EFFECT OF KILN ATMOSPHERE ON THE FIRING BEHAVIOUR OF CERAMIC BODIES

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INTRODUCTION

The ceramic tile industry is an energy-intensive industry, fundamentally in natural gas consumption, consuming a total of 13,400 GWh in 2020. The level of CO_2 emissions in the cluster amounts to 2,770,000 tCO_2/year, about 90% of which stem from natural gas combustion. In this context, the European Green Deal is aiming for an emissions reduction of 55% in relation to 1990 for 2030, and no emissions in 2050.

With these highly ambitious emissions reduction targets, the sector will need to radically change the technologies used in its production process. Options in this sense include using hydrogen in drying and firing processes as direct source of thermal energy by combustion. The great advantage of this process is that hydrogen combustion only produces water vapour and, if the energy for producing hydrogen comes from a renewable source, there is no direct CO_2 emission. This therefore highlights the great interest in achieving the decarbonisation targets set.

However, in addition to the need to produce hydrogen, its use as fuel in industrial processes requires detailed study to determine the effect that the gaseous atmosphere resulting from the use of hydrogen as fuel has on the physico-chemical reactions that the materials to be processed are going to undergo. This study sets out the results obtained in a controlled temperature tube furnace, designed to study the influence of kiln atmosphere on the firing behaviour of ceramic bodies.

RESULTS AND DISCUSSION

The sintering curves [1] and fluorine emissions (determining fluorine content before and after firing, using a selective electrode [2]) were determined of a spray-dried powder for red-firing stoneware tile, using three gaseous mixtures and modifying N_2 and H_2O contents. For this, an electric tube furnace, together with a liquid evaporative generator, was used (Figure 1). In every case, a gas circulation flowrate of 0.01 m^3/min was used.

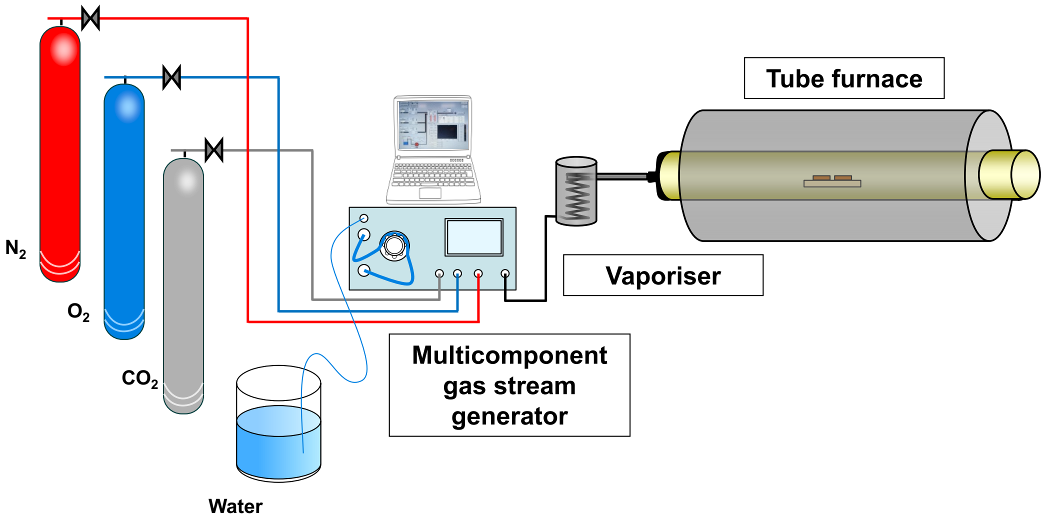

Figure 1. *Scheme of the test equipment.*

The three atmospheres were designed to reproduce (and even go beyond) the increase in water vapour that would be obtained in a roller kiln on replacing natural gas with hydrogen (Table 1). The vitrification diagrams obtained under these conditions are shown in Figure 2.

Atmosphere (% vol)	**1 (10% H_2O)**	**2 (30% H_2O)**	**3 (50% H_2O)**
O_2	10	10	10
CO_2	10	10	10
N_2	70	50	30
H_2O	10	30	50

Table 1. *Atmospheres used.*

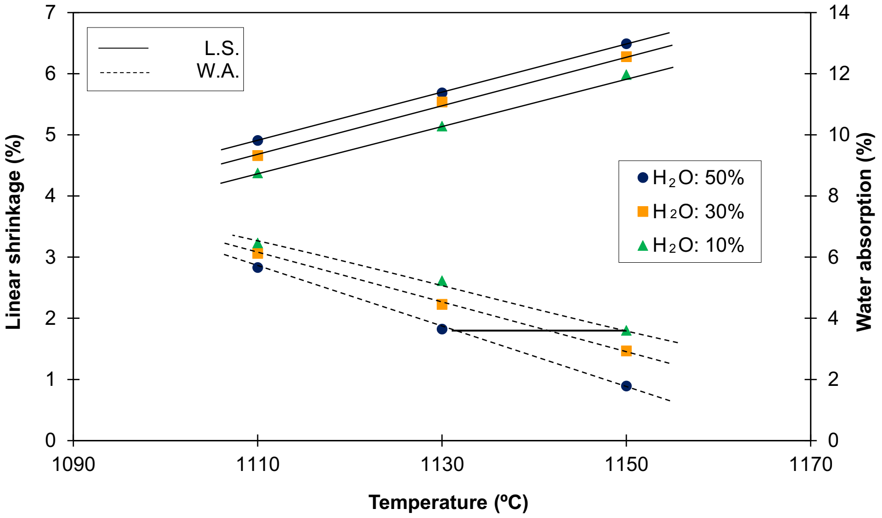

***Figure 2**. Vitrification diagrams of spray-dried powder for red-firing stoneware tile for three test atmospheres.*

The figure shows an increase in red-firing stoneware tile densification with the rise in water vapour partial pressure in the furnace atmosphere, which increased as firing temperature rose. This was because liquid phase viscosity decreased as water vapour content increased in the viscous glass. Indeed, a rise in water vapour concentration in the furnace atmosphere raised its concentration in the viscous melt, which led to rupture of Si-O-Si bonds and to the formation of silanol groups (Si-OH) [3][4]. On the one hand, this considerably lowered glassy phase viscosity [4] and, on the other, it increased cation silicon diffusivity in the glass [3], favouring quartz dissolution. These phenomena raised glassy phase content (more quartz dissolved) and glass viscosity decreased. Both factors increased the rate of viscous flow sintering, the mechanism responsible for densification of red-firing stoneware tile.

Indeed, comparison of the microstructures of the test pieces fired at 1150ºC in extreme water vapour concentrations (10 and 50%vol) reveals significant differences in their porous texture (Figure 3). The piece fired with the richest atmosphere in water vapour exhibited the greatest densification. In fact, water absorption decreased from 3.6% to 1.8%, which would allow firing temperature to be lowered by more than 15ºC (Figure 2).

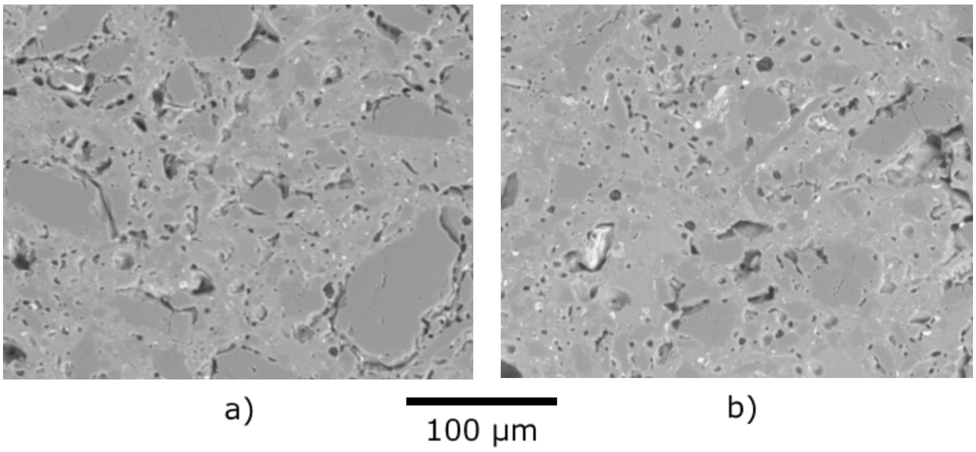

Figure 3. *SEM micrographs of the red-firing stoneware tile fired at 1150ºC, in different furnace atmospheres: a) 10 vol% of water vapour and b) 50 vol% of water vapour.*

In contrast, the increase in water vapour content associated with the use of hydrogen instead of natural gas led to a significant rise in fluorine emissions, as shown in Figure 4. This was because water vapour reacted with the fluorine present in the piece, forming HF and therefore raising fluorine emission [2].

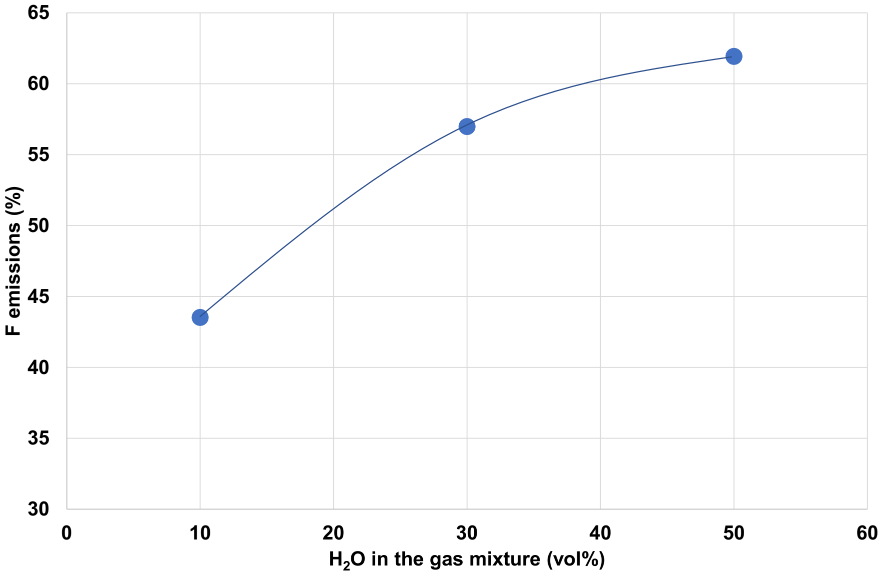

Figure 4. *Variation of the fluorine emissions (percentage fluorine emitted with respect to fluorine present in the unfired piece) at a firing temperature of 1130ºC with water vapour content in the gas mixture.*

ACKNOWLEDGEMENTS

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