NEW COMPOSITIONS FOR A LOW-CARBON CERAMIC INDUSTRY

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1. INTRODUCTION

Reducing greenhouse gases (GHG) is a key objective in meeting international challenges aimed at mitigating climate change (20% reduction by 2020 and 40% by 2030). The Roadmap for moving to a low-carbon economy published by the European Commission in 2011 sets out the target emissions reductions for industrial sectors, which include the ceramic sector, the objective being to reduce CO2 emissions by 34 to 40% in 2030 and by 83 to 87% in 2050. In this context, the present study reports four lines of experimentation, focused on modifying tile composition formulations to reduce CO2 emissions.

2. LOW-TEMPERATURE AND/OR FAST-FIRING COMPOSITIONS

This line of study pursues development of stoneware tile, porcelain tile, and earthenware tile formulations based on raw materials and fluxing waste (compounds with phosphorus and recycled glasses), which reduce energy consumption in the firing stage, by drastically lowering the firing temperature and/or shortening the firing cycle.

The following phosphorus-containing compounds were studied: hydroxyapatite ($Ca_5(PO_4)_3(OH)$) [1], phosphoric acid (H_3PO_4) [2], and calcium phosphate ($Ca_3(PO_4)_2$). The glasses introduced into the compositions to lower their sintering temperature were packaging glass (mixture of glasses with different colours), packaging glass scrap (mixture of glasses with different colours, together with other types of impurities), and fluorescent lamp glass [3]. The phosphorus compounds and recycled glasses were studied in different clay matrices: kaolin, national white clay, and national red clay. To achieve drastic decreases in firing temperature, the mixtures consisted of 50% clay matrix and 50% fluxing material.

Some of the formulated compositions, specifically those containing hydroxyapatite and fluorescent lamp glass are detailed in Table 1. The vitrification diagrams of these compositions are shown in Figures 1 and 2. The compositions with hydroxyapatite yielded surprising results, in principle, as those with the greatest fusibility were the ones that contained kaolin (a highly refractory raw material), particularly the composition in which kaolin was the only plastic component. This composition (HA-C) was the only one in this series that exhibited high fusibility. However, it led to very high shrinkages as a result of its bad pressing performance (dry bulk density of 1.29 g/cm^3). With regard to the glass-containing compositions, the one that provided the best results was the national white clay-containing composition (VF-AB), as it vitrified at low temperatures with moderate firing shrinkage. This was due to high closed porosity, possibly as a result of the large amount of glass. This composition was fully characterised, determining its proneness to deform by pyroplasticity. The result was similar to that of current red-firing stoneware tile and porcelain tile compositions, so that this line of formulation was deemed of great interest in significantly lowering firing temperature relative to that of current compositions and, hence, reducing firing-related emissions (for this composition in particular, such emissions would decrease by about 25%).

Composition	HA-AB	HA-ABC	HA-AR	HA-C	VF-AB	VF-ABC	VF-AR
National white clay	50	25	-	-	50	25	-
Kaolin	-	25	-	50	-	25	-
National red clay	-	-	50	-	-	-	50
Hydroxyapatite	50	50	50	50	-	-	-
Fluorescent lamp glass	-	-	-	-	50	50	50

Table 1. *Compositions based on hydroxyapatite and recycled fluorescent lamp glass (% by weigt).*

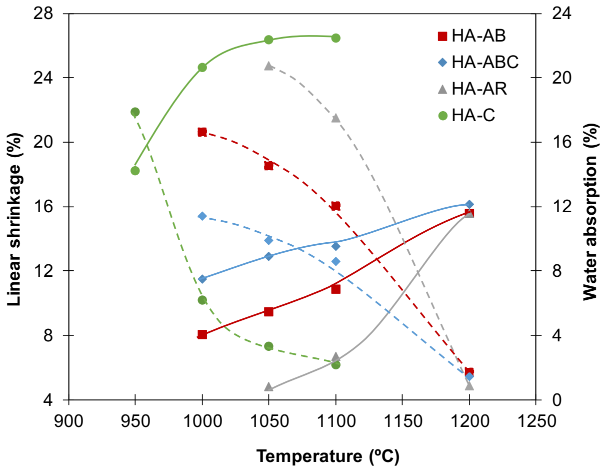

Figure 1. *Vitrification diagrams of the compositions with hydroxyapatite.*

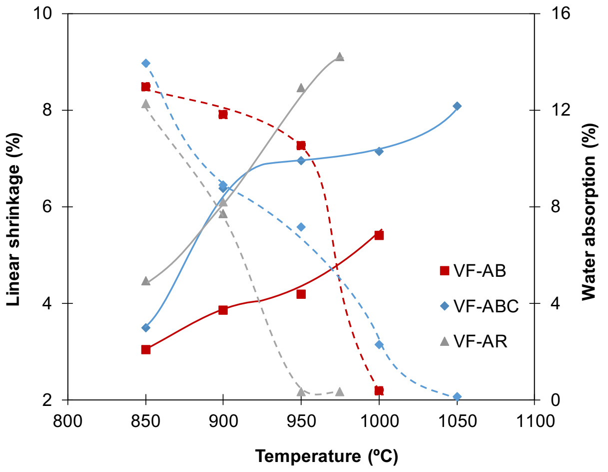

Figure 2. *Vitrification diagrams of the compositions with fluorescent lamp glass.*

3. CARBONATE-FREE EARTHENWARE TILE COMPOSITIONS

In this course of action, earthenware tile compositions were formulated without raw materials liable to release CO_2 by thermal decomposition and with a lower firing temperature than current compositions, while holding characteristic earthenware tile properties such as high dimensional stability, high porosity, and low moisture expansion. The formulated compositions were based on the use of wollastonite [4] and on the incorporation of highly fusible raw materials (recycled glass and talc) in order to lower firing temperature. Some of the formulated compositions are listed in Table 2, while Table 3 details their main characterisation results. As wollastonite is much more expensive than calcium carbonate, one of the criteria used in determining the optimum composition was minimising the amount of wollastonite without excessively adversely affecting firing behaviour. In view hereof, the optimum composition was deemed to be W13V which, as Table 3 shows, allowed firing-related CO_2 emissions to be reduced by practically 50% compared to those of the carbonate-containing composition used as a reference.

Composition	STD	W18	W16V	W10V	W13V
National 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	22
Wollastonite		18	16	10	13
Fluorescent lamp glass	-	-	5	5	5

Table 2. *Formulated earthenware tile compositions (% by weight).*

Composition	STD	W18	W16V	W10V	W13V
Temperature (ºC)	1140	1140	1100	1100	1100
Linear shrinkage (%)	0.2	1.9	2.6	2.6	2.5
Water absorption (%)	16.5	10.9	10.8	10.8	11.0
Moisture expansion (‰)	0.76	0.54	0.79	0.92	0.80
∆ L.S. (40 ºC) (%)	0.3	0.5	0.5	0.8	0.7
CO_2 emission from $CaCO_3$ (kg CO_2/m^2 $_{fired}$)	1.37	0.13	0.12	0.06	0.08
CO_2 emission from natural gas (kg CO_2/m^2 $_{fired}$)	2.55	2.13	2.02	2.03	2.04
Emissions reduction (%)		42	45	47	46

Table 3. *Properties of the formulated earthenware tile compositions.*

4. FRITLESS GLAZE COMPOSITIONS

In regard to fritless glazes, formulations were obtained with different finishes: glossy, satin, and matt, both for porcelain tile and for earthenware tile. The glazes were based on the use of raw materials with high fusibility, which in addition provided a wide firing range: nepheline, spodumene, etc. The compositions that yielded the best results, as well as the firing temperature, gloss, and appearance of the resulting fired glazes, are detailed in Table 4. The use of these glazes would allow the CO_2 emissions related to the overall ceramic tile manufacturing process to be reduced by about 2 to 13% (the highest percentages being for the earthenware tile compositions owing to their greater frit content).

Raw material	ESM-19 (% by weight)	ESM-11 (% by weight)	ESM-25 (% by weight)	ESM-28 (% by weight)
Wollastonite	14	8	4	7
Nepheline	-	68	35	42
Spodumene	78	-	30	38
ZnO	-	4	9	5
Zircon	-	12	14	-
Kaolin	8	8	8	8
T (ºC)	1180	1180	1100	1100
Gloss (60º)	6	60	87	27
APPEARANCE	Semi-transparent matt	Glossy white	Glossy white	Semi-transparent satin matt
				

Table 4. *Formulated glazes.*

5. COMPOSITIONS WITH HIGH MECHANICAL STRENGTH

Ceramic body formulations with high mechanical strength were developed to reduce tile thickness. The introduction of typical organic binders used in the sector, in amounts of 0.3 to 0.5% by weight increased dry mechanical strength by 30 to 70%, which would allow tile thickness to be reduced by about 30% (and overall CO_2 emissions by practically the same percentage).

To increase fired mechanical strength, actions were undertaken in regard to the body composition and process variables (degree of milling and forming conditions). The influence of the composition was studied in red-firing compositions for stoneware and earthenware tile. In the stoneware tile compositions, composition fusibility was modified by using different clays from the Villar region (presumably owing to the change in quartz content). Mechanical strength increased by up to 80% (Figure 3), thus enabling thickness and CO_2 emissions to be potentially reduced by 35%. The figure suggests that this increase stemmed mainly from the decrease in water absorption and not from the change in quartz and clay mineral content. In the earthenware tile compositions (Table 5), the carbonate content was modified by changes in the clay content from the Mas Vell region, no important changes being observed in mechanical strength.

Finally, the influence of the forming conditions and degree of milling in the different types of compositions was studied. The results, detailed in Table 6, show that it was possible to potentially reduce tile thickness and CO_2 emissions by up to 15% on increasing the degree of milling. In contrast, the tested increase in dry bulk density was less effective.

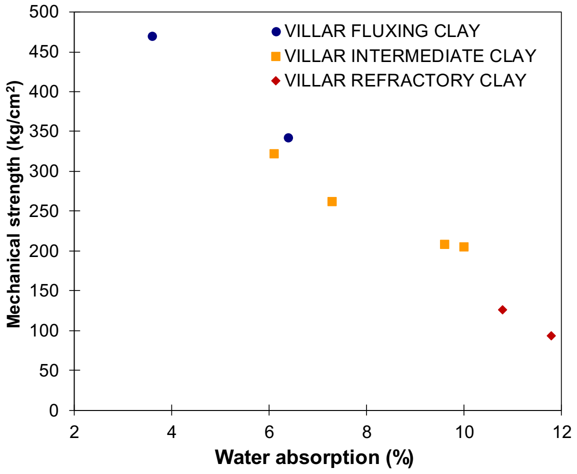

Figure 3. *Mechanical strength of the stoneware tile compositions with different fusibility.*

Composition	40M 60V	60M 40V
Carbonate content (%)	10	15
RM at 1080ºC (kg/cm²)	170	190
RM at 1110ºC (kg/cm²)	190	200

Table 5. *Mechanical strength (RM) of the earthenware tile compositions with different carbonate contents.*

Composition	Red-firing stoneware tile		Red-firing earthenware tile		White-firing earthenware tile	Porcelain tile
Modified variable	Dap	R	Dap	R	Dap	Dap
Variation (g/cm³ / %)	0.05	4	0.05	4	0.05	0.05
Increase in RM (%)	10	25	10	30	10	10
RE (%)	5	12	5	14	5	5

Table 6. *Increase in mechanical strength (RM) and decrease in thickness and CO_2 emissions (RE) by modifying milling (residue on 63 µm sieve, R) and forming (dry bulk density, Dap) conditions.*

6. ACKNOWLEDGEMENTS

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7. REFERENCES

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