TOWARDS A LOW-CARBON ECONOMY IN THE CERAMIC SECTOR: CIRCULAR ECONOMY STRATEGIES

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INTRODUCTION

The ceramic tile industry is an energy-intensive industry, fundamentally in natural gas consumption, accounting for a total of 13.400 GWh in 2020. The level of CO_2 emissions in the cluster lies at 2,770,000 tCO_2/year. In this context, the European Green Deal [1] pursues a 55% reduction in emissions relative to 1990 by the year 2030, and zero emissions in 2050.

With such ambitious emissions reduction targets, the sector will need to radically modify the technologies used in its production process. As about 90% of the cluster's CO_2 emissions come from natural gas combustion [2], it is clear that achievement of a drastic reduction in emissions will require replacing natural gas as the source of thermal energy. The existing options include electrification of the processes (using renewable energy sources) and, more recently, use of hydrogen as direct source of thermal energy by combustion.

The above might lead to the conclusion that decarbonisation of the sector only needs to be considered from the viewpoint of production processes. However, this is not so. The design of new materials and ceramic compositions with lower energy consumption and/or reduced CO_2 emissions would not only contribute to mitigating the remaining 10% emissions, but it would also lower natural gas consumption and, therefore, its related emissions.

In fact, these new materials and compositions can be key to reducing the economic impact that the electrification of the processes or the progressive replacement of natural gas with hydrogen would involve.

This study sets out the results obtained in different research lines based on ceramic materials, many of which favour the changeover to a circular economy by incorporating waste and reducing the extraction of natural raw materials, while also using processes with lower environmental impact, in order to contribute to the targeted emissions reductions.

As noted above, natural gas combustion is responsible for 90% of the emissions, the spray-drying and firing stages accounting for the greatest gas consumption. Most of the research lines considered in this study focus, therefore, on lowering gas consumption in these two stages:

- Spray-drying stage:
    - Obtainment of ceramic suspensions with very high solids content from new mixtures of deflocculants.
- Firing stage:
    - Development of glass-based formulations with high fusibility that reduce energy consumption in the firing stage.
    - Formulation of wall tile compositions without carbonates.
    - Study of the suitability of alkali-activated materials and silico-calcareous products as alternatives to ceramic wall tiles.

A further line pursues emissions reduction by development of formulations with high mechanical strength to make tiles slimmer.

And, finally, a sixth line consists of developing porcelain stoneware tile formulations based on Spanish and Portuguese raw materials (reducing transportation-related emissions).

EXPERIMENTAL

Ceramic compositions were prepared by wet milling. The resulting suspensions were dried under infrared lamps and then deagglomerated by dry milling.

The rheological behaviour of the suspensions was characterised by obtaining their deflocculation curves with a GALLENKAMP viscometer with no. 30 torsion wire using a cylinder of 1.75-cm diameter.

The pressing and firing behaviour of the compositions was determined by forming test pieces by pressing at a moisture content of 5.5 ± 0.1% at different pressing pressures. The test pieces were dried in an electric oven at 110 ºC, their bulk density was measured and they were fired in an electric laboratory kiln at different maximum temperatures. The test pieces were characterised by determining their linear shrinkage, bulk density, and water absorption. Finally, some of the compositions were characterised, determining their dry and/or fired mechanical strength (three-point bending test), moisture expansion (after autoclave treatment for 5 hours with water vapour pressure of 10.2 kg/cm^2), and/or proneness to deform by pyroplasticity.

RESULTS AND DISCUSSION

CERAMIC SUSPENSIONS WITH VERY HIGH SOLIDS CONTENT

The spray-drying stage is responsible for about 35% of the CO_2 relating to natural gas. Reducing these emissions requires raising suspension solids content, while holding the viscosity needed for proper development of the milling and spray-drying stages. This lowers the amount of water to be evaporated per tonne spray-dried powder and decreases the amount of thermal energy needed from natural gas to do so [3].

The solids contents in ceramic suspensions currently vary between 63 and 67%, depending on the type of composition, water, and deflocculants used. An average content of 65% was therefore assumed to be representative of current spray-drying conditions. In accordance with **Figure 1**, achieving solids contents of 72% would lead to a 30% reduction in the emissions associated with this stage.

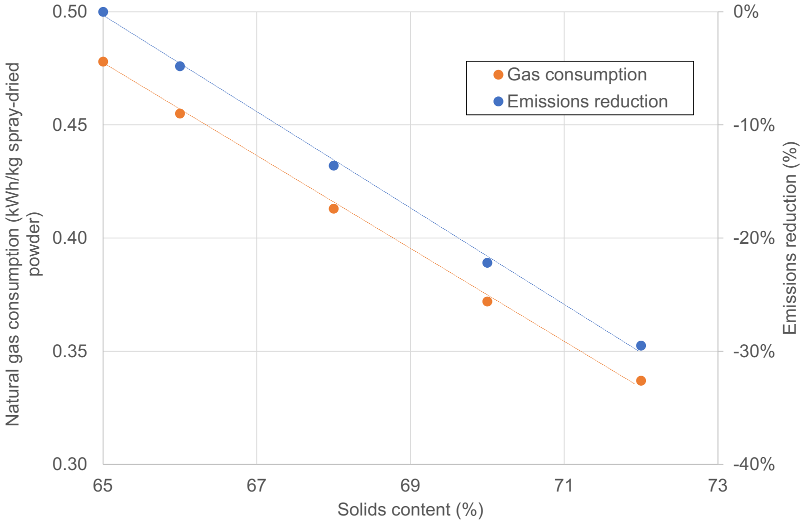

***Figure 1.** Gas consumption and emissions reduction as a function of solids content [3].*

Attempting to reach these solids contents requires, first, using water of very low hardness, such as that coming from reverse osmosis processes. But even with this water, it is necessary to use vigorous deflocculants to obtain high solids contents. Mixtures of three types of deflocculants were therefore studied to determine the maximum attainable solids content.

The three deflocculants used were, on the one hand, sodium tripolyphosphate (TPP) and sodium metasilicate (STM) (a mixture that provides lower viscosities than the liquid deflocculants used at present) and, on the other, a commercial deflocculant consisting of a mixture of phosphonates (MF, a powerful complexer of the flocculating divalent cations, calcium and magnesium). A mixture design with the three deflocculants was performed and the minimum viscosity for each mixture was determined, using a solids content of 70% (red-firing stoneware tile composition). The results were used to construct the diagram shown in Figure 2, which shows the most effective ternary mixtures for obtaining low viscosities. The optimum mixture consisted of 0.17% TPP, 0.17% MF, and 0.66% STM. Note that this mixture, in addition to being the one that provided the lowest viscosity (430 cP), exhibited practically zero thixotropy. With this mixture and a commercial liquid deflocculant (STD, with sodium silicate as major component), the evolution of minimum viscosity with solids content was determined, Figure 3.

The optimum mixture enabled a solids content of 71% to be achieved, while maintaining appropriate viscosity and thixotropy for the wet-milling and spray-drying processes. (In the case of usual deflocculants, such as test deflocculant STD, suspension stability at solids contents above 68% decreased significantly).

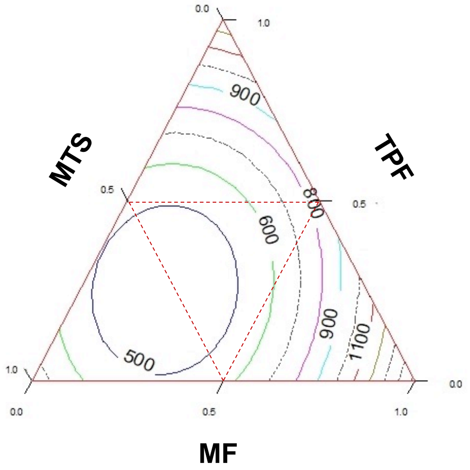

***Figure 2**. Representation in a triangular diagram of the iso-viscosity lines (cP), for combinations of the three deflocculants.*

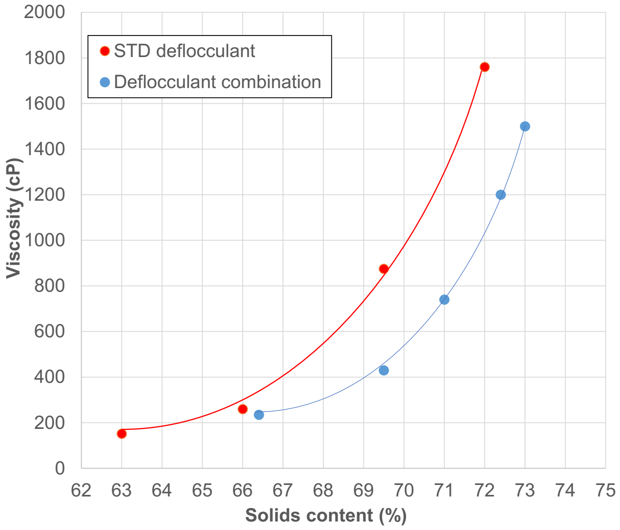

***Figure 3.** Variation of minimum viscosity with solids content for the standard deflocculant and for the optimum deflocculant mixture.*

In light of the above, it is deemed feasible to reach solids contents of 71%, which would allow the CO$_2$emissions in this stage to be reduced by 26% with respect to the average solids content used on an industrial scale of 65%. With current deflocculants, it is not deemed feasible to reach solids contents exceeding 71%.

FORMULATIONS WITH VERY HIGH FUSIBILITY

This line of study seeks to develop formulations of stoneware tiles and porcelain tile, based on glass from recycled fluorescent tubes, which reduces energy consumption in the firing stage by drastically lowering the firing temperature. Previous studies [4] verified the fluxing effect of this type of glass, at present without a clear alternative for valorisation. At a 10% glass percentage, a decrease in optimum firing temperature of between 20 and 30 ºC was obtained, depending on the type of composition. These studies also confirmed that the glass needed to be milled, either prior to its introduction into the composition or after mixing with the other raw materials, to avoid tile bloating during firing.

Based on these studies, compositions exclusively made up of clays and glass were formulated [5]. Figure 4 shows vitrification diagrams of the two compositions with the greatest fusibility, the composition containing 50% Spanish white-firing clay and 50% glass (VF-AB) standing out because it vitrified at very low temperature with moderate firing shrinkage. In contrast, the composition with red-firing clay (VF-AR) exhibited greater fusibility, as was to be expected because of the type of clay used (red-firing clay from the Villar del Arzobispo area) [6].However, it did not display acceptable dimensional stability for ceramic tile manufacture as it underwent high shrinkage and, in addition, high variation of shrinkage with temperature.

In general, given the low dry bulk density (Table 1) and high fusibility of the glass (formation of a large amount of glassy phase in a narrow temperature range), high shrinkage, in addition to high variation of shrinkage with temperature, was to be expected.

This is what was observed in the composition with red-firing clay, the low shrinkage of the composition with white-firing clay being anomalous. The fired bulk density values indicate that, in this last composition, much higher closed porosity was being generated, perhaps because these clays sinter at much higher temperatures than the range in which the glass generates a large amount of glassy phase. Compositions with other Spanish clays, involving both red-firing and white-firing clays, were prepared and the same trends were found. This warrants the conclusion that the type of clay considerably influenced firing behaviour and, particularly, the dimensional stability of these compositions with high fusibility.

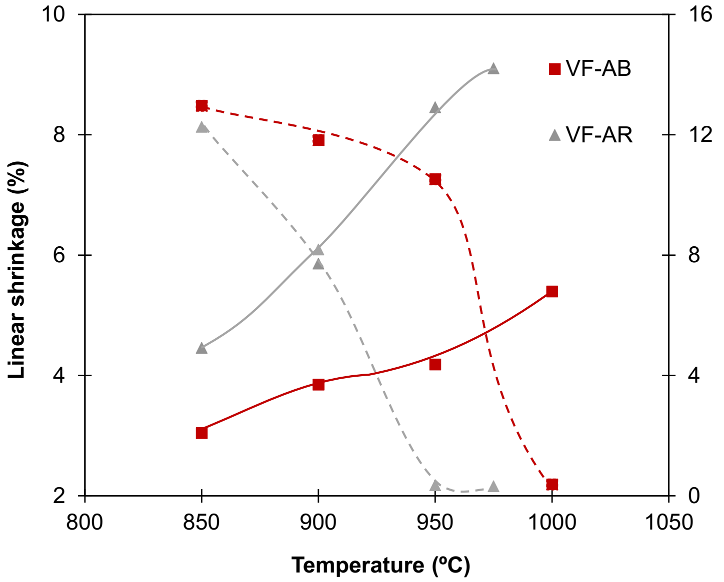

Figure 4. *Vitrification diagrams of the compositions with very high fusibility.*

Composition	VF-AR	VF-AB
Dry bulk density (g/cm³)¹	1.69	1.71
Temperature (ºC)	950	1000
Linear shrinkage (%)	8.4	5.4
Loss on ignition (%)	3.05	4.03
Bulk density (g/cm³)	2.26	2.08

[1] Test pieces formed with a moisture content of 5.5% (dry basis) at a pressing pressure of 250 kg/cm^2.

Table 1. *Required temperature for obtaining 0.5% water absorption and properties of the compositions at this temperature.*

Comparison of the decrease in firing temperature of composition VF-AB (with 50% glass) with those of previous studies [4] (5 and 10% glass) revealed a practically linear trend in temperature reduction with glass content (Figure 5), which was confirmed after preparing an intermediate composition with 30% glass. No compositions were formulated with glass contents above 50% and, therefore, with low clay contents, in order to keep dry mechanical strength within acceptable limits and not to raise closed porosity any further.

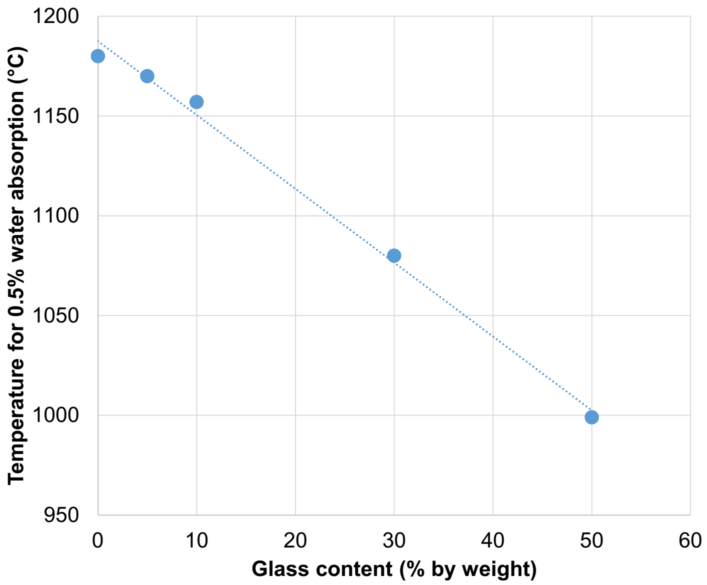

Figure 5. *Temperature required to obtain 0.5% water absorption as a function of glass content.*

The characterisation of this composition was completed, and acceptable values were obtained for dry mechanical strength and proneness to deform by pyroplasticity (Table 2). As was to be expected because of the low density, mechanical strength after firing was lower than the usual values in porcelain tile compositions, albeit still above the limit values of European standards for this type of product, 30 MPa [7].

Finally, the reduction in gas consumption was calculated that would be obtained during firing in relation to a representative cycle of those used in porcelain stoneware tile manufacture, Figure 6. For this, a theoretical model simulating energy transfer in single-deck roller kilns for ceramic tile firing was used [8], obtaining a reduction of 26%.

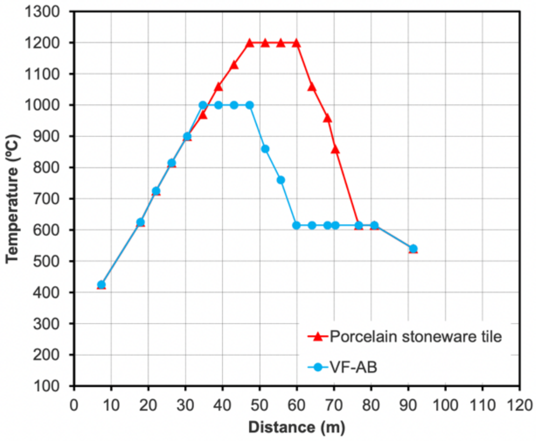

Figure 6. *Firing cycles used for calculating gas consumption in firing [8].*

Composition	Porcelain tile range	VF-AB
Dry mechanical strength (kg/cm^2)	25–30	25
Temperature (ºC)	1180–1200	1000
Bulk density (g/cm^3)	2.37–2.40	2.08
Mechanical strength (MPa)	60–70	52
Pyroplasticity index (cm^{-1}x10^5)	3.5–5.0	4.1
Gas consumption in firing (kWh/m^2)	9.4	6.9
Reduction in consumption (%)	-	26

Table 2. *Properties of composition VF-AB and usual range of values for porcelain tile compositions (laboratory scale data) and energy consumption*

CARBONATE-FREE WALL TILE COMPOSITIONS

In this line, wall tile compositions were formulated without raw materials that might release CO_2 by thermal decomposition and that had a lower firing temperature than that of current raw materials, while maintaining characteristic wall tile properties, such as high dimensional stability, high porosity, and low moisture expansion. The formulated compositions, some of which were already presented elsewhere [5], were based on the use of wollastonites in addition to the incorporation of recycled glass to lower the firing temperature. Table 3 details some of the formulated compositions. As the cost of wollastonites is much higher than that of calcium carbonate, one of the criteria used to determine the optimum composition was that the amount of this raw material needed to be as low as possible without, however, excessively impairing firing behaviour or the properties of the fired product.

Composition	STD	W18	W16v	W10v	W5v
Spanish white clay	40	40	40	40	40
Imported white clay	10	10	10	10	10
Kaolin	10	10	10	10	10
Calcium carbonate	15	-	-	-	-
Feldspathic sand	25	22	19	25	30
Wollastonite		18	16	10	5
Fluorescent lamp glass	-	-	5	5	5

Table 3. *Formulated wall tile compositions (% by weight).*

The sintering diagrams of these compositions, Figure 7, evidence a rise in linear shrinkage and a reduction in water absorption as wollastonite content decreased. This was due to the absence of the carbonate decomposition reaction, together with greater sintering of these compositions, Figure 8. This greater sintering was partly due to the partial or total absence of the expansion that occurred in the case of composition STD around 1000 ºC, associated with crystalline phase formation in the carbonate-containing compositions [6]. It may be noted, however, that in no event did a sufficiently high variation in shrinkage with temperature occur that could significantly reduce tile dimensional stability. Indeed, Table 4 shows the properties of the fired tiles and shrinkage increase that occurred in a range of 40 ºC, it being observed that this was at most 0.8% and solely in the composition with the lowest wollastonite content (W5v). In contrast, the moisture expansion did make this composition unfeasible from a technical viewpoint, because it could possibly cause problems of delayed crazing.

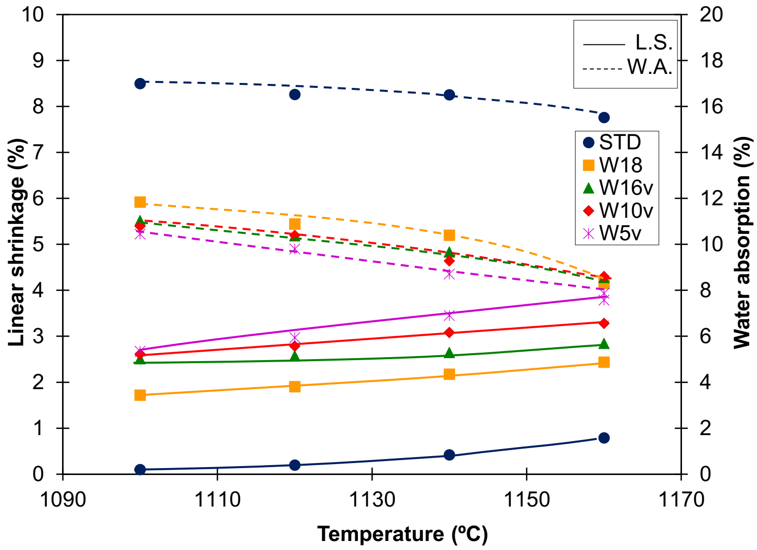

***Figure 7.** Sintering curves of the wall tile compositions.*

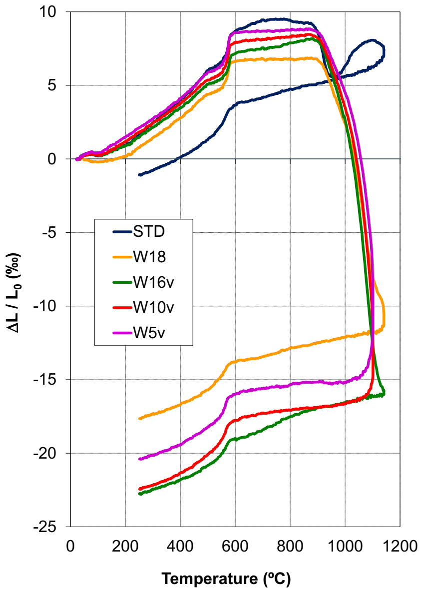

***Figure 8.** Expansion–shrinkage curves of the wall tile compositions.*

Composition	STD	W18	W16v	W10v	W5v
Temperature (ºC)	1140	1140	1140	1100	1100
Linear shrinkage (%)	0.2	1.9	2.6	2.6	2.8
Water absorption (%)	16.5	10.9	10.4	10.8	10.4
Moisture expansion (‰)	0.76	0.54	0.44	0.79	1.30
Δ L.S. (40 ºC) (%)	0.3	0.5	0.1	0.5	0.8

***Table 4.** Properties of the formulated wall tile compositions.*

In light of the above, composition W10v was a technically feasible alternative to the current compositions with carbonates, in addition to the advantage of no emissions exhibiting a firing cycle with lower natural gas consumption. Indeed, for the calculations with the aforementioned model [8], it was assumed that this composition would not require use of low heating rates in the carbonate decomposition range and its optimum firing temperature was lower than that of the compositions with carbonates. However, the cost related to the raw materials in this formulation was calculated, which resulted in an almost 100% increase over that of composition STD owing to the higher cost of commercial wollastonites compared to calcium carbonates. These wollastonites are mainly used in ceramic frit and glaze manufacture, so that they must exhibit very low chromophore oxide (Fe_2O_3 and TiO_2) contents. For this study, it was assumed that the degree of whiteness of the white-firing wall tile bodies was not a limiting factor (although it must obviously stay within acceptable levels). A search was there made for cheaper wollastonites, accepting higher Fe_20_3 contents.

The low-cost wollastonite listed in Table 5 was thus located, which not only had a greater iron content, but also a lower calcium content and a greater loss on ignition owing to the presence of carbonates).

This wollastonite was used to prepare formula W10v again (Wbc10v), entailing a lower increase in cost (practically half that found with the standard wollastonite) but a greater variation in shrinkage with temperature and greater moisture expansion (Table 6). This was consistent with its lower calcium content. To compensate this, the composition was reformulated, raising the low-cost wollastonite content to 13% (equalling the CaO content in the W10v formula), with the aim of achieving the properties of this composition, but still at a lower cost. This last formulation, Wbc13v, exhibited appropriate properties for making it a technically feasible alternative to the carbonate-containing compositions, albeit with greater shrinkage.

In regard to cost, a more thorough calculation was made, calculating not only the cost of the materials but also the cost of natural gas (associated with firing) and the cost of the emission rights. The results, shown in Table 7, evidence a considerable decrease in the emissions associated with firing compared to those of a conventional wall tile, with an extra cost of about 22%. This extra cost would be even lower, if the reduction in indirect costs relating to the increase in production that could be obtained as a result of the reduced firing cycle, already mentioned previously, were taken into account. Note, moreover, that this extra cost was not calculated with respect to production total cost, because only the aforementioned costs were taken into account. This is why the calculated increase would be considerably lower if it were calculated with respect to the total cost. It may further be highlighted that a gradual reduction of this value is expected as a result of the progressive increases in natural gas and emission rights costs observed recently.

Oxide	Wollastonite	Low-cost wollastonite
SiO_2	51.0	55.0
Al_2O_3	0.3	0.3
CaO	44.5	35.0
MgO	1.3	1.0
Fe_2O_3	0.3	1.0
L.O.I.	1.2	5.0

***Table 5**. Chemical composition of the wollastonites used in this study.*

Composition	STD	W10v	Wbc10v	Wbc13v
Temperature (ºC)	1140	1100	1100	1100
Linear shrinkage (%)	0.2	2.6	2.6	2.5
Water absorption (%)	16.5	10.8	10.8	11.0
Moisture expansion (‰)	0.76	0.79	0.92	0.80
Δ L.S. (40 ºC) (%)	0.3	0.5	0.8	0.7

***Table 6.** Properties of the wall tile compositions with the two types of wollastonite.*

Composition	STD	Wbc13v
CO_2 emissions from $CaCO_3$ (kg CO_2)	1.37	0.08[1]
CO_2 emissions from natural gas (kg CO_2)	2.55	2.04
Total CO_2 emissions (kg CO_2)	3.92	2.12
Reduction of total CO_2 emissions (%)	-	46
Raw materials cost (€)	0.66	1.13
Natural gas cost firing process (€)	0.35	0.28
Emission rights cost (€)	0.24	0.12
Joint cost (€)	1.25	1.53
Joint extra cost (%)	-	22

[1] CO_2 relating to the carbonate content of low-cost wollastonite.

Table 7. *Emissions and costs (all per m^2 fired tile, calculated with an average emission rights price of €60/t CO_2, corresponding to September 2021) associated with composition STD and with the optimum composition containing low-cost wollastonite.*

ALKALI-ACTIVATED MATERIALS AND SILICO-CALCAREOUS PRODUCTS AS ALTERNATIVES TO CERAMIC WALL TILES

The two lines mentioned above (stoneware tile and porcelain tile compositions with high fusibility and wall tile compositions without carbonates) would allow energy consumption and CO_2 emissions to be reduced, while maintaining current manufacturing processes. In addition, as already noted above, they would help significantly in the transition to firing processes in electric kilns or with hydrogen in full or partial replacement of natural gas, on lowering energy consumption and, in the case of wall tiles, also avoiding carbonate-related emissions.

Nevertheless, it has been sought to take a further step in reducing emissions by considering a radical change in processes and products: making products "without firing". The two types addressed involve alkali-activated materials [9, 10] and silico-calcareous products [11]. Both types are valid alternatives to ceramic bricks and, moreover, in the case of silico-calcareous products, they are much more widely used than clay bricks in Northern Europe (particularly in Germany and the United Kingdom). In both cases, the possibility was assessed of using them as alternatives to ceramic wall tiles, for which test pieces were prepared by pressing as forming process. The materials and composition preparation in the alkali-activation process have already been described elsewhere [10], so that only the materials and obtainment process of silico-calcareous products will be described.

Traditionally, these products were obtained from mixtures of quartz with CaO and water, which were formed by pressing. The resulting items were then set in an autoclave. For this study, the pieces remained for 5 hours under a water vapour pressure of 10 bar. With high-pressure water vapour, hydrated lime reacts with the surface of the silica particles, forming crystalline phases of hydrated calcium silicate (hCS). These phases act as binders, uniting the silica particle aggregates. With a view to maximising the mechanical strength, first, the influence of the amount of CaO-quartz and that of quartz particle size was studied in order, secondly, try to replace quartz with different types of waste.

Figure 9 shows the mechanical strength of the resulting compositions. The values exceeded the required minimum for wall tiles (12 MPa, [7]) when the CaO content was equal to or higher than 20% for the larger-sized quartz (d_{95}: 130 µm) and for the intermediate-sized quartz (d_{95}: 100 µm). The compositions prepared with the smaller-sized quartz (d_{95}: 10 µm) provided lower mechanical strength values as well as a greater variation with CaO content, particularly in the range in which stabilisation with the larger-sized quartzes was observed. This is logical if the already mentioned "hardening" mechanism is taken into account: formation of crystalline phases at the surface of the quartz particles that act as a bond between them. Indeed, the larger the size of the quartz, the lower is the specific surface area and, therefore, the smaller is the number of bonds required to obtain appropriate mechanical strength. This would explain why, from a certain percentage of CaO on, an increase in mechanical strength with larger-sized quartzes was no longer observed, whereas this was in fact the case with smaller-sized quartzes.

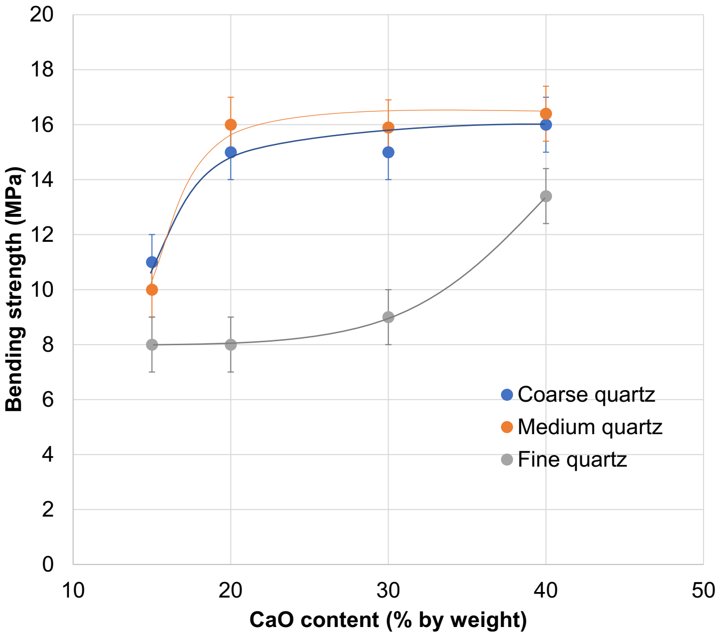

Figure 9. *Bending strength of the silico-calcareous product compositions as a function of their CaO content.*

In view of these results, the composition made up of 80% (coarse or medium) quartz and 20% CaO was chosen as the most appropriate for use as an alternative to wall tile compositions, seeking, in a second stage to replace this quartz with waste and other types of raw materials. A study was therefore carried out of quartz replacement with clay and with the following types of waste: porcelain tile scrap, recycled window glass, recycled fluorescent lamp glass, and sand from iron foundry processes (all having a particle size below 200 µm).

Bending strength values around 13–14 MPa were obtained in all cases except for that of the recycled window glass, in which the pieces exhibited cracking after the autoclave, possibly owing to some reaction associated with the high solubility of this type of glass. The fact that the other wastes provided similar mechanical strength values (albeit slightly lower than quartz), regardless of silica content, could imply some other type of reaction between the hydrated lime and the waste, in addition to the formation of crystalline phases between calcium and silica.

Taking into account the limit value already noted of wall tile mechanical strength (12 MPa), all the waste-containing silico-calcareous product compositions, except that which contained window glass and the aforementioned compositions with larger-sized quartzes, were valid.

The same occurred with the alkali-activated materials, in which ITC has recently manged to increase bending strength from 16 MPa [10] to values above 30 MPa, by modifying the composition and particle size distribution of the starting materials, also enabling them to be prepared from waste, and fine-tuning the variables of the forming process to obtain better properties.

It is clear that to be a feasible alternative to wall tiles, these products need to contain a vitreous coat that seals the surface. This requires development of frits with a very low melting temperature, as conventional frits would involve firing at temperatures similar to current ones, so that the reduction in CO_2 emissions associated with these materials (about 90% of the overall process on suppressing the spray-drying and firing stages) would decrease significantly.

A literature search was therefore carried out on fluxing compositions that could be used in these types of products. As a result of this search, two different systems were selected: "$BaO-B_2O_3-SiO_2$" and "$ZnO-B_2O_3-Na_2O-SiO_2$" and the following frits were obtained, Table 8.

Frit		**A**	**B**
Oxide (% by weight)	SiO_2	6	15
	B_2O_3	39	28
	BaO	55	-
	Na_2O	-	14
	ZnO	-	43
Glaze appearance (T= 700 ºC)			

Table 8. *Chemical composition of the frits and finish obtained in the wet application on a ceramic biscuit.*

The main problem posed by the use of a low-temperature frit in glaze compositions is that the organic matter contributed by carboxymethylcellulose (CMC) and kaolin decomposes in the same range of temperatures in which glaze sealing takes place, so that greyish vitreous coats were obtained (***Table*** 8). Neither the reduction in CMC and kaolin content nor the design of firing cycles with low rates to favour decomposition of the organic matter were able to eliminate the greyish appearance, the only alternative being dry application of these frits as grit (with particle sizes below 200 µm). However, the pieces obtained exhibited significant changes in shade and gloss for variations in firing temperature of 10–20 ºC (around 700 ºC) when they were applied on substrates obtained by alkali activation, and they produced spalling on application to the silico-calcareous bodies. The study therefore needs to be continued, modifying frit formulations and application conditions to achieve acceptable finishes.

DEVELOPMENT OF FORMULATIONS WITH HIGH MECHANICAL STRENGTH TO REDUCE TILE THICKNESS

One way of mitigating overall emissions is by developing formulations with high mechanical strength to reduce tile thickness. Very slim ceramic slabs (3-5 mm) are currently available, but ceramic slab use as flooring requires greater thicknesses, the minimum thickness used in floor tiles being 8 mm for glazed stoneware tile and 6–7 mm for porcelain tile in domestic uses.

Obtaining suitable materials for manufacturing tiles with low thickness requires achieving high dry as well as high fired mechanical strength. In the dry state, the introduction of organic binders (customarily used in the sector), in percentages by weight between 0.3% and 0.5%, raised mechanical strength between 30% and 70%, which would allow tile thickness to be reduced by 30% (and overall CO_2 emissions by practically the same amount).

To increase fired mechanical strength, both the composition and process variables (degree of milling, forming conditions) were adjusted. In the red-firing stoneware tile compositions, composition fusibility was modified by using different clays from the Villar area (presumably with different quartz contents) [5]. This enabled mechanical strength to be raised by up to 80% (Figure 10) and, therefore, tile thickness and CO_2 emissions to be reduced by 35%.

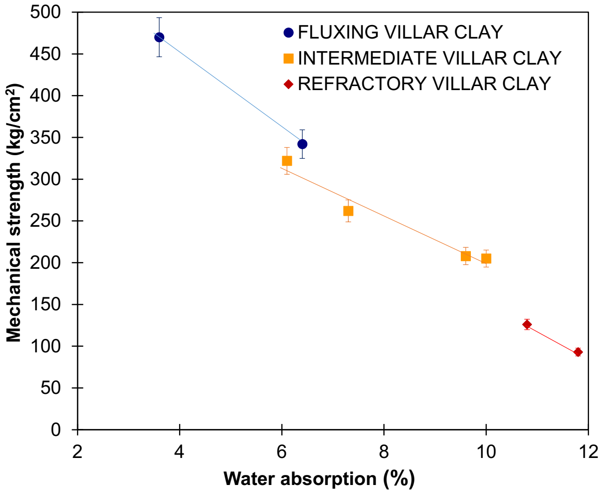

***Figure 10**. Bending strength of different Villar clays (firing temperatures between 1120 and 1160 ºC).*

The figure indicates that the increase stemmed mainly from the decrease in water absorption, in addition to the quartz content (smaller in the clay with the greatest fusibility).

In the red-firing wall tile compositions, such high increases in mechanical strength could not be attained. The greatest increase in this type of compositions (about 30%) was obtained on reducing the residue on a 63-µm sieve from 8% to 4% by weight. This would allow emissions to be reduced by 14% [5].

Analysis of the white-firing compositions revealed that the best results were obtained by modifying the raw materials mixture. Thus, in the case of porcelain stoneware tile, the influence of the type of feldspar and clay and of the percentage of each component was studied (clay–feldspar–feldspathic sand mixtures), obtaining a maximum bending strength of 82 MPa for a mixture made up of 35% imported clay with high alumina content and 65% extra quality sodium feldspar, which, if it is taken into account that current compositions provide laboratory-scale values between 60 and 70 MPa, would allow tile thickness and overall emissions to be lowered by between 8% and 16%.

Finally, it was in the white-firing wall tile compositions that the greatest emissions reductions were achieved. This was because the compositions with wollastonite mentioned above were used, and it was sought to increase their mechanical strength by adding alumina and using clays with high alumina content (Table 9) in order to foster formation of calcium aluminosilicates. It is clear that this approach is going to raise costs significantly, which is why a detailed study of these products was carried out.

Composition	STD	W13v	AW-1	AW-2	AW-3	AW-4
Spanish white clay	40	40	40	-	-	-
Imported white clay	10	10	10	40	-	-
Kaolin	10	10	10	-	-	-
High-alumina imported white clay	-	-	-	-	35	30
Calcium carbonate	15	-	-	-	-	-
Feldspathic sand	25	22	22	20	15	15
Low-cost wollastonite	-	13	-	-	-	-
Wollastonite	-	-	13	20	25	30
Glass	-	5	5	-	-	-
Alumina	-	-	-	20	25	25

Table 9. *Formulated wall tile compositions (% by weight).*

Table 10 details the properties of the compositions, showing that this line of formulation was highly effective in raising mechanical strength and reducing wall tile thickness and moisture expansion. The high porosities (despite the absence of carbonates), together with the excellent properties, appear to indicate that adding alumina combined with high wollastonite contents provided high crystalline phase content in the fired tiles. However, these compositions are not economically feasible at present because of the high cost of the raw materials (Table 10), particularly of the aluminas. Even so, the increase in cost would be much higher if it had not been partly offset in the case of compositions AW-3 and AW-4 by the 23% reduction in tile thickness.

Despite the costs associated with this line of formulation for white-firing wall tile compositions, it was explored because it provides technical results of great relevance and opens up the way to optimising the formulation by adjusting the raw materials contents, particularly of alumina, and/or locating other types of alumina with lower costs.

Composition	STD	W13v	AW-1	AW-2	AW-3	AW-4
Temperature (ºC)	1140	1100	1100	1140	1140	1140
Linear shrinkage (%)	0.2	2.5	2.6	1.9	1.5	1.2
Water absorption (%)	16.5	11.0	10.8	16.3	18.7	19.2
Moisture expansion (‰)	0.76	0.80	0.70	0.52	0.28	0.20
Δ L.S. (40 ºC) (%)	0.3	0.7	0.5	0.2	0.1	0.1
Mechanical strength (MPa)	25	28	30	35	42	42
Reduction in thickness (%)	-	5	9	15	23	23
Emissions reduction (%)	-	48	49	46	46	46
Raw materials cost (€)	0.66	1.13	1.15	3.06	3.14	3.28
Natural gas cost in firing (€)	0.35	0.28	0.28	0.29	0.30	0.29
Emission rights cost (€)	0.24	0.12	0.12	0.13	0.13	0.13
Joint cost (€)	1.25	1.53	1.55	3.48	3.56	3.71
Joint extra cost (%)	-	22	24	178	185	196

Table 10. *Properties and costs (all per m^2 fired tile, calculated with an average emission rights cost of €60/t CO$_2$, corresponding to September of 2021) of the formulated wall tile compositions.*

DEVELOPMENT OF PORCELAIN STONEWARE TILE FORMULATIONS BASED ON SPANISH AND PORTUGUESE RAW MATERIALS

In all the above lines considered, emissions reduction was calculated based on the direct emissions of the process. However, there is a second type of emission, involving indirect emissions, relating to the electric power consumed in the process and the emissions associated with transportation of the raw materials from their origin to the manufacturing plants. If total emissions are calculated, taking into account indirect emissions by means of the Life Cycle Assessment methodology [12], the extraction and transportation of the raw materials account for 11% of total emissions (considering total tile production in Spain). However, this percentage rises to 26% in the case of porcelain stoneware tile.

A sixth line was therefore studied, consisting of the development of porcelain tile formulations based on Spanish and Portuguese raw materials (Table 1), with a view to mitigating emissions relating to transportation. Nevertheless, if the differing impacts on emissions from the various types of transport (truck, train, sea transport of medium volume and sea transport of large volume) per tonne raw material are taken into account, none of the compositions proposed allow any emissions reduction.

This is because the clays and feldspars imported from the Ukraine and Turkey are transported in vessels with large volumes, with lower related emissions than transport by truck of Spanish white clays, and vessels with medium volumes in the case of clays and feldspars from Portugal (Table 12). This line of formulation is not, therefore, useful for lowering emissions at present, but it has been included in case, in the future, trucking might be carried out in electric vehicles using electricity from renewable sources.

Composition	STD	GPB-1	GPB-2	GPB-3
Spanish clay 1	15	20	-	-
Spanish clay 2	-	25	25	-
Portuguese clay	-	-	20	45
Ukrainian clay	30	-	-	-
Turkish sodium feldspar	45	-	-	-
Portuguese lithium feldspar	-	45	55	55
Feldspathic sand	10	10	-	-
CO_2 emissions (kg CO_2 eq/m^2)	2.5	2.6	2.7	2.8

Table 11. *Formulated porcelain stoneware tile compositions (% by weight) and emissions related to raw materials transportation.*

Transport	Emission factor
Truck	0.0702
Electric train	0.0127
Diesel train	0.0253
Vessel with medium load	0.0083
Vessel with high load	0.0039

Table 12*. Emission factors of the different types of transport (kg CO_2/(t raw material km)).*

OVERALL IMPACT OF THE STRATEGIES CONSIDERED

In order to be able to identify the best CO_2 emissions reduction strategies for each type of tile, the following figures depict the reductions achieved (only for the valid strategies from a technical viewpoint), calculated with the Life Cycle Assessment methodology [12]. The figures show that the most effective strategies are as follows: lowering porcelain tile peak firing temperature, reducing the thickness of red-firing stoneware and wall tile, and using carbonate-free compositions (with low-cost wollastonite) for white-firing wall tiles.

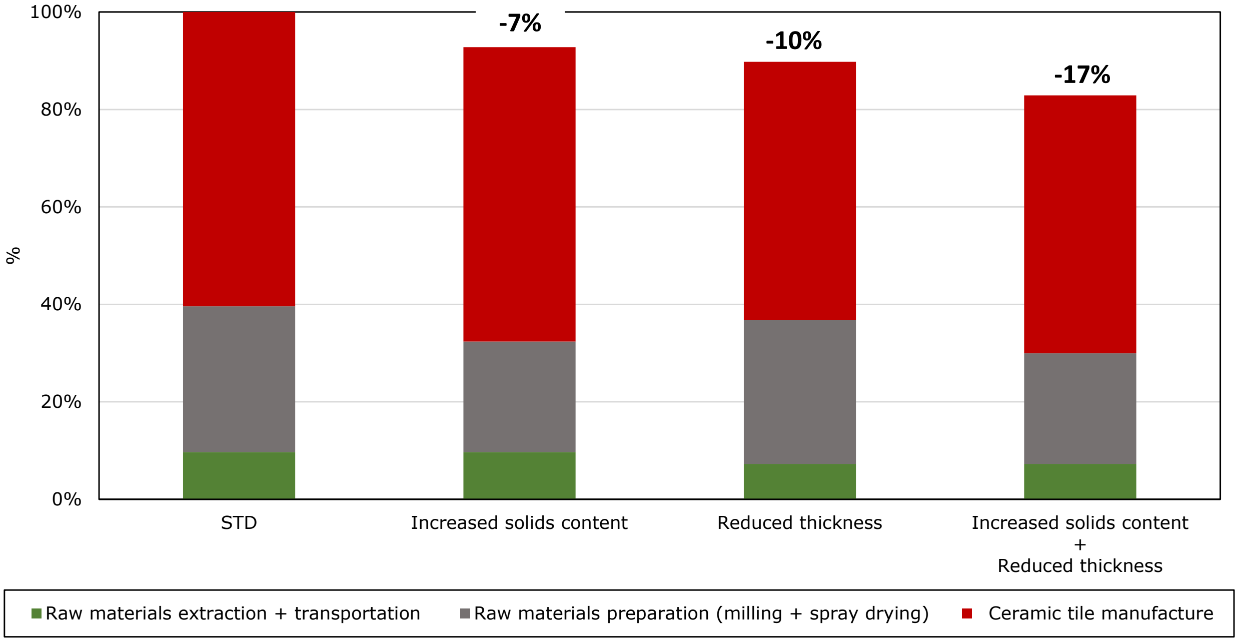

Figure 11. *Emissions reductions achieved with the different strategies in red-firing stoneware tiles.*

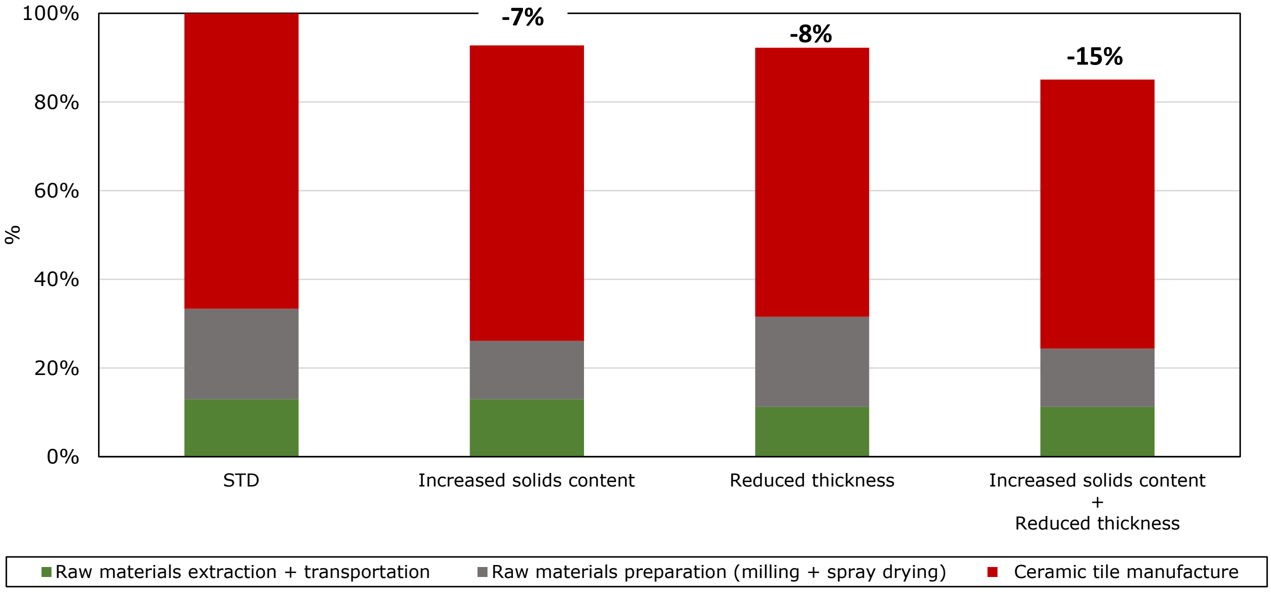

Figure 12. *Emissions reductions achieved with the different strategies in red-firing wall tiles.*

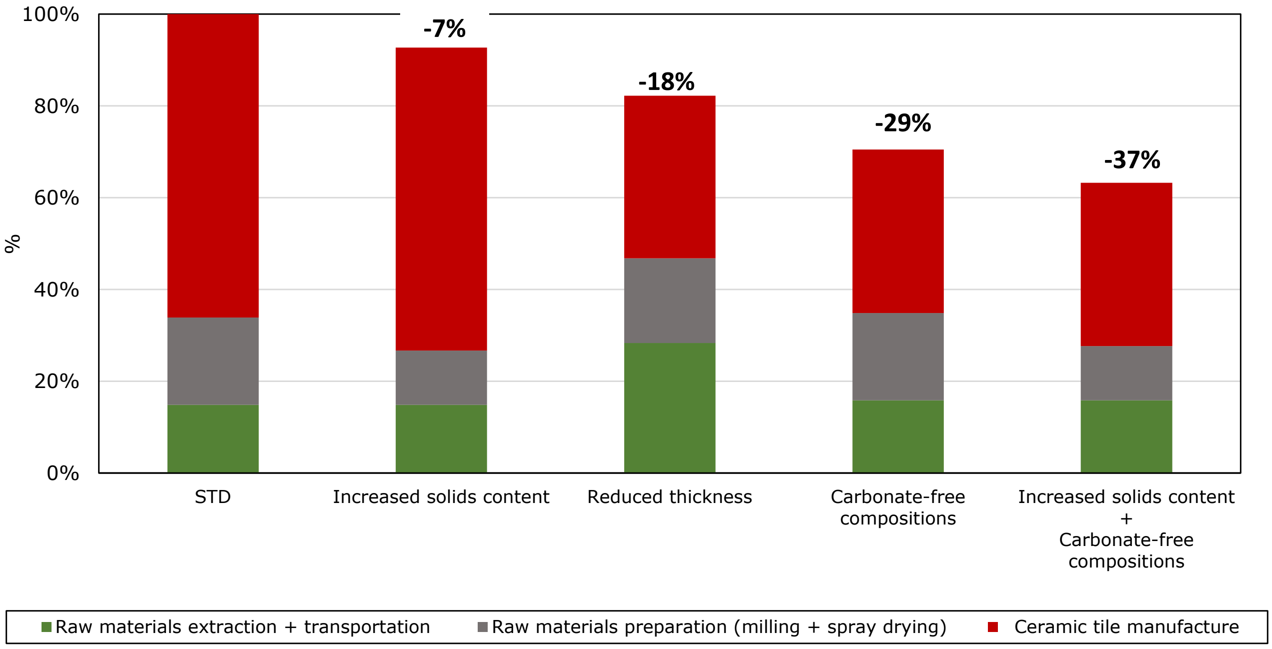

***Figure 13**. Emissions reductions achieved with the different strategies in white-firing wall tiles.*

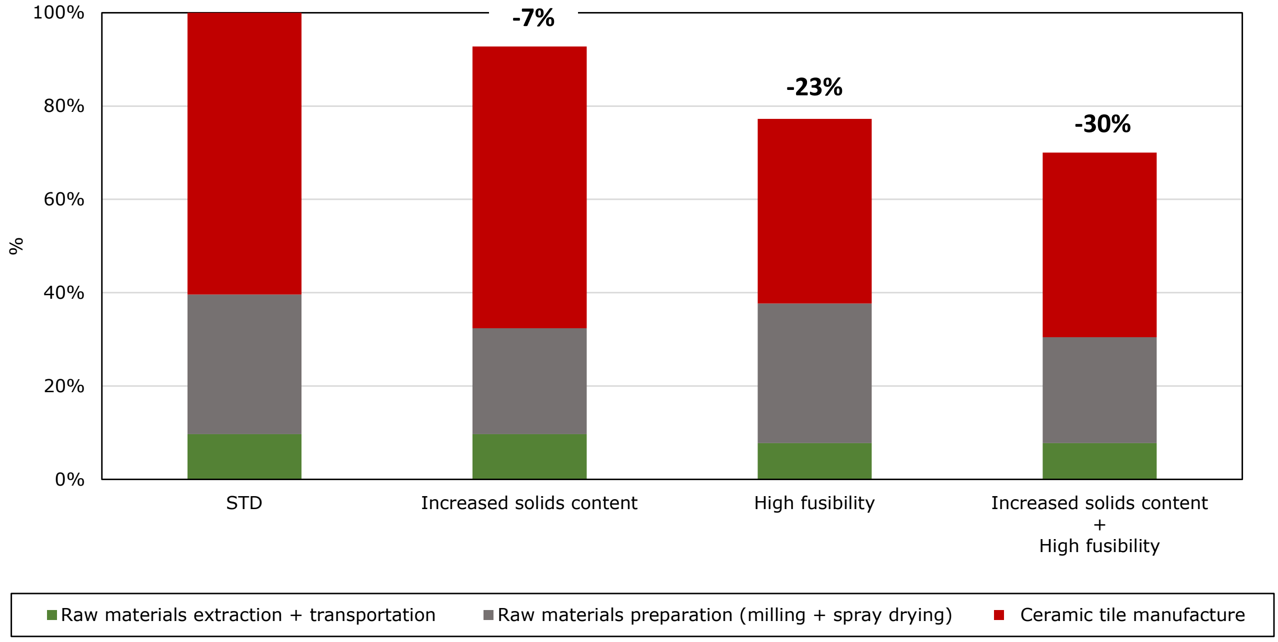

***Figure 14.** Emissions reductions achieved with the different strategies in porcelain stoneware tiles.*

According to these figures, the combined application of increased solids content (applicable to all the types of tiles) and of the differentiated strategies of greatest impact for each type of tile would allow overall emissions to be reduced by percentages varying from 15% for red-firing wall tile to 37% for white-firing wall tile (with intermediate reductions for red-firing stoneware tile and porcelain tile). It is clear that, to achieve the proposed emissions reductions in the European Green Deal, none of these strategies is sufficient, it being necessary to change over to electric processes or use hydrogen as fuel.

That is precisely why it must not be forgotten that most of these strategies can be very helpful in enhancing the feasibility of these new processes by reducing energy consumption.

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