REDUCING THE ATMOSPHERIC EMISSIONS OF CO_2 DURING THE FABRICATION OF SINGLE-FIRED POROUS TILES

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1. ABSTRACT

Large amounts of carbon dioxide are emitted into the atmosphere during the fabrication of ceramic tiles. In the ceramic industry, the combustion of natural gas produces CO_2, a subject of international control due to its environmental damage. Furthermore, the thermal decomposition, during firing, of carbonates used in the bodies contributes to increasing CO_2 emissions.

The objective of this work was to contribute to the reduction of atmospheric emissions of carbon dioxide in the fabrication of single-fired porous tiles. This type of ceramic tiles usually presents 40% higher CO_2 emissions than the average values emitted during the fabrication of other types of ceramic tiles. The presence of carbonates (usually calcite) in the composition of porous tiles is responsible for increasing natural gas consumption during firing and, together with the CO_2 produced by thermal decomposition of the carbonates, contributes to generating high levels of carbon dioxide emissions – in general above 320 kg CO_2/ton of fired product.

The work was developed in two parts. In the first part, two industrial compositions for the fabrication of single-fired porous tiles were processed by the dry route. The compositions were milled in hammer and ball mills and, after that, they were granulated in an Eirich microgranulator. The performances of the dry route compositions were compared to those of the industrial compositions prepared by ball milling and spray drying. The results showed that the dry route process produces good results, considering the technological behaviour of the bodies during the fabrication and the properties of the final product. The dry route process has the potential to reduce the CO_2 emissions arising in the fabrication of porous tiles by 30%, owing to the absence of the spray drier in this route.

In the second part, compositions of porous bodies were developed reducing or eliminating the presence of carbonates in the initial mixtures. Several raw materials and compositions were evaluated, considering their performances during the fabrication and the characteristics required for porous tiles, according to the international standard ISO 13.006.

The results suggested that reductions up to 60% in CO_2 emission, in comparison with the traditional compositions and process, are possible, without adversely affecting the technical characteristics of the final product.

In view of the necessary efforts in the next years to improve the sustainability of the ceramic tile industry, the developed product is an important alternative for increasing energy efficiency and reducing atmospheric emissions in the ceramic sector.

2. INTRODUCTION

The continuous growth of ceramic tile production in the last few decades has led to a significant increase in carbon dioxide emissions into the atmosphere. In the ceramic tile sector, CO_2 is generated in different stages of the fabrication process, especially due to fuel combustion. In Brazil, natural gas is the main fuel used in the ceramic sector and its consumption has increased by more than 60% in the last ten years[1], as shown in Fig. 1.

The atmospheric emissions of CO_2 have been the subject of international control policies in the last years because they are directly related to the greenhouse effect and global warming.

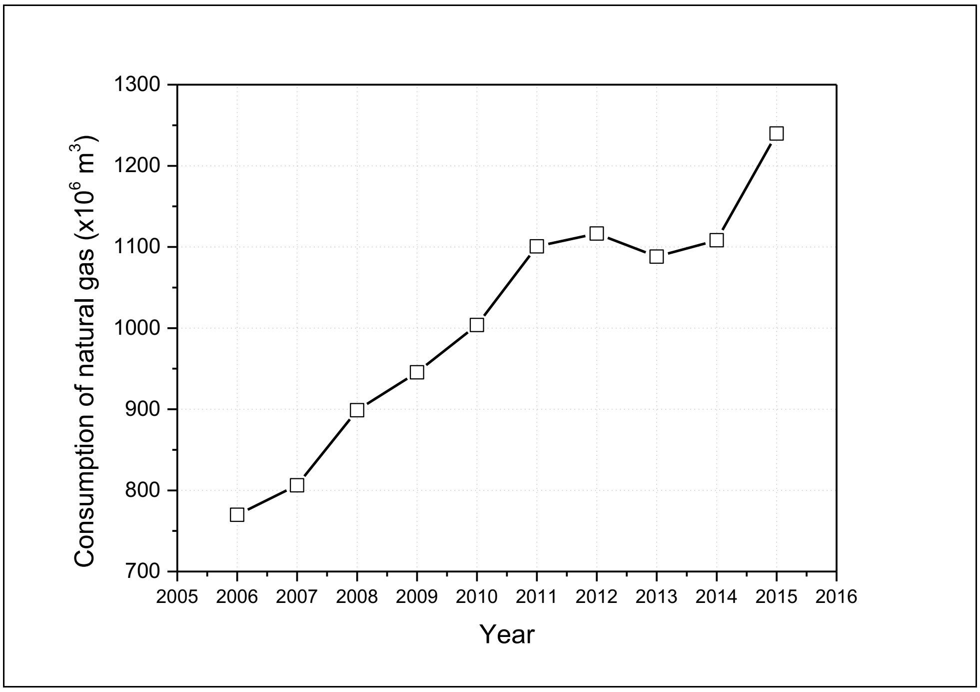

***Figure 1**. Evolution of natural gas consumption in ceramic tile production in Brazil[1].*

Considering the different classes of ceramic tiles, porous tiles (BIII) stand out because of the high level of atmospheric emission. This type of ceramic tiles presents 40% higher CO_2 emissions than the average values emitted in the fabrication of the other types of ceramic tiles[2]. The presence of carbonates (usually calcite) in the compositions of porous tiles is responsible for the increase in natural gas consumption during firing and, together with the CO_2 produced by thermal decomposition of the carbonates, contributes to generating high levels of carbon dioxide emissions - in general above 320 kg CO_2/ton of fired product[2].

Porous tiles are intended for wall cladding. For this reason, they are characterized by great dimensional precision, while the mechanical properties are less important. Their high porosity (specified by water absorption higher than or equal to 10%) contributes to the adhesion with mortar during installation. The usual way to achieve the required properties - high dimensional precision and high water absorption after firing – consists of using compositions containing high levels of calcium carbonates processed by the wet route and single firing.

The wet route is traditionally used in the production of porous tiles because it represents the classic way to achieve a small particle size and good homogeneity of the batches after milling. Calcium carbonate[3] (calcite) is responsible for dimensional precision. In some cases, calcareous clays[3] may be used in the batches as a source of calcium carbonates.

Previous works[4,5] have studied the role of calcium carbonates in porous tiles. During firing, calcium carbonates decompose into calcium oxide and carbon dioxide between 850°C and 950°C. The decomposition is strongly affected by particle size[6]. The calcium oxide obtained is very reactive and generally interacts with decomposed clays and quartz to generate crystalline phases (anorthite, gehlenite, wollastonite, etc.). The new phases have lower densities than the precursor phases, so that a small expansion is produced in the bodies during their formation (Fig. 2). The expansion partially compensates the firing shrinkage, so that, in general, the resultant linear firing shrinkage is lower than 1.5%. However, as discussed before, the presence of calcium carbonates in the bodies contributes to increasing the atmospheric emission of carbon dioxide.

In view of the general situation described, the main objective of this work was to contribute to the reduction of atmospheric emission of carbon dioxide in the fabrication of single-fired porous tiles. To achieve this, the possibility of producing single-fired porous tiles by the dry route, without the presence of calcium carbonates in the body composition, was studied.

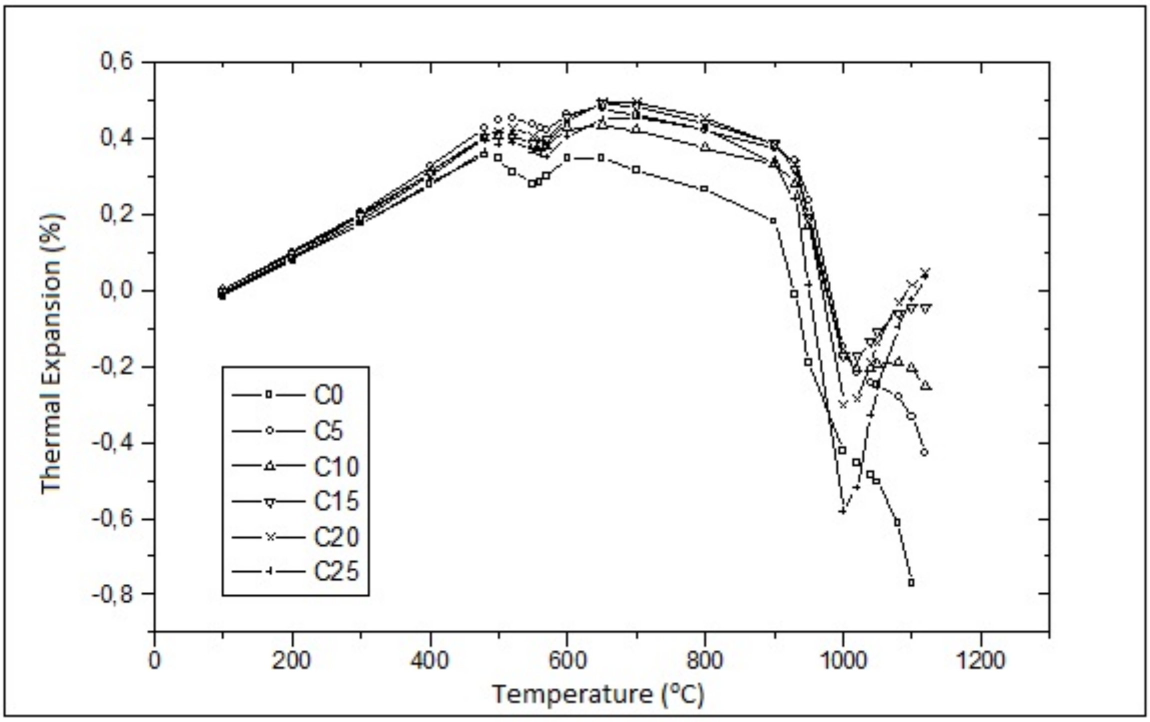

Figure 2. *Effects of the content of calcium carbonate (C0= 0% calcite; C5= 5% calcite,…, C25= 25% calcite) in the dimensional behaviour of single-fired porous tiles[4].*

3. METHODOLOGY

In the first part of the work, the feasibility of producing single-fired porous tiles by the dry route was studied. The literature[7] indicates that the average emission of CO_2 in the dry route is 40% lower than in the traditional process, the wet route. The main difference is due to the spray drier used in the wet route and absent in the dry route, which is responsible for a significant portion of the consumption of natural gas and, consequently, CO_2 emission.

To verify the potential of the dry route, in this work two industrial compositions (WR-1 and WR-2) intended for single-fired porous tile manufacture were processed by the dry route and their performances were compared to the original compositions prepared industrially by the wet route. Initially, the chemical and mineralogical compositions of the industrial compositions were determined by x-ray fluorescence and x-ray diffraction. The same compositions then were milled in hammer and dry ball mills, using the same raw materials as in the batches prepared industrially by the wet route. The dry route milling was conducted in such a way as to achieve similar particle size distribution to the industrial slurries. The particle size distributions were determined by the sedimentation technique (Sedigraph III Plus).

The dry milled compositions (DR-1 and DR-2) were granulated in an Eirich microgranulator, tested in a previous study by the same authors[8]. The dry route granulation was carried out with the addition of 12.5% water to generate the granules. After that, the granules were dried at 60°C to obtain two different moisture contents: 6.5% (similar to the industrial compositions prepared by spray drying) and 9.0% (according to the conclusions drawn in previous works[8] to improve the deformation of the granules in the pressing process).

The performances of the dry route compositions (DR-1 and DR-2) were compared with those of industrial compositions prepared by ball milling and spray drying (WR-1 and WR-2). Their grain size distributions were analysed by vibratory sieving during 10 minutes and their flow properties were determined by the Hausner ratio. Then, prismatic bodies of 60 x 20 x 6 mm were pressed at 300 kgf/cm^2 in an automatic laboratory press. The green bodies were characterized by the following analyses: bending strength after drying at 110°C; linear drying shrinkage, bulk density after drying. The bodies were subsequently fired at different temperatures in 35-minute firing cycles. The water absorption and linear firing shrinkage of the bodies were determined. Finally, the loss on ignition, bending strength, chromatic coordinates, thermal expansion coefficient and moisture expansion (2 hours under pressure of 5 kgf/cm^2) of the bodies fired at 1100°C, were evaluated.

In the second step of this work, different raw materials were tested as alternatives to replace calcite in a typical composition for the production of single-fired porous tiles. Table I shows the planned batches, where the feasibility of direct substitution of calcite by several raw materials was evaluated.

The compositions were prepared by the dry route, similar to the first part of this work. The milling was performed in hammer and ball mills. However, considering the number of tests and their exploratory nature, in this part the granulation was carried out in laboratory sieves with 7.0% moisture. Prismatic bodies were pressed at 300 kgf/cm^2 and the following analyses were performed: bulk density after drying, bending strength after drying, water absorption, linear firing shrinkage, bending strength after firing, thermal expansion coefficient, chromatic coordinates and moisture expansion. The bodies were fired in 35-minute cycles and the maximum temperature was the temperature needed to achieve linear firing shrinkage between 1.0 and 2.0%.

Raw materials (%)	STD	RC 1	RC 2	RC 3	RC 4	RC 5	RC 6	RC 7	RC 8	RC 9	RC 10
Clay A016	16	18.2	16	16	16	16	16	16	16	16	16
Clay A017	14	15.9	14	14	14	14	14	14	14	14	14
Clay MP029	3	3.4	3	3	3	3	3	3	3	3	3
Kaolin	15	17.0	15	15	15	15	15	15	15	15	15
Talc	8	9.1	8	8	8	8	8	8	8	8	8
Phyllite	32	36.4	32	32	32	32	32	32	32	32	32
Calcite	12	-	-	-	-	-	-	-	-	-	-
Quartz	-	-	12	-	-	-	-	-	-	-	-
Diopside	-	-	-	12	-	-	-	-	-	-	-
Wollastonite	-	-	-	-	12	-	-	-	-	-	-
Sanitaryware chamotte	-	-	-	-	-	12	-	-	-	-	-
Porcelain tiles chamotte	-	-	-	-	-	-	12	-	-	-	-
Lime	-	-	-	-	-	-	-	12	-	-	-
Agalmatolite	-	-	-	-	-	-	-	-	12	-	-
Feldspar	-	-	-	-	-	-	-	-	-	12	-
Gypsum	-	-	-	-	-	-	-	-	-	-	12

Table I. *Tested batches to replace calcite in the single-fired porous tile composition.*

4. RESULTS

The chemical and mineralogical analysis of the industrial compositions prepared by the wet route is presented in Table II. Both bodies present high CaO and LOI values, as usually found in typical compositions for single-fired porous tile manufacture. In the mineralogical analysis, we can see the presence of calcite in contents higher than 10% in the two compositions. The main difference between WR-1 and WR-2 is the SiO_2/Al_2O_3 ratio, higher in WR-2 owing to its higher quartz content. WR-1 contains a larger proportion of kaolinite.

Fig. 3 shows a plot of the particle size distributions of WR-1 and WR-2 (industrially processed) together with the same compositions prepared in the laboratory, by dry milling, (DR-1 and DR-2). The results indicated that the particle sizes obtained in the milling by the dry route, in general, were very similar to those obtained industrially by wet milling.

The granules obtained in the dry route process achieved good flow properties, as shown in Table III by the Hausner ratio. The results are related to the granulation system used, which is able to generate granules of similar shape and sizes in comparison to the granules obtained by spray drying. Similar results were obtained in previous works described in the literature[8] with the same granulation system. Table III indicates that the flow properties of DR-1 and especially DR-2 are slightly lower because their fractions of fine granules are higher than in WR-1 and WR-2. In the case of DR-2, the composition with a lower clay mineral content, the increase in the moisture content contributes to reducing its Hausner ratio.

Elements (%)	WR-1	WR-2
LOI	9.81	9.98
SiO_2	59.46	61.22
Al_2O_3	17.63	14.28
Fe_2O_3	1.64	2.10
TiO_2	0.86	1.00
CaO	6.30	7.76
MgO	1.66	0.70
Na_2O	-	-
K_2O	2.44	2.34
P_2O_5	0.12	0.09
MnO	0.01	-
Kaolinite	27	19
Quartz	35	44
Mica muscovite	18	17
Microcline	2	2
Calcite	11	14
Talc	5	-

Table II. *Chemical and mineralogical analysis of the studied industrial bodies for single-fired porous tile manufacture.*

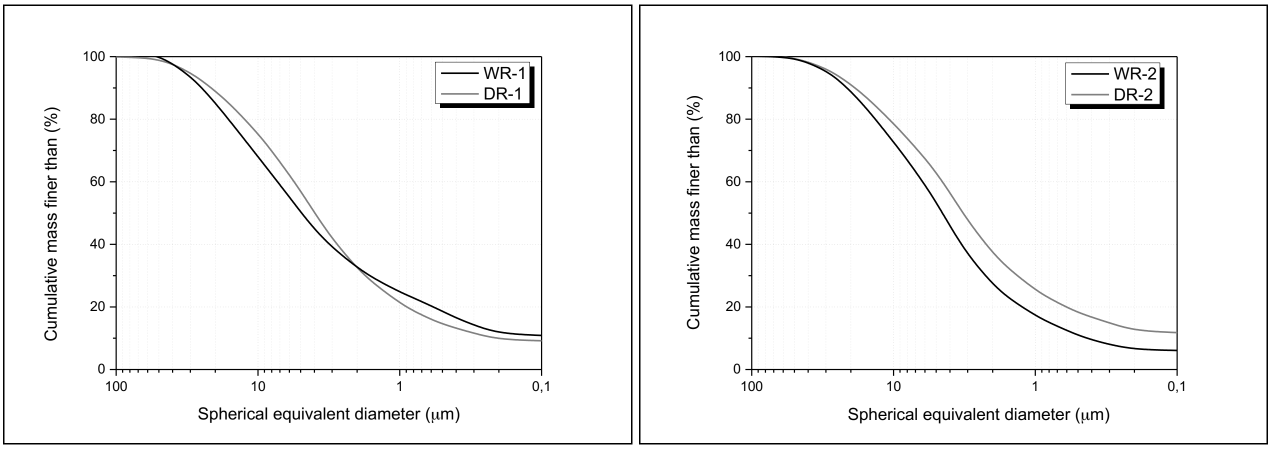

Figure 3. *Particle size distribution of the wet route (WR-1 and WR-2) and dry route (DR-1 and DR-2) bodies.*

Characteristics	WR-1	DR-1		WR-2	DR-2	
Moisture content (%)	5.8	6.4	9.4	6.1	6.0	9.3
Fraction > 500 μm (%)	16.7	9.5	8.4	13.4	11.0	11.1
Fraction between 180 – 500 μm (%)	75.1	60.2	58.4	74.4	42.7	43.2
Fraction < 125 μm (%)	3.1	14.4	15.7	5.1	28.6	24.5
Hausner ratio	1.120	1.185	1.170	1.165	1.205	1.270

Table III. *Characterization of the powders prepared by the wet and the dry route.*

The results of the characterization of the pressed bodies are presented in Table IV. The first significant result observed is the increase in the bulk density of the green bodies prepared by the dry route. Independently of the moisture content of their granules, compositions DR-1 and DR-2 presented bulk densities noticeably higher than WR-1 and WR-2. This can be explained by the characteristics of the granules prepared by the dry route[8].

The higher bulk density strongly influenced the behaviour of the bodies. Linear drying shrinkage of DR-1 and DR-2 was higher, especially for the compositions containing higher moisture contents. However, high moisture content is important for enhancing deformation of the granules prepared by the dry route[9]. The results of bending strength after drying show that the deformation of the granules is higher in the compositions DR-1 and DR-2 when they were pressed with moisture content around 9,0%. Higher deformation of the granules during pressing reduces the intergranular porosity of the green bodies, so that the modulus of rupture of the bodies after drying is much higher than DR-1 and DR-2 containing around 6.0% moisture in the pressing stage.

Characteristics		WR-1	DR-1		WR-2	DR-2	
Moisture content (%)		5.8	6.4	9.4	6.1	6.0	9.3
Bulk density after drying (g/cm^3)		1.91	2.06	2.07	1.90	2.05	2.12
Linear drying shrinkage (%)		0.05	0.16	0.26	0.07	0.20	0.37
Modulus of rupture after drying (MPa)		3.6	3.4	5.0	3.4	4.5	6.3
Water absorption – 1100°C (%)		16.7	13.7	11.5	17.3	17.1	12.2
Linear firing shrinkage – 1100°C (%)		1.8	1.3	1.2	1.4	0.7	0.5
Modulus of rupture – 1100°C (MPa)		22.0	17.4	24.5	22.0	17.1	23.8
Loss on ignition – 1100°C (%)		9.9	10.1	10.0	10.2	10.2	10.3
Thermal expansion coeff. (10^{-7} °C^{-1})		68.8	68.5	69.8	71.3	73.0	72.4
Moisture expansion (mm/m)		0.05	0.04	0.11	0.08	0.02	0.02
Chromatic coordinates	L*	76.7	72.8	71.8	68.0	64.9	63.3
	a*	7.7	9.1	9.2	10.5	12.2	12.8
	b*	19.0	19.6	20.0	19.6	20.4	20.8

Table IV. *Characterization of the bodies prepared by the wet and the dry route.*

The behaviour of the bodies during firing is shown by the vitrification curves (Fig .2). The characterization of the fired bodies at 1100°C is indicated in Table IV. Considering the importance of the dimensions for single-fired porous tiles, the results obtained by the bodies prepared by the dry route are very interesting. They show the feasibility of producing porous tiles with a water absorption equal to or lower than that of the wet route bodies, obtaining considerably lower firing shrinkages. The result is probably a consequence of the higher bulk density of the green bodies DR-1 and DR-2.

The mechanical behaviour of the fired bodies provides new evidence that DR-1 and DR-2 did not present acceptable deformation of the granules during pressing with 6.0% moisture. Despite the fact that their water absorptions were lower than that of WR-1 and WR-2, they presented a lower modulus of rupture. The problem is completely solved when the granules of the same compositions prepared by the dry route were pressed with a moisture content around 9.0%.

As expected, the powder preparation route did not affect the thermal expansion and moisture expansion of the fired bodies. Firing colours of the bodies prepared by dry route are relatively darker, probably as a result of their lower porosity. In any event, the differences are not significant.

Besides the technical results discussed, the dry route process represents an important contribution to enable single-fired porous tiles to be produced in a more sustainable way. The change from the wet route to the dry route alone allows a reduction of at least 22% natural gas consumption and, consequently, 22% decrease in carbon dioxide emission in the production of single-fired porous tiles.

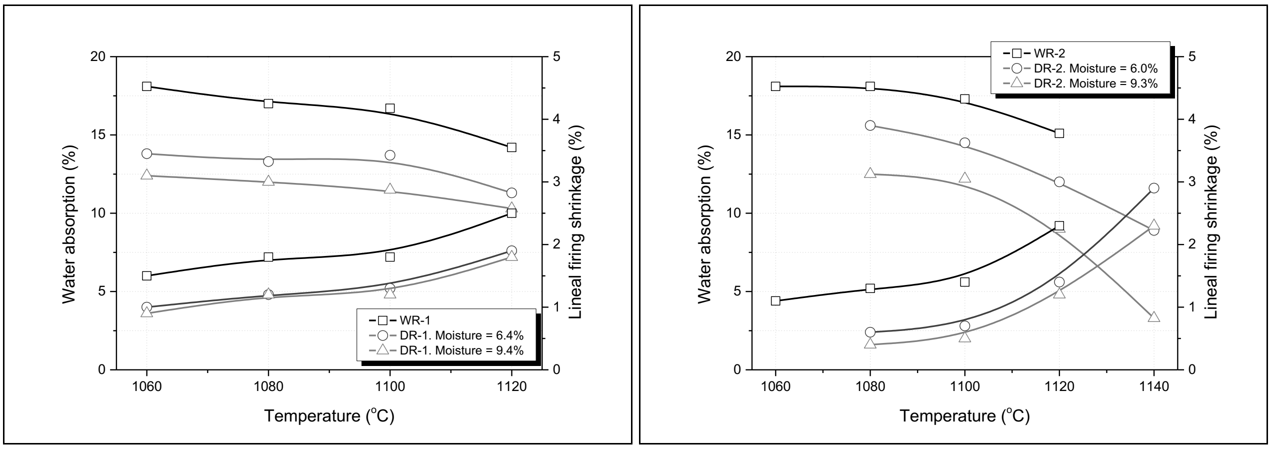

***Figure 4.** Vitrification curves of the bodies prepared by the wet and the dry route.*

In the second part of the work, in an attempt to substitute, partially or totally, the calcite present in the standard compositions (STD), several raw materials were tested. RC1 was an attempt to eliminate the calcite in which the proportion between the others raw materials was maintained. In RC2–RC10 new raw materials were introduced to replace the calcite. The results are presented in Table V.

The results obtained with the incorporation of quartz, diopside, chamottes, agalmatolite and feldspar in substitution for calcite have shown two technical difficulties: the decrease in the modulus of rupture and the increase in the moisture expansion of the fired bodies. The differences between the bodies, probably related to the formation of crystalline phases during firing, were very significant. On the other hand, the raw materials that incorporated calcium in the bodies achieved similar results to the STD composition. Consequently, the replacement of calcite with wollastonite, lime and gypsum could be considered as a way of avoiding the atmospheric emissions of CO_2 from calcium carbonate decomposition.

Wollastonite is the best option to avoid impairment of the modulus of rupture after firing and, at the same time, is very effective in keeping moisture expansion controlled. The feasibility of its incorporation into single-fired porous tiles is just limited by economic reasons.

The presence of lime and gypsum in the compositions also led to good results. The bending strength of the fired bodies as not as high as in the body containing wollastonite; however, it is sufficient for porous tiles. On the other hand, gypsum liberates sulphur during firing and these gases may cause some problems for the kiln and the atmosphere. Lime is a better option, because water is its only decomposition product. However, lime, in most cases, is obtained from the calcination of calcium carbonates. Thus, sources of industrial wastes of lime could be considered in the sequel of the project.

The reactions that take place when the alternative sources of calcium – wollastonite, gypsum and lime – were used were not studied in the present work. However, they will the object of future studies.

The feasibility of the elimination of calcite by these raw materials has the potential to reduce the emissions of 110 kg CO_2/ton (including the CO_2 generated and the energy needed to complete the decomposition process), accounting for 48% of the emissions of carbon dioxide involved in the production of porous tiles. The combination of the two strategies presented in this study – dry route process and replacement of calcite by other sources of non-carbonated calcium – allows a reduction of approximately 60% of the atmospheric emission of carbon dioxide in the production of single-fired porous tiles.

Characteristics		STD	RC 1	RC 2	RC 3	RC 4	RC 5	RC 6	RC 7	RC 8	RC 9	RC 10
Bulk density after drying (g/cm^3)		1.98	1.97	1.96	2.00	1.95	1.94	1.93	1.82	1.97	1.92	1.92
Modulus of rupture after drying (MPa)		2.3	2.7	1.9	2.0	2.5	2.2	2.0	3.7	2.5	1.7	3.2
Firing temperature (°C)		1120	1100	1100	1100	1100	1100	1080	1100	1100	1100	1070
Water absorption (%)		16.7	14.1	15.4	14.3	13.7	13.6	14.4	19.1	13.4	14.7	15.5
Linear firing shrinkage (%)		0.9	1.6	0.9	1.6	1.8	1.7	1.7	1.0	1.1	1.3	2.1
Modulus of rupture after firing (MPa)		23.7	16.8	10.8	16.5	25.2	17.7	16.7	19.8	13.8	12.4	18.1
Loss on ignition (%)		11.8	7.6	7.2	7.8	7.1	6.5	6.6	9.6	6.9	6.3	9.9
Thermal expansion coefficient ($10^{-7}\,°C^{-1}$)		68.3	63.2	68.6	69.2	70.2	63.4	67.7	68.4	59.5	58.9	67.7
Moisture expansion (mm/m)		0.12	1.34	1.34	0.91	0.28	1.23	1.24	0.26	1.23	1.22	0.43
Chromatic coordinates	L*	76.0	80.3	81.7	80.7	77.1	80.9	80.3	78.4	82.4	81.8	78.7
	a*	6.7	6.6	6.0	6.4	7.1	6.1	6.3	6.9	5.9	6.0	7.4
	b*	16.3	13.4	12.4	13.5	15.3	13.2	13.8	14.5	12.1	12.7	15.4

Table V. *Characterization of the bodies prepared to replace calcite in single-fired porous tiles.*

5. CONCLUSIONS

- The results showed the possibility of producing high-quality single-fired porous tiles, reducing at least 60% of the carbon dioxide emissions into the atmosphere. The use of the dry route process and the replacement of calcite by non-carbonated raw materials in the compositions were the strategies used to achieve that;
- The dry route process achieved better results with the pressing of granules containing 9.0% moisture to promote their deformation. Under these conditions, the mechanical behaviour of the bodies before and after firing were better;
- Single-fired porous tiles produced by the dry route achieved the desired water absorption with higher dimensional stability compared to the same compositions processed by wet route;
- The replacement of calcite by wollastonite, lime or gypsum represents promising alternatives for reducing carbon dioxide emissions without impairing the properties of the resulting bodies;
- The reactions that take place during firing when wollastonite, lime and gypsum are used to replace calcite and the compatibility between sources of raw materials, formulations and costs of production will be the studied in future works.

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