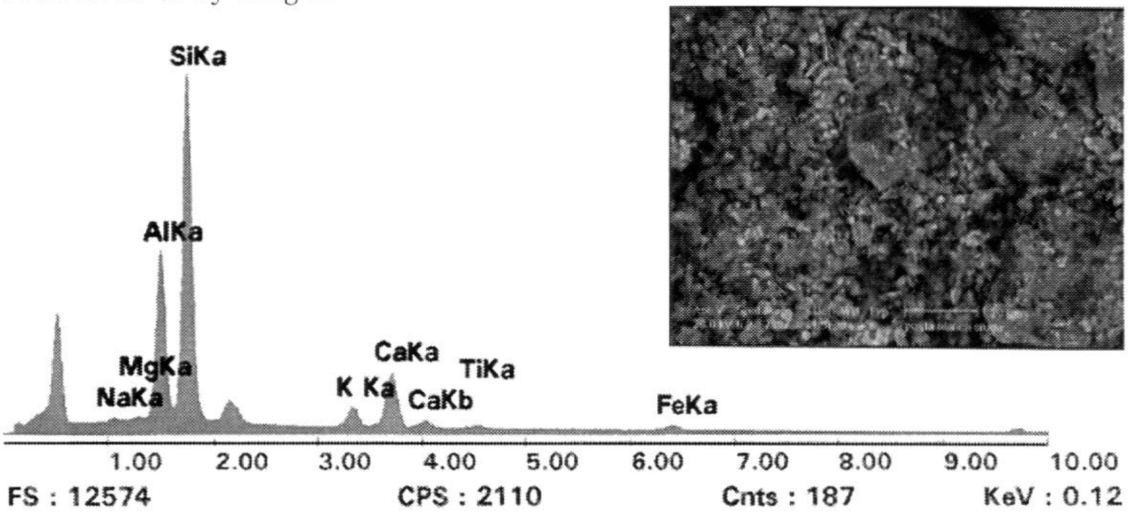


Fig. 8. SEM micrograph of the unfired white tile body sample and EDAX microanalysis.

As in the case of the values obtained from microanalysis carried out on the red tile body, here there is also evidence of phases which will modify the kiln atmosphere during heat treatment, due to the presence of organic matter, carbonates and sulphates, as mentioned earlier, although some of their contents changed (less iron and magnesium, for example, in the last case).

3.2 Gas measurements in an industrial kiln during a standard porous, single-fire production process.

The O_2 percentage in the firing cycle intervals was determined for a single-firing industrial kiln, with a gas analyzer. The results are shown on the schematic in Fig. 9.

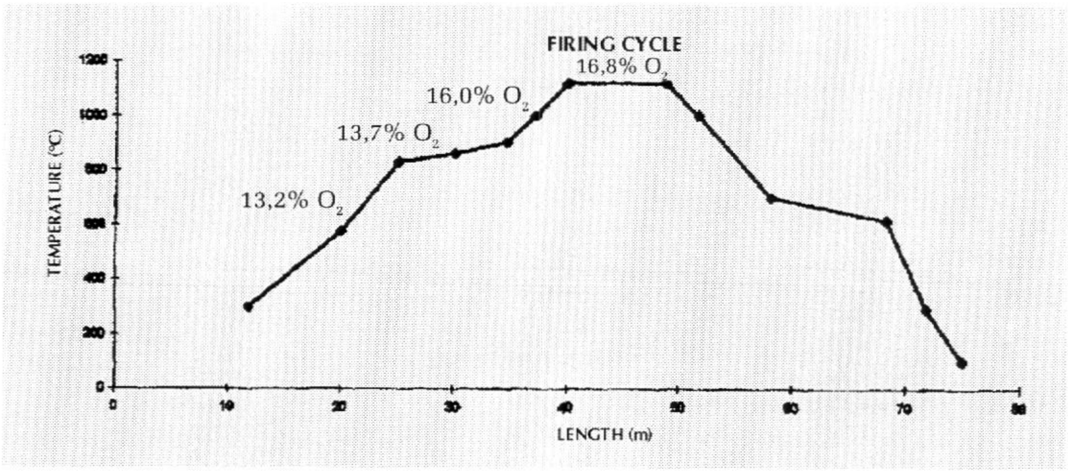


Figure 9. Measurements obtained in an industrial kiln during a standard porous, single-firing production process.

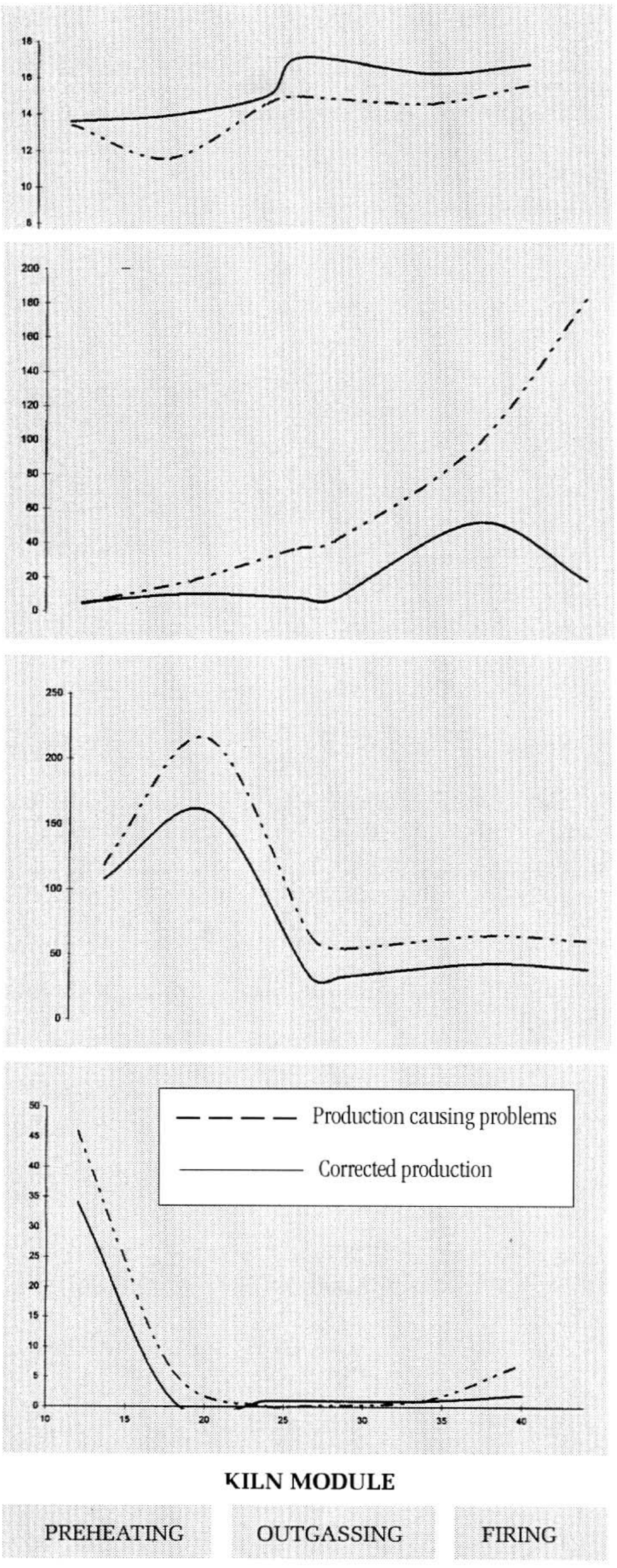


Figure 10. Measurements obtained in an industrial kiln during a standard production process.

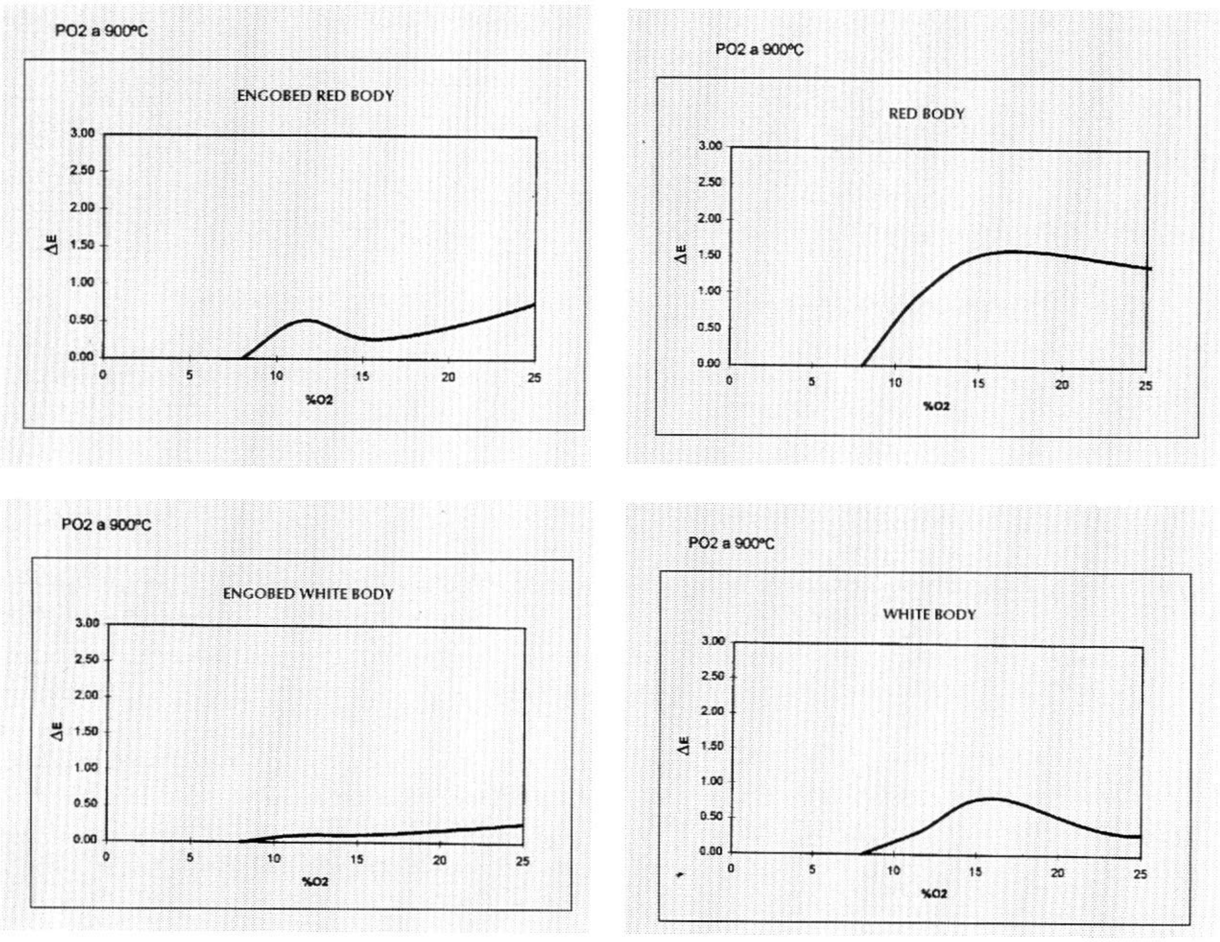


Figure 11. Measurements obtained of oxygen partial pressure on the red and white tile bodies.

The effectiveness of the firing atmosphere correction was verified, using the gas analysis data of one day's single fire production, when changes were noticed and corrected in the colours of fired glazed tile, determining the percentages of O_2, SO_2, NO_2 and CO for each kiln module area: the preheating, outgassing and firing area. The results obtained during the appearance of these faults and, after these had been corrected using gas regulation, are shown in Fig. 10. They show the direct influence exerted by kiln atmosphere on the physico-chemical variables of the tiles.

3.3. Influence of oxygen partial pressure on colorimetric properties.

The heat-treatment experiments were carried out in a tubular electric kiln, whose arrangement is shown in Fig. 3, using different porous, single-fire, red and white tile bodies, with and without engobe, varying the oxygen pressure and relating its influence to colorimetric measurements.

Plots of % O_2 versus firing temperature were obtained. The fired specimens were subjected to colorimetric analysis, and the Lab. parameters were found. These were used to calculate the colour variation parameter (áE), whose formula is (12):¬X197

$$\Delta E = \sqrt{(L - L^*)^2 + (a - a^*)^2 + (b - b^*)^2}$$

Fig. 11 shows the values of ΔE againnst various percentages of O_2 measured at 900°C inside the firing chamber, just beside the ceramic bodies. In all cases it was observed thet the value of ΔE was constant for percenteges of O_2 above about 15%. These results suggest that, working in atmospheres with these percenteges of O_2, there will be few changes in the colour of such materials.

Similar results were obtained in the values analyzed at 1050°C.

3.4. Influence of oxygen partial pressure on structural properties.

Using X-ray diffraction, analysis was carried out on the red and white tile bodies, with and without engobe, fired in the tubular electric kiln (Fig. 3), varying oxygen partial pressure.

The results obtained show the following:

- The presence was observed of major crystalline phases of zircon, $ZrSiO_4$ (ASTM file no. 6-0266) and quartz, SiO_2 (ASTM file no. 33-1161), in the engobes of both the red and white bodies. No modification was observed of the number of crystalline phases in the various O_2 percentages analyzed.

- However, in the engobe on the white body, the main zircon peak was more intense when the O_2 percentages in the combustion chamber atmosphere went from about 5 to 15%. This peak did not become any more intense at higher measured percentages of O_2, but it did move slightly towards higher 2Θ values (Fig. 12a). This could indicate a certain structural distortion in the zircon owing to a more oxidising atmosphere.

- In XRD analysis on the red body, the most intense crystalline phases found were those of quartz and anorthite, $CaAl_2Si_2O8$ (ASTM file no. 41-1486). Worth pointing out is the development of a phase of pseudowollastonite α-$CaSiO_3$ (ASTM file no. 31-0300), in the specimen fired at an oxygen pressure of about 15% in the combustion chamber. This had not been observed in the samples fired at lower oxygen percentages (Fig. 12b).

- In XRD analysis on the white body, the most intense crystalline phases were those of quartz and anorthite. No apparent structural change caused by atmospheric variation inside the combustion chamber was observed.

4. CONCLUSIONS

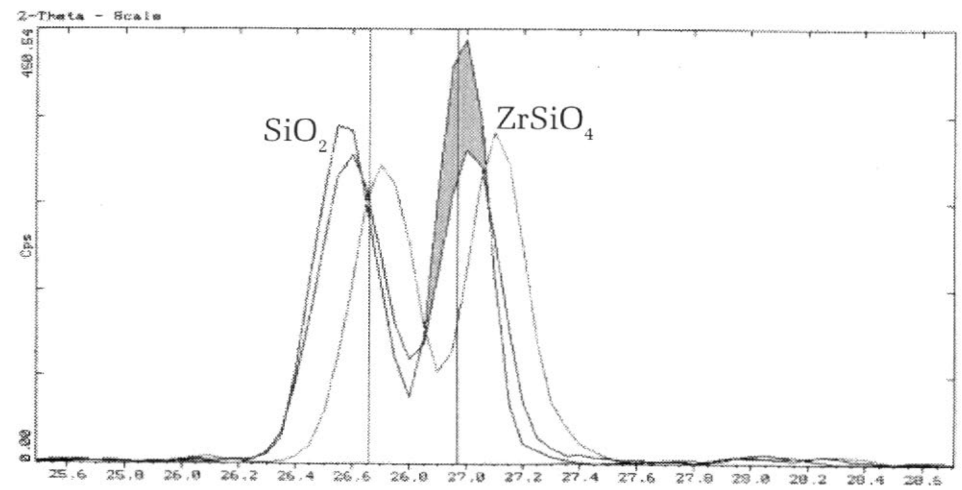
The experimental results obtained allow drawing the following conclusions:

1- The influence has been established of the nature of the atmosphere in the combustion chamber of an industrial kiln on colour changes in porous, single-fired ceramic tile.

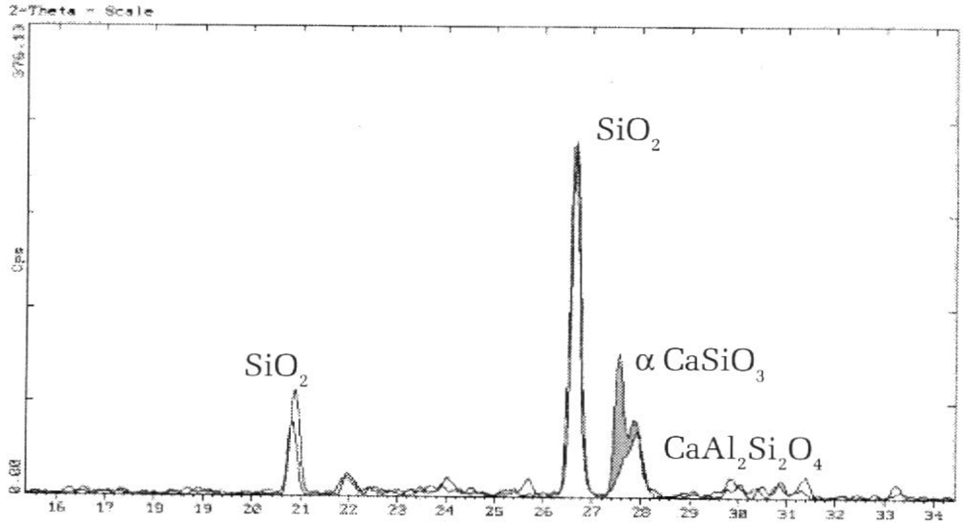
2- An experimental technique was developed, allowing the influence of the oxygen partial pressure to be correlated to certain physico-chemical variables of porous, single-fired ceramic tile bodies, with and without engobe.

3- This paper opens up a fresh line of prospective research into the influence of oxygen partial pressure on different ceramic products and their decoration.

4- Since sensor technology is accessible and economical, it will foreseeably be swiftly implemented in the ceramic industry.



12a



12b

Figure 12. XRD analysis of a red (12a) and white tile body (12b) with engobe.

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