

IMPACT OF USING HYDROGEN IN FIRING CERAMIC TILES. A PRACTICAL VIEW.

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ABSTRACT

Among the different technologies that can contribute to decarbonising the ceramic industry is the use of hydrogen as fuel, as hydrogen combustion generates no CO₂ emissions. However, hydrogen combustion entails a series of changes in the firing process that require in-depth study. It is thus necessary to adapt both the ceramic products and the operational variables in industrial equipment, in order to avoid production and quality problems in the end product.

This paper sets out the results obtained in the simulation of an industrial kiln using different mixtures of natural gas and hydrogen, followed by an analysis of how kiln atmosphere influences the firing behaviour and properties of ceramic glazes and bodies. Different types of tiles and glazes are considered.

1. INTRODUCTION

The ceramic tile industry is an energy-intensive industry, fundamentally in natural gas consumption, with a total consumption of 13,400 GWh in 2020. The industry cluster's level of CO₂ emissions is 2,770,000 tCO₂/year, of which about 90% comes from natural gas combustion. In this context, the European Green Deal envisages a 55% reduction in emissions relative to 1990 levels for the year 2030, and zero emissions in 2050.

In light of such ambitious emissions reduction targets, the sector will need to radically modify the technologies used in its production process. Among the existing options is the use of hydrogen as a direct source of thermal energy by combustion in drying and firing processes. The great advantage of this process is that combustion only produces water vapour and, if the energy for hydrogen production comes from a renewable source, no direct emission of CO₂, therefore making it of great interest in meeting decarbonisation targets.

However, in addition to the need to produce hydrogen, its use as fuel in industrial processes requires detailed study in order to understand the influence that the gaseous atmosphere resulting from using hydrogen as fuel has on the physico-chemical reactions that the materials being processed will undergo. This study sets out the results obtained in a tube furnace with controlled temperature, designed to study the influence of kiln atmosphere on the firing behaviour of ceramic glazes and bodies.

2. THEORETICAL STUDY

From a technical standpoint, the technology for using hydrogen as fuel in industrial processes is not very mature, and detailed study is required in order to understand the influence that this change in fuel will have on the physico-chemical reactions that the materials being processed are going to undergo, the possible effects on the construction materials in industrial facilities, as well as on process variables and air emissions, without adversely affecting resulting product quality.

Although H₂ could, in principle, be used in processes in which natural gas is currently used, the great challenge ahead lies in adapting existing plants to this new fuel since, from a technical viewpoint, natural gas and hydrogen exhibit very different characteristics. One of these is the heating value (HV), that of hydrogen being 3–4 times lower than that of natural gas. Consequently, for the same power, 3–4 times the amount of hydrogen needs to be fed into the system. It also means that it will be necessary to redesign and adapt the kiln and burner feed ducts, or it may even require replacing today's combustion units with others that are able to handle this volume flow rate. Flame rate and temperature also change, these being higher, possibly raising the NO_x emissions associated with combustion gases, NO_x being a particularly harmful gas for health. This parameter becomes very critical at flame temperatures above 1400°C. In addition, hydrogen combustion will also generate a greater amount of water vapour, compared to that resulting from natural gas combustion, and it is not known how this might affect resulting product quality and the building elements inside the kiln.

From a combustion standpoint, using hydrogen or hydrogen mixed with natural gas as fuel affects combustion variables and flame temperature profile, geometry, and rate, as well as heat transfer towards the material.

Figure 1 shows how the lower heating value (LHV) of the resulting mixture varies, per unit volume, as well as how the composition of the gases formed in the full combustion of different mixtures of natural gas and hydrogen (CO_2 , H_2O) varies [1].

Adding hydrogen to natural gas significantly changes the resulting mixture properties, in particular the energy properties, because, when hydrogen is incorporated into the mixture, the mixture heating value decreases. Since hydrogen exhibits a lower heating value per unit volume, as more hydrogen is introduced, the energy contained per unit volume progressively decreases. It may be observed that, under standard conditions, when 20% hydrogen per volume is reached in the mixture, this results in a 14% drop in heating value. If this percentage is raised to 50% hydrogen by volume in the mixture, the heating value decreases by 35%.

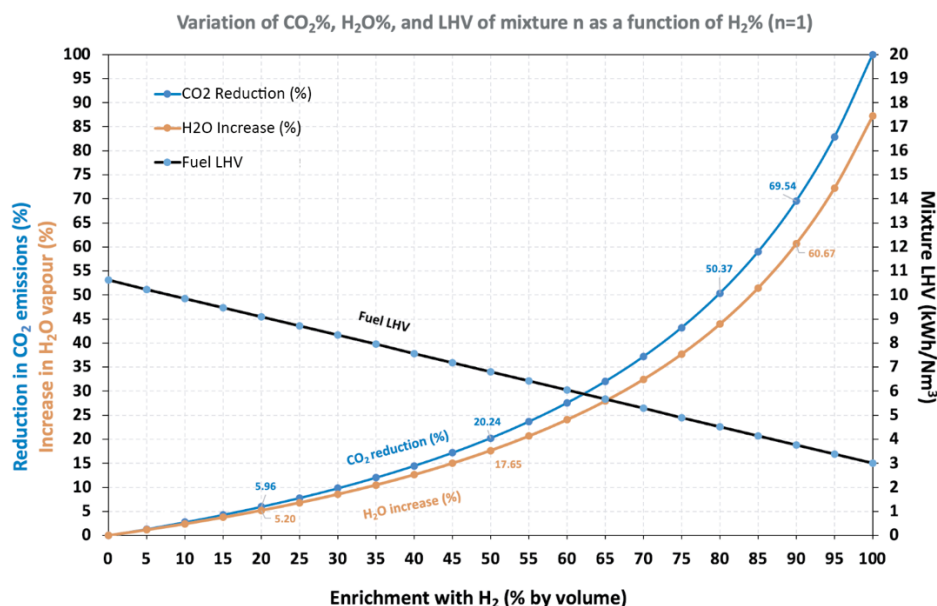


Figure 1. Variation of the lower heating value (LHV) and of the composition of the complete combustion products (CO_2 , H_2O) for different mixtures of natural gas and hydrogen.

On the other hand, mixtures very rich in hydrogen need to be used to significantly reduce CO_2 emissions. Adding 20% hydrogen by volume to the natural gas mixture only lowers the resulting CO_2 by 6%. In order to achieve a reduction of the order of 50% CO_2 , mixtures with more than 80% hydrogen need to be used.

With regard to the variation in percentage of H_2O vapour in the combustion chamber, the use of hydrogen-rich mixtures leads to water vapour enrichment in the gases. For example, in a mixture of 20% hydrogen, the rise in H_2O is 5.20%, compared with that generated in natural gas combustion (in absolute value, the amount of water vapour would go from 18.5% to 19.5%). And if 100% hydrogen were used, water vapour in the combustion products would increase by 87.3% (in this case, in absolute value, the amount of water vapour would go from 18.5% to 34.7%).

The present study focuses on this last case: the influence of kiln atmosphere on the firing behaviour of ceramic glazes and bodies. Specifically, studies were designed with three atmospheres, which included the percentages of water vapour that would be generated with natural gas (18.5%) and with natural gas and hydrogen, as well as with mixtures of even higher water vapour percentages on working with 100% hydrogen (34.7%).

3. EXPERIMENTAL

The influence of kiln atmosphere on the firing behaviour of ceramic glazes and bodies was studied, using an electric tube furnace together with a liquid evaporative generator (Figure 2). A gas circulation flowrate of $0.01 \text{ m}^3/\text{min}$ was used in every test. The thermal cycle consisted of heating at a rate of $15^\circ\text{C}/\text{min}$ with a 6min dwell at peak temperature.

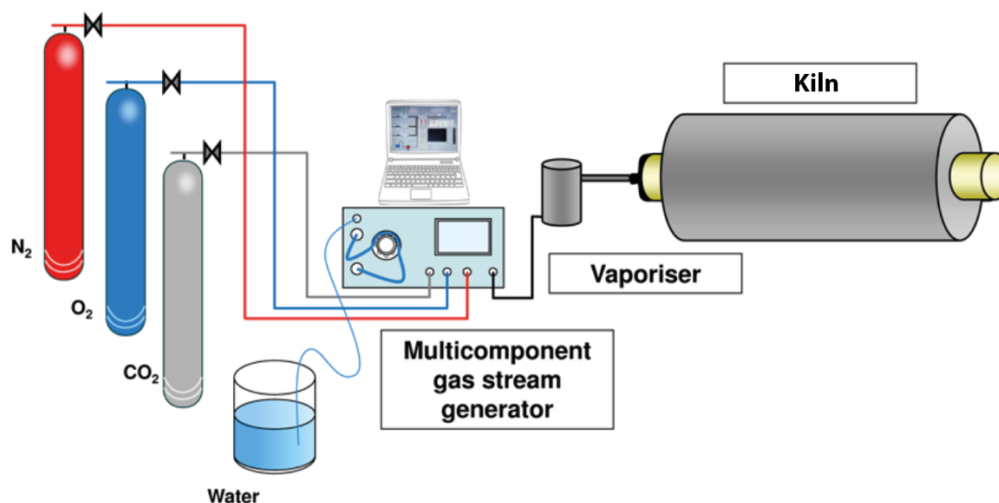


Figure 2. Scheme of the test equipment.

Three atmospheres were designed in order to reproduce (and even exceed) the increase in water vapour content in a roller kiln resulting from replacing natural gas with hydrogen (Table 1). As already remarked above, water vapour concentrations can vary from 18% in natural gas combustion to 35% in the case of using pure hydrogen.

Atmosphere	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
O ₂	10	10	10
CO ₂	10	10	10
N ₂	70	50	30
H ₂ O	10	30	50

Table 1. Atmospheres used.

Three types of ceramic bodies were used: a spray-dried powder for red-firing stoneware tile, a spray-dried powder for porcelain stoneware tile, and a spray-dried powder for red-firing earthenware tile. The body sintering curves were obtained for each atmosphere used [2], microstructure was observed by SEM-EDX, and the fluorine emissions were calculated (determining fluorine content before and after firing with a selective electrode [3]).

With regard to the ceramic glazes, suspensions of three types of frits were prepared: transparent for earthenware tiles, opaque for earthenware tiles, and matt for porcelain stoneware tile. The suspensions were applied on a laboratory scale in the case of the transparent and opaque glazes on a red earthenware tile body and in the case of the matt glaze on a porcelain stoneware tile body. The coated pieces were fired at 1110°C in the case of the red earthenware tile body and at the optimum firing temperature in the case of the porcelain stoneware tile body in the firing atmospheres used previously. Colour and gloss were determined of the resulting fired glazed test pieces and their microstructure was observed by SEM-EDX. In addition, glaze test specimens were prepared and fired under the same conditions in order to subsequently determine their expansion coefficients. The sealing temperature of each glaze in the three test atmospheres was also determined.

4. RESULTS AND DISCUSSION

4.1 RED-FIRING STONEWARE TILE COMPOSITION

The sintering curves of the spray-dried stoneware tile powder are shown below [4]. Densification of the red-firing stoneware tile with rising water vapour partial pressure in the kiln atmosphere increased more markedly as firing temperature rose, owing to the decrease in liquid phase viscosity as water vapour content in the viscous glass increased.

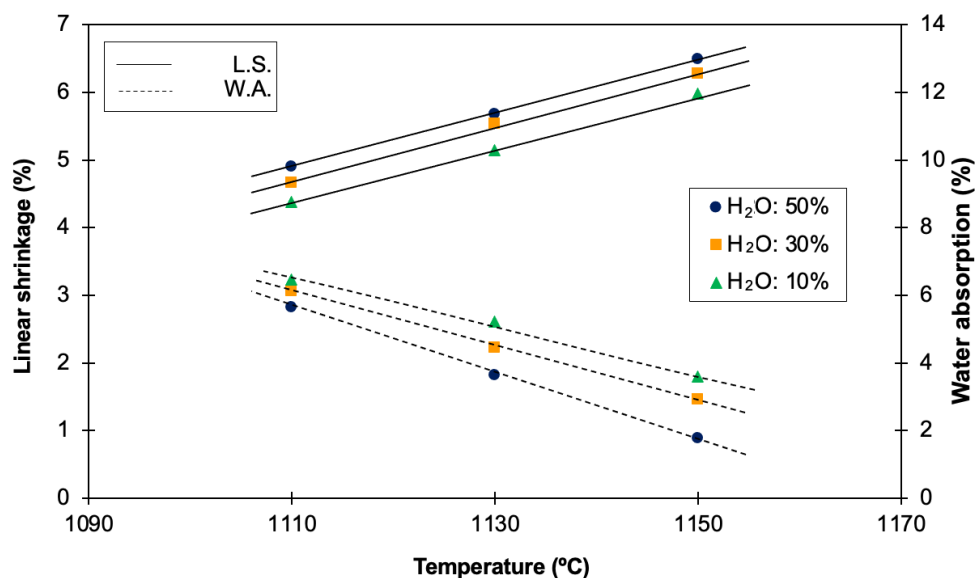


Figure 3. Sintering curves of the spray-dried red-firing stoneware tile powder at three water vapour concentrations.

Indeed, the increase in water vapour concentration in the kiln atmosphere entailed a higher water vapour concentration in the viscous liquid mass. This led to rupture of the Si–O–Si bonds and to formation of silanol groups (Si–OH) [4][5], which on the one hand considerably reduced glass phase viscosity [5] and, on the other, increased silicon cation diffusivity in the glass [4], favouring quartz dissolution. These phenomena raised glass phase content (more quartz dissolved) and lowered glass viscosity. Both factors increased the viscous flow sintering rate, the mechanism responsible for red-firing stoneware tile densification. This was confirmed by comparing the microstructures of the test specimens fired at 1150°C under extreme water vapour concentrations (10 and 50 vol%). They exhibited significant differences in their porous texture (Figure 4), the piece fired in the highest water vapour atmosphere displaying 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 20°C (Figure 3 and Table 2).

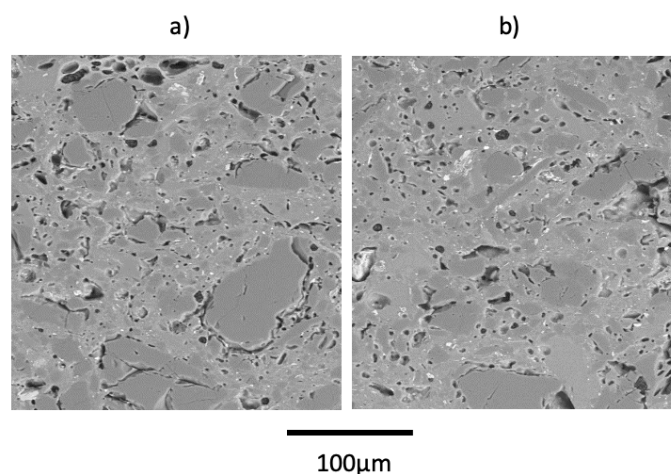


Figure 4. SEM micrographs of the red-firing stoneware tile fired at 1150°C, in different kiln atmospheres: a) 10 vol% water vapour and b) 50 vol% water vapour.

In addition to the temperature required to reach the 3% water absorption mentioned above, Table 2 details the properties of the pieces at this temperature.

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Temperature (°C)	1158	1148	1137
Linear shrinkage (%)	6.2	6.2	6.0
Water absorption (%)	3.0	3.0	3.0
Bulk density (g/cm ³)	2.380	2.380	2.360
Mechanical strength (MPa)	48±3	47±3	46±3
Modulus of elasticity (GPa)	51±1	51±2	49±2
Pyroplasticity index (cm ⁻¹ × 10 ⁵)	2.3	2.1	2.2

Table 2. Firing temperature at which the piece reached 3% water absorption and properties at this temperature.

The results obtained indicate that there were no significant changes associated with the kiln atmosphere. In contrast, the increase in water vapour content with the use of hydrogen instead of natural gas significantly raised fluorine emissions, as Figure 5 shows. This was because water vapour reacted with the fluorine present in the piece, forming HF and thus increasing fluorine emissions [3].

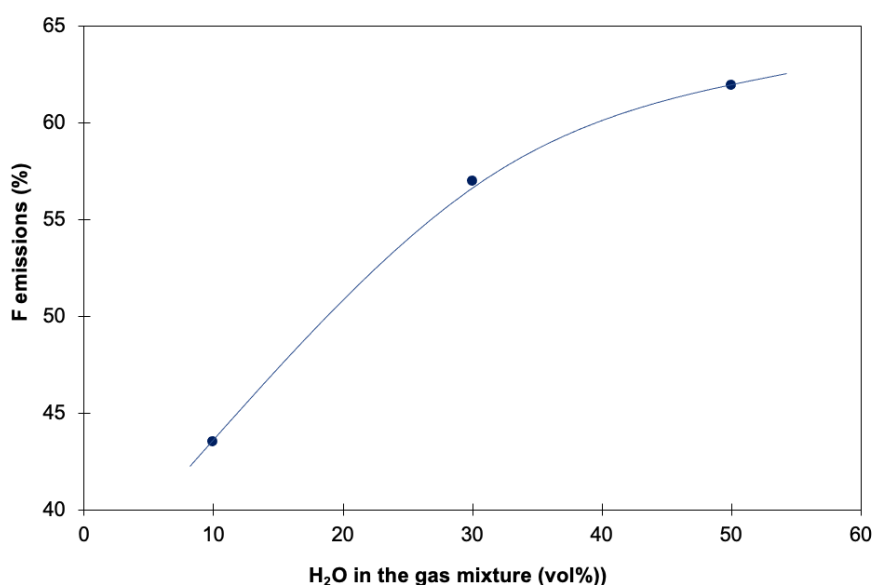


Figure 5. Variation of fluorine emissions (percentage of fluorine emitted with respect to the fluorine present in the unfired piece) at a firing temperature of 1130°C with water vapour content in the gas mixture.

4.2 RED-FIRING EARTHENWARE TILE COMPOSITION

The sintering curves of the spray-dried earthenware tile powder are shown in Figure 6, while Table 3 details the properties of the pieces at 1110°C, the typical firing temperature for red-firing earthenware tiles in industrial practice.

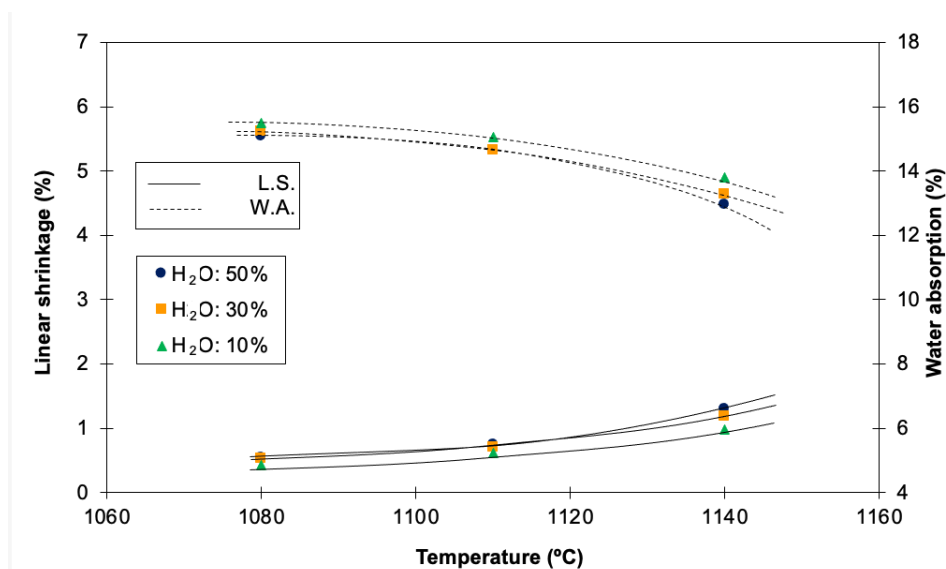


Figure 6. Sintering curves of the spray-dried red-firing earthenware tile powder for the three water vapour concentrations.

The results obtained indicate that, in this type of composition, there was a small increase in fusibility, but neither the mechanical properties nor moisture expansion varied significantly as a function of kiln atmosphere. This was due to the smaller amount of viscous liquid phase that developed, compared to that in the red-firing stoneware tile, which led water vapour concentration to influence this type of composition less.

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Linear shrinkage (%)	0.62	0.70	0.74
Water absorption (%)	15.1	14.6	14.8
Bulk density (g/cm ³)	1.902	1.908	1.912
Mechanical strength (MPa)	27 ± 1	26 ± 1	27 ± 1
Modulus of elasticity (GPa)	24 ± 1	24 ± 1	24 ± 1
Moisture expansion (‰)	0.6	0.6	0.6

Table 3. Properties of the spray-dried red-firing earthenware tile powder at a temperature of 1110°C

4.3 PORCELAIN STONEWARE TILE

The effect of kiln atmosphere on the firing behaviour and properties for a water absorption of 0.5% (industrial firing conditions for porcelain stoneware tile) is shown in Figure 7 and Table 4. As occurred with the spray-dried red-firing stoneware tile powder, the increase in water vapour content in the gas stream raised fusibility, which enables firing temperature to be lowered. Indeed, as water vapour pressure in the kiln atmosphere increased, water vapour concentration rose in the material's abundant liquid phase, lowering liquid phase viscosity. This phenomenon, in turn, raised sintering rate and quartz dissolution. As a result, firing temperature needs to be reduced to keep tile porosity at the pre-set value.

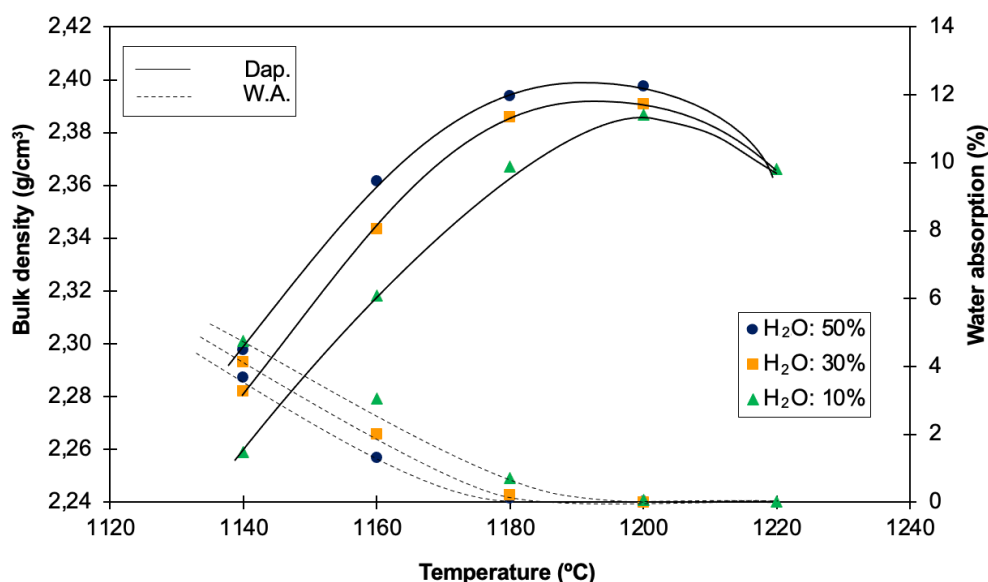


Figure 7. Sintering curves of the spray-dried porcelain stoneware tile powder for the three water vapour concentrations.

On the other hand, as in the case of the spray-dried red-firing stoneware tile powder, the properties of the pieces at the same water absorption exhibited no significant changes as a result of kiln atmosphere except for density which, as with maximum density, also increased slightly with water vapour concentration. These changes in density indicate that the closed porosity generated during the sintering process decreased as water vapour pressure increased. Indeed, analysis of the material's microstructure shows that, in the test specimen fired at the highest temperature and lowest water vapour pressure, the number and size of closed pores and pore sphericity rose (Figure 8). This suggests that the effect of firing temperature on the closed porosity generated during porcelain tile sintering was greater than the decrease in viscosity stemming from the increase in water vapour pressure [6].

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Temperature(°C)	1183	1175	1170
Linear shrinkage (%)	7.5	7.4	7.5
Water absorption (%)	0.5	0.5	0.5
Bulk density (g/cm ³)	2.370	2.382	2.382
Mechanical strength (MPa)	73 ± 4	74 ± 4	72 ± 4
Modulus of elasticity (GPa)	68 ± 3	68 ± 3	68 ± 3
Pyroplasticity index (cm ⁻¹ x 10 ⁵)	2.3	2.4	2.5

Table 4. Firing temperature at which the piece reached 0.5% water absorption and properties at this temperature.

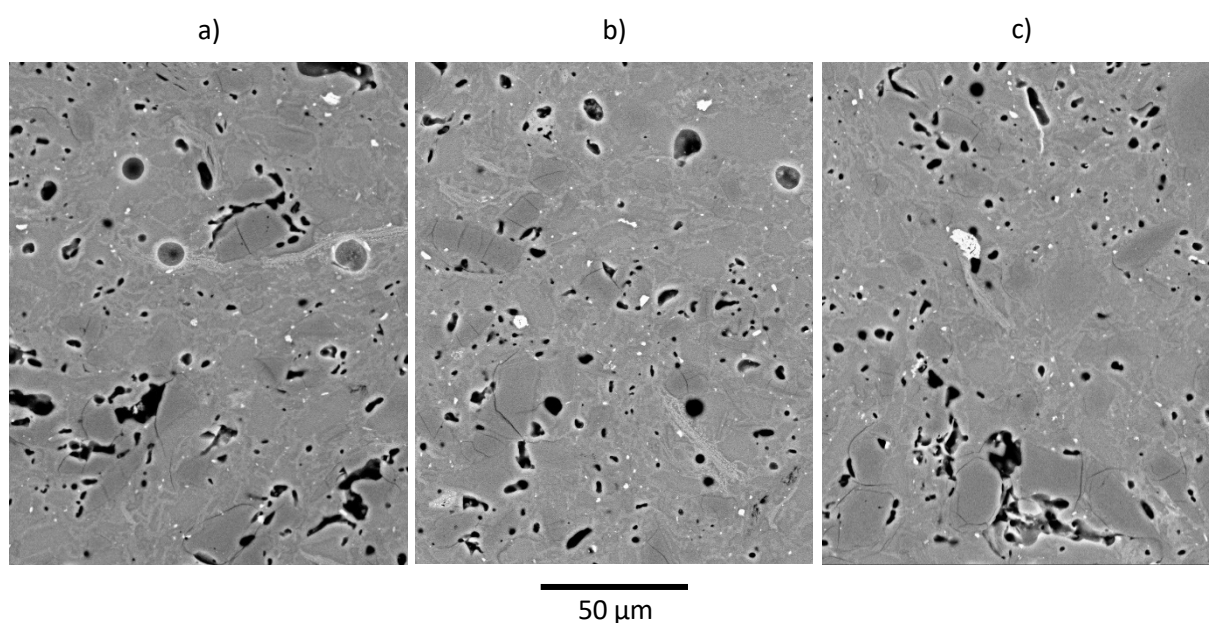


Figure 8. SEM micrographs of the porcelain stoneware tile fired at different kiln temperatures in different atmospheres: a) 1183°C and 10 vol% water vapour; b) 1175°C and 30 vol% water vapour; c) 1170°C and 50 vol% water vapour.

4.4 TRANSPARENT GLAZES FOR EARTHENWARE TILE

As was to be expected as a result of the influence observed on the viscosity of the liquid phase generated in the porcelain stoneware tile and stoneware tile compositions, water vapour concentration also influenced the resulting transparent glaze characteristics. The following figure shows the variation of gloss with the rise in water vapour concentration. A significant increase in gloss may be observed when water vapour concentration rose from 10 to 30%, which subsequently decreased slightly at higher concentrations.

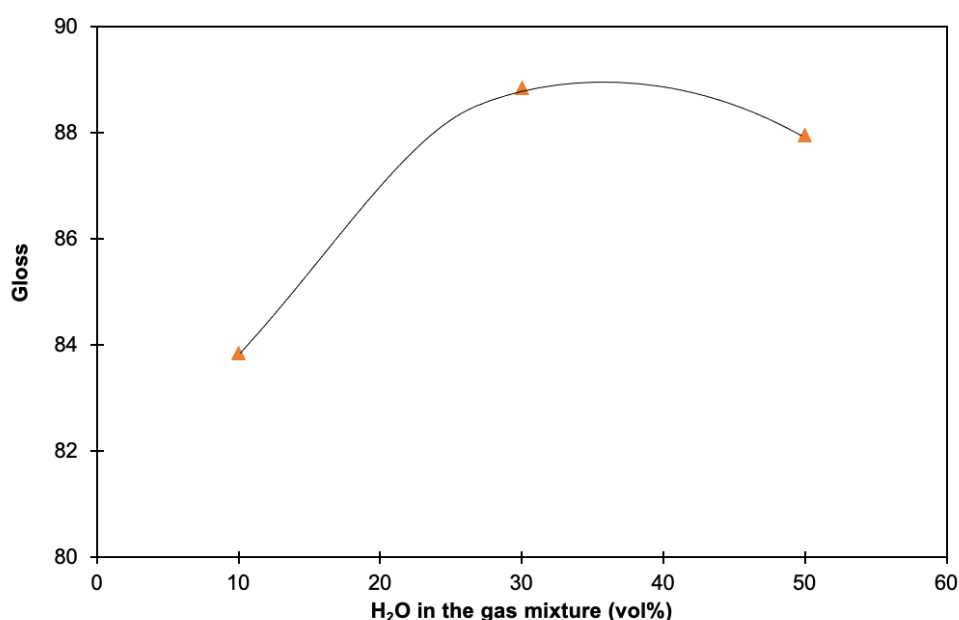


Figure 9. Gloss variation of the transparent glaze fired at 1110°C with water vapour content in the gas mixture. Gloss measured at 60°.

Sealing temperature also changed as water concentration rose, as Figure 10 and Table 5 show. In this case, the effect developed at the highest water concentration, at which sealing temperature decreased by about 20°C in relation to the other two atmospheres. In addition, as may be observed in Figure 10, in which the gloss measured at an angle of 80° (appropriate angle for very low gloss) is plotted, the sealing at lower temperature paralleled an early onset of glossy glaze development.

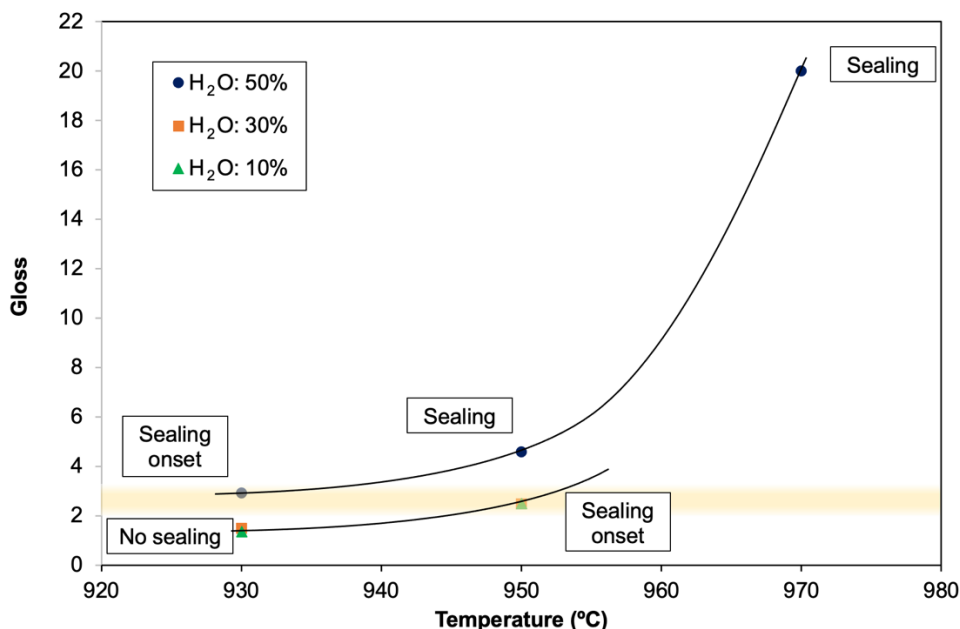


Figure 10. Evolution of the gloss measured at an angle of 80° in the glaze sealing temperature range.

The variation in gloss with increasing water vapour pressure in the kiln atmosphere correlated with the crystallised area in the surface of the vitreous coat (Figure 11 and Figure 12). This behaviour developed because a moderate decrease in viscosity of the glass phase favoured surface crystallisation of hardystonite (calcium and zinc silicate) in the glaze (b in Figure 11 and in Figure 12). In contrast, an excessive decrease in viscosity led to dissolution of the previously devitrified crystalline phase (c in Figure 11 and in Figure 12). Therefore, the crystal crystallisation/dissolution phenomena, whose rate increased as glass phase decreased, determined fired glaze surface appearance.

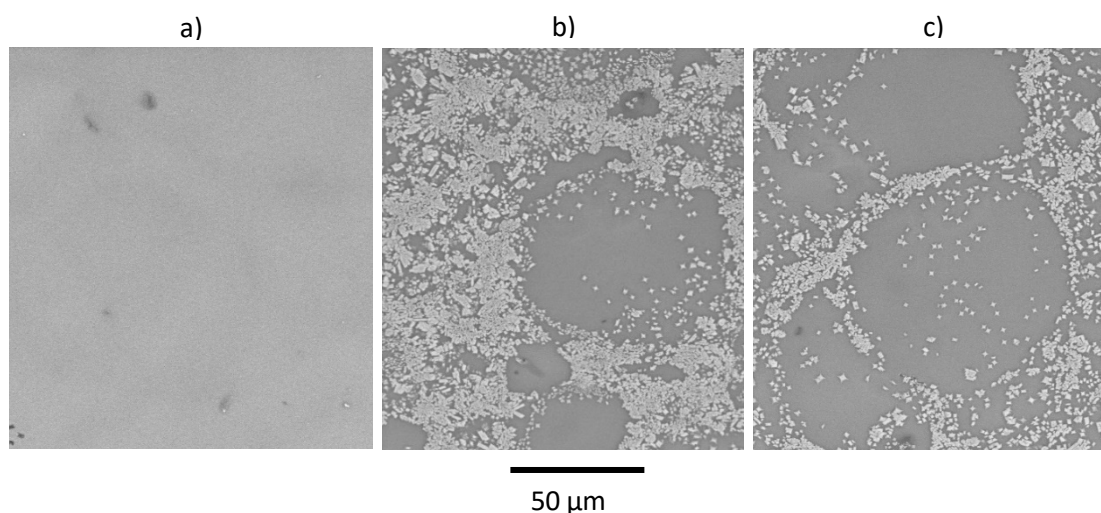


Figure 11. SEM micrographs of the surface of the transparent glaze fired at 1100°C in different kiln atmospheres: a) 10 vol% water vapour; b) 30 vol% water vapour; c) 50 vol% water vapour.

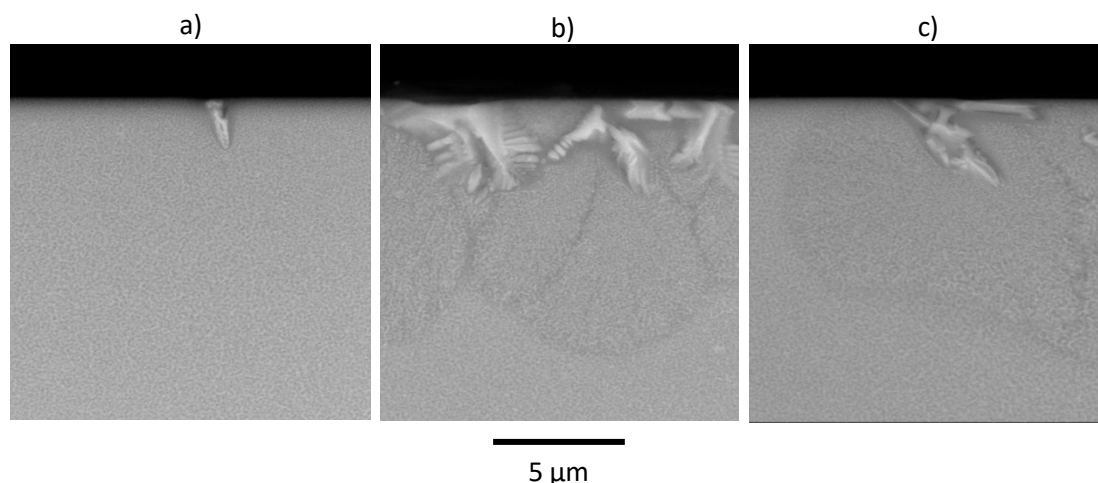


Figure 12. SEM micrographs of the surface of the transparent glaze fired at 1100°C in different kiln atmospheres: a) 10 vol% water vapour; b) 30 vol% water vapour; c) 50 vol% water vapour.

To complete the study of the influence of water vapour concentration during firing on glaze properties, in addition to the sealing temperatures and gloss values already discussed, Table 5 details the chromatic coordinates, which did not vary significantly. The table also includes the dilatometric analysis data, which again reveal a slight rise in fusibility in the 30–50% water vapour range, judging by the softening temperatures.

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Sealing temperature (°C)	950	950	930
Chromatic coordinate L*	90.3	90.6	90.8
Chromatic coordinate a*	-1.4	-1.9	-1.8
Chromatic coordinate b*	-2.5	-2.6	-2.5
Gloss (β) angle 60°	84	89	88
α_{50-300} (°C ⁻¹ ·10 ⁷)	62	58	60
Transformation temperature (°C)	653	652	649
Softening temperature (°C)	790	790	773

Table 5. Sealing temperature and properties of the vitreous coats obtained with the transparent glaze at a firing temperature of 1110°C.

4.5 OPAQUE GLAZES FOR EARTHENWARE TILE

As in the case of the transparent glazes, opaque glaze gloss increased as water vapour concentration rose from 10 to 30%, after which it decreased slightly at higher concentrations (Figure 13). The effect on sealing temperature was also noted, this being even greater than in the transparent vitreous coat (Figure 14).

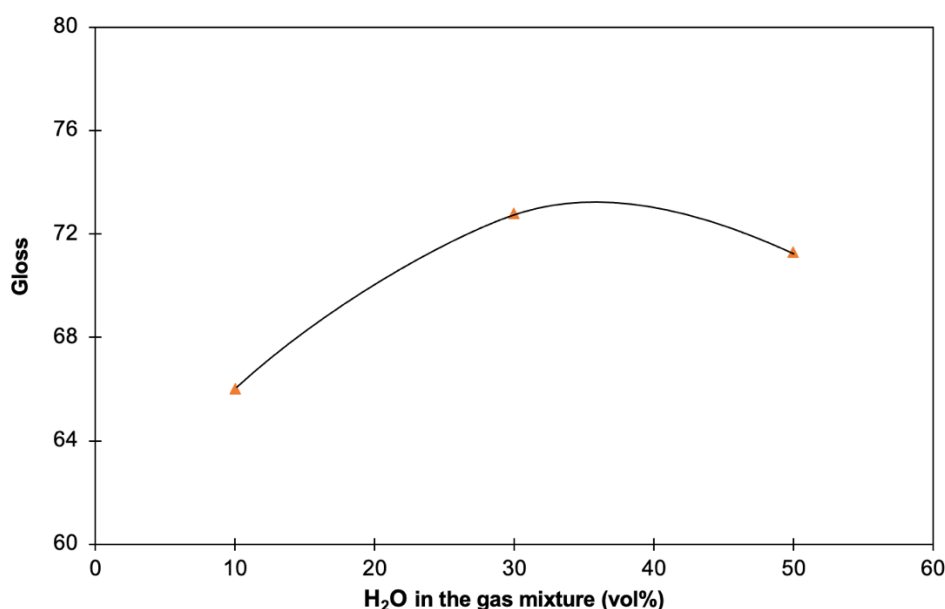


Figure 13. Gloss variation of the opaque glaze fired at 1110°C with water vapour content in the gas mixture. Gloss measured at 60°.

In regard to the surface microstructure of the vitreous coat (Figure 15), as water vapour pressure rose in the kiln atmosphere and, with it, water vapour concentration in the glaze surface, the zircon crystals became less evident, probably because they sank more deeply into the glaze and/or as a result of their partial dissolution. In both cases, the decrease in glass phase viscosity, mainly close to the surface, favoured both phenomena. These changes in microstructure and glass phase viscosity were responsible for the changes in gloss.

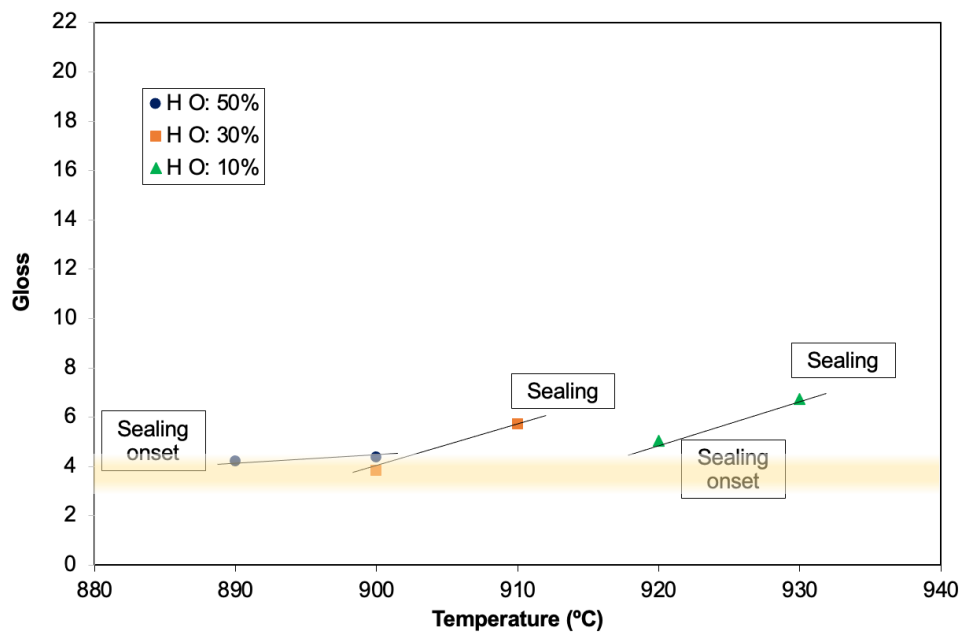


Figure 14. Evolution of the gloss measured at an angle of 80° in the glaze sealing temperature range.

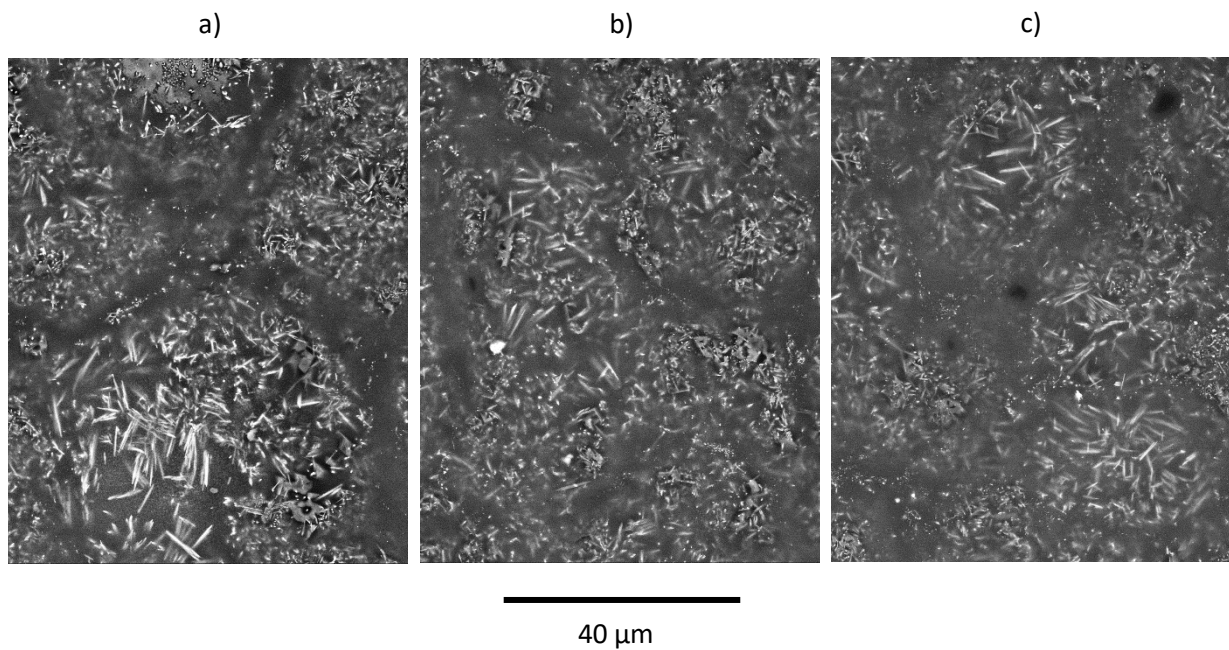


Figure 15. SEM micrographs of the surface of the opaque glaze fired at 1100°C in different kiln atmospheres: a) 10 vol% water vapour; b) 30 vol% water vapour; c) 50 vol% water vapour.

The internal microstructure of the vitreous coat (Figure 16) consisted of dark areas that contained acicular zircon crystals and, in smaller amounts, of irregularly shaped dark crystals of some (calcium and/or magnesium) silicate. These areas, with high calcium and zinc content, were surrounded by a clear glass phase from which numerous acicular zircon crystals had devitrified. Both areas exhibited phase separation, with interconnected drops. As water vapour pressure in the kiln atmosphere increased, the number of dark areas decreased; however, they were large and preferentially concentrated in the uppermost area of the vitreous coat.

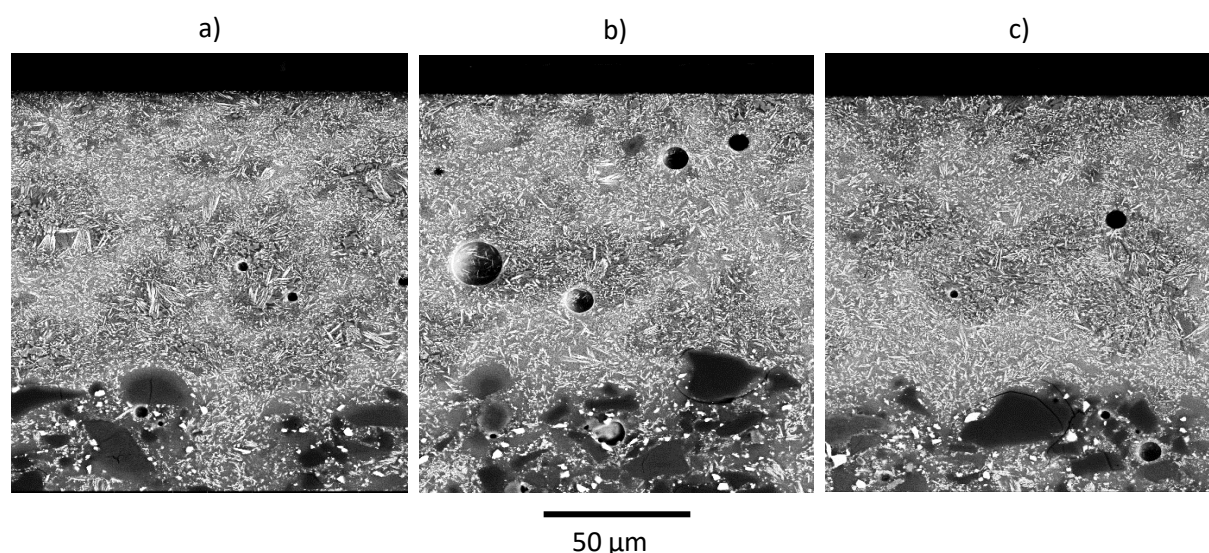


Figure 16. SEM micrographs of the cross-section of the opaque glaze fired at 1100°C in different kiln atmospheres: a) 10 vol% water vapour; b) 30 vol% water vapour; c) 50 vol% water vapour.

To complete the study of the influence of water vapour concentration during firing on resulting glaze properties, in addition to the sealing temperatures and gloss values already discussed, Table 6 details the chromatic coordinates and dilatometric analysis data. In this case, no significant variation of any of these parameters was observed.

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Sealing temperature (°C)	920	900	900
Chromatic coordinate L*	92.2	92.1	91.9
Chromatic coordinate a*	-0.3	-0.4	-0.4
Chromatic coordinate b*	0.1	0.0	0.0
Gloss (β) angle 60°	66	73	71
α_{50-300} (°C ⁻¹ ·10 ⁷)	62	60	60
Softening temperature (°C)	906	906	906

Table 6. Sealing temperature and properties of the vitreous coats obtained with the opaque glaze at a firing temperature of 1110°C.

4.6 MATT GLAZES FOR PORCELAIN STONEWARE TILE

To round off the study of the influence of water vapour concentration on the properties of the resulting glazes, a matt glaze for porcelain stoneware tile was selected as it required higher firing temperatures than the previous ones and provided a very different finish. In this case, the properties were studied by taking into account the variation in fusibility of the porcelain tile body discussed above, which caused the optimum firing temperature to decrease with the increase in water vapour concentration. Table 7 shows that, in this case, changes in gloss were not observed, which is logical in light of the low values obtained, as a matt glaze was involved, and the aforementioned decrease in firing temperature.

	H ₂ O: 10%	H ₂ O: 30%	H ₂ O: 50%
Sealing temperature (°C)	1130	1130	1120
Temperature (°C)	1183	1175	1170
Chromatic coordinate L*	91.1	91.0	90.8
Chromatic coordinate a*	-0.3	-0.2	-0.2
Chromatic coordinate b*	3.6	3.6	3.6
Gloss (β) angle 60°	7	8	8
Gloss (β) angle 85°	36	37	35
α_{50-300} (°C ⁻¹ ·10 ⁷)	60	62	62
Softening temperature (°C)	1065	1060	1070

Table 7. Sealing temperature and properties of the vitreous coats obtained with the matt glaze at the firing temperature required to reach a water absorption of 0.5% in the porcelain stoneware tile body.

5. CONCLUSIONS

The study conducted on the effect of kiln atmosphere on the firing behaviour of different types of ceramic bodies and glazes allowed the following conclusions to be drawn:

- In the case of porcelain stoneware tile and red-firing stoneware tile bodies, the increase in water vapour partial pressure facilitated sintering, so that optimum firing temperature decreased. In the case of red-firing earthenware tile, no significant changes were observed, owing to the smaller amount of glass phase that developed in this type of composition. In contrast, the increase in water vapour partial pressure raised fluorine emissions.
- In the resulting ceramic glazes, a greater effect of water vapour pressure was again observed in the glazes that exhibited more glass phase, namely the transparent and opaque glazes, no significant changes being noted in the studied matt glaze. In the transparent and opaque glazes, the changes in glass phase viscosity modified the glass and crystalline phases present, as well as the gloss, in the fired glaze, gloss increasing in the fired pieces as water vapour pressures rose.

6. ACKNOWLEDGEMENTS

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