I O U R N A L O F

Ceramic Processing Research

Effect of alkaline-earth oxides on firing behaviour of monoporosa wall tile bodies

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For the production of ceramic wall tiles, effective sintering has become increasingly important in recent years to reduce firing times and/or peak firing temperatures and thus cope with high energy costs and environmental issues. This study was aimed to investigate the effects of alkaline-earth oxides on the fast-firing behaviour of wall tile bodies. To this end, several body formulations with different amounts of calcite and magnesite were prepared and fast fired under laboratory conditions. The sintering behaviour of the representative formulations was evaluated using a double-beam non-contact optical dilatometer (ODHT). Thermal properties were characterised by TG-DTA. Phase and microstructural analyses were performed by XRD and SEM, respectively. The results showed that an optimum combination of the aforementioned earth alkalines has a considerable influence on lowering the peak firing temperature, shortening the firing cycle and improving the glaze quality by lowering the decomposition temperature of carbonates in the formulations.

Key words: Alkaline-earth oxides, Monoporosa Wall tile, Firing behaviour, Fast firing, Decomposition.

Introduction

In the ceramic tile industry, body formulations are usually developed and optimised by trial and error [1]. The technical expertise of this industry has been a critical factor in developing the production processes and materials. In the last two decades, since the involvement of single firing for floor and porcelain tiles has increased, the use of traditional double firing has given rise to the use of fast double and single firing. Fast-firing methods and the manufacture of single fired (monoporosa) wall tiles require careful attention regarding the selection of raw materials, mixture design, particularly the role of specific components and the consequences of modification or substitution. The trend has recently moved towards larger-sized wall tiles measuring up to 300×900 mm in length and approximately 8 mm in thickness with high aesthetic and decorative appeal.

Wall tile bodies principally consist of two types of components: reactive and inert components [2]. The reactive materials used in wall tile bodies are clays and kaolin, which provide plasticity and desirable mechanical strength for both green and dried body pieces. The inert materials, mainly quartz, pegmatites and feldspars, increase the refractoriness of wall tile bodies, reduce linear shrinkage during firing and also regulate the SiO_2/Al_2O_3 ratio, which is an important parameter for mullite formation. Feldspar can also be used as a fluxing agent. Other fluxing modifiers, such as talc, wollastonite, calcite and dolomite, are introduced in controlled amounts to decrease the melting point of bodies through the formation of a eutectic system with alkaline feldspars [3].

A wall tile body has characteristic features, such as little or no firing shrinkage and compatible thermal expansion coefficients between bisque and glaze. These features are required when fast single (monoporosa) firing is the selected production process. In monoporosa firing, the bisque and glaze must be fired simultaneously for up to 40-50 min. in roller furnaces according to the size of the ceramic product. To reduce the peak firing temperature of ceramic materials, flux-forming additives, both natural (feldspars, nefeline syenite, etc.) and synthetic (including industrial wastes), are widely used. Therefore, research in the field of sintering intensification, i.e., the formation of anorthite in calcium-containing ceramic mixtures due to various mineralising additives, which makes the formation of low-temperature mixtures possible, is of clear scientific and practical interest [4]. Calcite acts as a stabilising flux by expanding and lowering the firing range. The influence of magnesia containing fluxes, such as talc, magnesite, dolomite and chlorite as sintering promoters, on the vitrification behaviour of different compositions has already been studied by several researchers. It has been reported that

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the concurrent presence of alkaline and alkaline-earth oxides promotes the development of a less viscous liquid phase, which improves the densification kinetics of floor and porcelain tiles at sufficiently high temperatures [5]. The fluxes added to tile bodies exist in different forms, e.g., carbonates (calcite, dolomite and magnesite). Carbonates are decomposed to CaO and MgO during firing. These oxides react with the other raw materials, resulting in the formation of desirable mineral phases, promoting a more effective melting of the raw materials and improving the technological properties of the final products [6]. It has also been reported that the use of magnesite as a fluxing agent in porcelain tile not only reduces the peak firing temperature but also narrows the firing range [7]. Thus, wall tile manufacture requires using calcium oxides to produce crystalline calcium phases (silicates and aluminosilicates) during the firing stage, which provide tiles with their characteristic properties [8]. According to the literature, the decomposition reaction of calcium carbonate occurs at approximately 900 °C. In contrast, the decomposition of magnesium carbonate starts at approximately 650 °C. Similar behaviour is expected for limestone and dolomite, which leads to active CaO and MgO-CaO, respectively, depending on the peak firing temperature and the firing cycle chosen [9]. It is clear that the decomposition temperature can be reduced with magnesium carbonate-containing bodies and provides short-firing cycles as well.

The most noteworthy aspect of monoporosa firing is the fact that the decomposition of carbonates overlaps with the softening of glaze, which can produce glaze defects during fast single firing. Thus, a soaking time at the degasification temperature is needed to allow CO_2 to evolve without causing defects. Furthermore, unreacted calcium or magnesium oxides after firing should be avoided because they are liable to exhibit carbonatation or hydration during use, resulting in a characteristic defect of ceramic tiles known as delayed crazing. Largesized wall tiles, because of the glazes used, require long firing cycles and usually exhibit delayed cracks. It has been shown that CaO hydrates at a high rate in the presence of water, while MgO shows a slower rate of hydration [10]. Achieving little or no moisture expansion is also an important factor to consider when producing wall tiles [5]. Carbonates, particularly calcite, are effective in decreasing moisture expansion due to the formation of anorthite [11]. Moisture expansion value should be < 0.06% (EN 14411) to avoid surface defects.

The aim of the study was to develop fast-firing wall tile bodies with special attention to the role that alkalineearth oxides, namely calcia and magnesia, play in the fast-firing behaviour and the resultant technological characteristics of the final product. Body preparation of the wall tiles was conducted under laboratory conditions, and the firing behaviour of the end product were explored.

Materials and Methods

Experimental procedure

The main raw materials employed to prepare the various formulations in this study are listed in Table 1. The experimental method used was similar to that most commonly used in single-fired wall tile manufacture. Mixtures were ball milled and homogenised by wet processing in ball mills; the rejects screened through a 63-µm aperture constituted approximately 3 wt. % of the total solids. The suspensions were then dried in an oven at 110°C and humidified and sieved down to 1 mm before forming. Powders with a moisture content of 5-6 wt. % were pressed under 310 kg/cm^2 of pressure into samples with dimensions of $100 \text{ mm} \times 50 \text{ mm} \times 6 \text{ mm}$. For firing, industrial parameters were preferred, namely, 35 min. for firing time (from cold to cold) and 1150°C for peak firing temperature. Firings were achieved in a laboratory-type roller furnace (Nannetti ER 30, Italy). The measurements performed on the fired tiles included those pertaining to linear shrinkage and water absorption. Additionally, flexural strength was determined using a three-point bending test (Gabrielli S.R.L, Italy) at a loading rate of 1 mm.min⁻¹. The chromatic coordinates (L^*, a^*, b^*) of all of the fired tiles were measured using a Minolta CR-300 series chromometer.

For thermal characterisation, samples were heated in a TG-DTA (Netzsch STA 409 PG, Germany) in air

Table 1.	. (Chemical	anal	ysis	of	the	raw	mat	eria	ls

Oxide	Clay 1	Clay 2	Clay 3	Kaolinite	Quartz	Calcite	Magnesite
SiO ₂	59.17	59.47	63.71	68.24	97.46	2.87	10.15
TiO ₂	1.14	1.25	0.74	0.41	-	_	0.13
Al_2O_3	23.70	22.29	14.84	20.73	1.31	1.01	2.31
Fe_2O_3	3.46	4.25	6.28	1.85	0.08	0.21	1.12
CaO	0.18	0.23	2.17	0.09	0.04	52.97	6.93
MgO	0.68	0.65	1.66	0.03	0.03	0.42	35.66
Na ₂ O	0.17	0.15	0.76	_	0.45	_	0.27
K ₂ O	2.60	2.54	2.62	0.10	0.33	0.08	0.04
L.o.I.*	8.17	8.93	6.90	8.21	0.23	42.13	42.72
Total	100	100	100	100	100	100	100

*L.o.I. Loss on Ignition.

from room temperature to 1200 °C at a heating rate of 10 °C.min⁻¹. Thermal expansion coefficients were measured by a dilatometer (Netzsch DIL 402 PC), and the firing behaviour of the bodies was monitored using a double-beam, non-contact optical dilatometer (Misura ODHT-HSM 1600/80, Expert System Solutions, Italy). Phase analyses were conducted to identify the major crystalline phases by XRD (Cu-K_a radiation, working at 40 kV, 30 mA, with a scanning velocity of 2°C/min.) using a Rigaku Rint 2000 (Japan) series diffractometer. Fractured and etched surfaces (5 wt. % hydrofluoric acid solution at room temperature for 30 s) of the selected samples were examined under SEM (Zeiss Supra at 20 kV, Japan) fitted with an EDS (Oxford Inst. Inca Energy).

Body formulations

Several body compositions containing different ratios of CaO/MgO were developed according to the Seger approach and by adjusting the $(Al_2O_3 + SiO_2)/alkali$ ratios. When preparing the body compositions, the silica content of the clays was also taken into account. Amongst the raw materials, clay 3 helps to promote sintering activity. The oxide compositions of standard (STD) and the investigated formulations (CM and CRM) are listed in Table 2. The calcite- and magnesitecontaining compositions were classified into the CM group, referring to the increasing molar ratio of magnesia/calcia. Therefore, the RO + R₂O content of the bodies was maintained at an optimum value, but the

Table 2. Chemical composition of the investigated tile bodies.

RO/R₂O ratio was also increased to achieve more effective sintering. In contrast, the RO (CaO + MgO) content was maintained at a value between 0.56-0.68. The MgO/CaO ratio was increased to observe the influence of MgO on the properties of the bodies. The adjusted ratios of calcia/magnesia in the CM bodies were 0.75 : 0.25, 0.5 : 0.5 and 0.25 : 0.75, respectively. In the second group of the formulations, the CRM bodies were developed with magnesia instead of calcia, with the molar values calculated according to the Seger formulation (Table 3). In all of the formulations, the SiO₂/Al₂O₃ ratio was increased to control the shrinkage behaviour. Furthermore, the (SiO₂ + Al₂O₃)/RO ratio was decreased for low-moisture expansion.

Results and Discussion

Physical and thermal properties

Fig. 1 shows the XRD spectra of the clays used in body formulations. The presence of illite, calcite, clinochlore, microcline and quartz can be observed. Since it is an illitic clay, the fluxing power of clay 3 is expected to be high, as confirmed by the presence of K_2O and Na_2O . Fig. 2 shows the thermal behaviour of the same clay. The DTA curve gives endothermic peaks at 536.4 and 759.8°C. Due to the considerably high CaO content of the clay, which also encourages the formation of anorthite, the second endothermic peak can be attributed to the decomposition of calcium carbonate.

Oxide	STD	CM1	CM2	CM3	CRM1	CRM2	CRM3
SiO ₂	59.10	58.65	59.22	59.84	61.27	62.03	62.74
TiO ₂	0.78	0.75	0.75	0.75	0.80	0.79	0.73
Al_2O_3	18.36	17.07	16.93	16.82	18.96	18.45	17.32
Fe ₂ O ₃	3.06	2.97	2.98	2.99	3.16	3.11	3.42
CaO	5.11	5.30	3.91	2.52	0.79	0.79	1.04
MgO	0.55	1.55	2.57	3.56	2.79	2.80	2.92
Na ₂ O	0.18	0.21	0.22	0.23	0.20	0.21	0.29
K ₂ O	1.62	1.64	1.64	1.65	1.64	1.64	1.64
L.o.I.*	10.96	11.61	11.51	11.38	10.12	9.91	9.64
Total	100	100	100	100	100	100	100

*L.o.I. Loss on Ignition.

Table 3. Formulations of investigated tile bodies.

Raw Material	STD	CM1	CM2	CM3	CRM1	CRM2	CRM3
Clay 1	26	26	26	26	26	26	18
Clay 2	25	25	25	25	25	25	10
Clay 3	10	10	10	10	10	10	22.6
Kaolinite	24	17.2	16.3	15.5	26.6	24	24
Quartz	6	10	11	12	6	8.6	9
Calcite	9	9	6	3	_	_	_
Magnesite	-	2.8	5.7	8.5	6.4	6.4	6.4



Fig. 1. XRD pattern of Clays(q: quartz, i: illite, m: microcline, c: calcite, cl: clinochlore).



Fig. 2. TG-DTA curves of Clay 3.

Table 4. Physical properties of the investigated tile bodies.

Technological property	Unit	Bodies						
	Unit	STD	CM1	CM2	CM3	CRM1	CRM2	CRM3
Flex Temperature	(°C)	1147	1140	1137	1125	1139	1129	1127
Water Absorption	(wt. %)	16.70	13.93	12.02	12.27	10.88	11.38	11.27
Firing Shrinkage	(%)	1.10	1.19	1.28	1.90	3.18	2.13	2.60
Breaking Strength	(kg/cm ²)	294.60	313.00	318.40	336.20	343.20	309.50	312.60
Moisture Expansion	(%)	0.06	0.03	0.03	0.03	0.02	0.03	0.02
α _(400°C) / 10 ⁻⁷ °C ⁻¹		65.12	75.21	79.52	83.33	68.21	76.70	79.26
Chromatic co-or	dinates							
L*		67.68	67.07	67.29	62.82	60.86	68.51	65.74
a*		9.15	8.97	8.05	6.44	8.68	7.37	7.82
b*		17.40	18.18	19.72	18.76	16.91	17.43	17.82

The linear shrinkage (%), water absorption (%) and flexural strength (kg/cm²) of the formulations are listed in Table 4. An high degree of firing shrinkage observed in CM and CRM compositions can be attributed to the progressive melting of the crystalline phases, which enriches the liquid phase with alkaline-earth oxides. Some authors have indicated that MgO reduces the melt viscosity of SiO_2 -Al₂O₃ glasses to a greater extent than CaO, which might explain the greater shrinkage of CM3 and CRM3 [12]. The water absorption values of

Formulations	Exothermic peak temperature (°C)	Endothermic peak temperature (°C)	Mass loss (wt. %)	Total mass loss (wt. %)
STD	998.1	94.3 528.5 572.2 783.8	1.09 3.24 - 6.01	10.34
CM1	943.0	93.4 530.9 566.0 799.9	1.29 4.58 - 4.87	10.74
CM2	943.0	93.3 528.4 569.9 787.4	1.42 5.04 - 4.29	10.75
CM3	932.1	95.1 532.0 565.0 775.0	1.59 6.82 - 2.17	10.93
CRM1	943.6	93.3 538.8 572.2 730.7	1.38 6.07 - 1.69	10.58
CRM2	948.0 1027.0	95.3 535.1 577.0 719.3	1.45 6.05 - 1.39	8.89
CRM3	998.1 1007.0	99.9 535.3 573.0 729.0	1.27 5.54 - 1.73	8.54

Table 5. The exothermic and endothermic peak temperatures and corresponding mass loss (%) values derived from TG-DTA analysis.

the designated bodies vary significantly (16.6-18.7%). The flexural strength of the CRM bodies also improved with densification, from 295 kg/cm² to 343 kg/cm². It is known that the strength of the ceramic bodies is related to the type and quantity of the crystalline phases present. Three different clays were used in both the standard and developed formulations. The reasonable potassium and calcium content of the highly illitic clay, i.e., clay 3, further promoted the formation of the phases present and, therefore, the high strength of the bodies.

The thermal expansion coefficients of the tile bodies are listed in Table 4. These expansion values show a gradual rise for both the CM and CRM compositions (Fig. 3). Although the values appear dilatometrically compatible with the commercial glaze used in standard tile formulations, it is evident that the thermal expansion coefficients of the CM3 and CRM3 bodies are considerably higher than those of the rest of the bodies. This may be attributed to the relatively high free quartz content in these bodies.

The moisture expansion values (%) were determined for 100x50x6 mm ceramic tiles, and the results showed that both the CM and CRM bodies are appropriate for use according to EN 14411 (Table 4).

The comparative temperature values of the peaks indicating both endothermic and exothermic reactions and the corresponding mass losses (wt. %) derived from the DTA-TG analysis are presented in Table 5. For the STD formulation, exothermic and endothermic peaks were observed at 94.3 and 528.5, 783.8, 998.1 °C, respectively. The TG curves of the STD and CM formulations clearly show a weight loss at approximately 780 °C, which correspond to the decomposition of CaCO₃ [13]. The first endothermic peak at 93.3 °C (mass loss approximately 1.5 wt. %) is due to the removal of physically adsorbed water, typical of kaolinitic materials. The second endothermic peak (mass loss of approximately 3 wt. %) indicates the removal of hydroxides. The third endothermic peak, at approximately 528.4 °C, is due to the dehydroxylation of the silicate lattice, which leads to the formation of metakaolinite (Al₂O₃,2SiO₂) [14]. The endothermic peak, at 570.1 °C, is associated with the allotropic transformation of quartz. The fourth endothermic peak is due to the thermal decomposition of calcite to form calcium oxide (CaO) and CO2. Its corresponding weight loss is approximately 6 wt. %. The small exothermic peak at approximately 950 °C is due to further disruption of the lattice and is probably related to the formation of new crystalline phases, such as Si containing γ -Al₂O₃ with a spinel structure or mullite [15]. The last exothermic peak observed at approximately 1000 °C was mainly due to formation of a new crystalline phase of mullite, as shown by XRD.



Fig. 3. (a) Thermal expansion curves of the STD and CM compositions and (b) derivative curves; (c) thermal expansion curves of the STD and CRM compositions and (d) derivative curves.

In the CRM compositions, the decomposition temperature showed a decreasing trend with an increase in the amount of magnesite (Table 5), which can be explained by the poorer thermal stability of magnesite compared with that of calcite [15].

Firing behaviour

Comparative firing curves of the STD, CM and CRM compositions are shown in Figs. 4 and 5, respectively. Note that the bodies were subjected to an industrial firing cycle. All of the graphs are plotted with time on the x-axis and both temperature and sintering percentage on the y-axis. The flex temperatures corresponding to the maximum amount of shrinkage and maximum sintering speed can be observed in the graphs for each composition. According to these dilatometric curves, the STD and CM bodies show expansion up to 970 °C (first flex point), which indicates that prior densification occurred. The maximum sintering speed of the STD body occurred at 1147 °C and 1141 °C for CM1, 1137 °C for CM2 and 1134 °C for CM3 formulation. The CRM bodies show maximum sintering speed at 1136 °C, 1129 °C and 1126 °C, respectively. It is evident that the incorporation of magnesite into the standard body composition led to a considerable decrease in the peak firing temperature. The maximum sintering speeds for CM compositions containing both calcite and magnesite occurred at temperatures approximately 13 °C lower than that of the standard body. As shown in Fig. 5, the CRM compositions also have lower values of the flex point

than those of the standard body. It appears that the magnitude of this effect depends on the amount of magnesite incorporation. The improved firing behaviour can be explained by the reduced eutectic temperatures. Thus, CRM1, CRM2 and CRM3 compositions with increasing amounts of magnesia exhibited lower firing temperatures. Moreover, the densification process occurs quickly in CM3 and CRM3 bodies. It was also shown that the CRM bodies experienced a considerable decrease in sintering temperature compared with the CM bodies, confirming the higher reactivity of the former with respect to the STD body.

For the bodies containing both calcite and magnesite, the maximum firing speed temperatures indicated a decrease in peak firing temperature with increasing magnesite content. During the firing cycle, the bodies continued to shrink, and the values reached a maximum of 0.4% for the STD body, 0.6% for CM1, 0.4% for CM2 and 1.2% for CM3. A small expansion occured at approximately 950 °C, as CaO reacted with the other oxides present to form a new crystalline phase, which is believed to be anorthite. It should be mentioned that the most important parameter to focus on when studying the thermomechanical behaviour of such bodies is not the total amount of shrinkage but rather the sintering rate. The differences in terms of the size stability and the behaviour that leads to deformations during firing are controlled by the sintering rate [5]. During fast firing, if the sintering rate is very high, the heat-transfer mechanisms create large differences in



Fig. 4. Firing behaviour of STD and CM compositions.



Fig. 5. Firing behaviour of STD and CRM compositions.

temperature between the sides and centre and even between the corners and sides of the tiles, and under the worst conditions, these stresses may lead to unrecoverable plastic deformation [16]. Therefore, the similarity between the developed compositions and the STD body with respect to the sintering rate is important to note.

X-ray diffraction analysis

The representative XRD spectra of the investigated bodies fired at 1150 °C are shown in Figs. 6 and 7. The quartz (JCDPS file 046-1045) and anorthite (JCDPS file 041-1486) were the main phases detected. The formation of the anorthite phase is also supported by the firing curves obtained by the optical dilatometer during a continuous heating ramp. Fig. 6 shows that the compositions with magnesite instead of calcite contained mullite (JCDPS file 015-0776) as well. According to the literature, on the introduction of alkaline-earth oxides into mixtures containing kaolinitic clay, the rate of mullite crystallisation increases [17]. Clay 3 is believed to play an important role in mullitisation because of its relatively higher content of iron oxide and potassium oxide. MgO is one of the most important additives that stimulates the formation of mullite at low temperature. It is known that magnesium and iron oxides enhance the formation of mullite [2, 7]. In both CM and CRM compositions, a small amount of the spinel phase was also observed. The comparison of these bodies,



Fig. 6. XRD spectra of the STD, CM1, CM2 and CM3 compositions.



Fig. 7. XRD spectra of the STD, CRM1, CRM2 and CRM3 compositions.

corresponding to high clay content, indicates that by an exothermic metakaolin decomposition reaction, spinel phase remained at about 1000 °C. A small amount of spinel phase can be understood for the compositions with low mullite crystallisation.

Microstructural analysis

SEM images of the fractured and etched surfaces of the selected formulations are presented in Fig. 8. It can be observed that anorthite phase is in the form of spheroidal crystals [5]. The observed microstructures and low firing temperatures of the investigated bodies indicate that solid-state reactions occur in the systems. In addition, Fig. 8(b) shows that quite a few mullite crystals occurred in the CM bodies. These crystals are well known to have an effect on final properties. Mullite (3Al₂O₃·2SiO₂) is the thermodynamically favoured phase because it possesses a lower crystallisation activation energy than anorthite and gehlenite [18]. It generally exhibits two morphologies: in addition to the well-known elongated needle-shaped mullite (also called secondary mullite because it forms later during the firing process), mullite crystals also occur as fine crypto-crystalline mass of scaly patches



(a)





(c)

Fig. 8. A typical SEM image showing Q: quartz; A: spheroidal anorthite crystals and M: mullite crystals taken from the fractured and etched surface of (a) STD, (b) CM2 and (c) CRM2 formulations.

(primary mullite). The size and shape of mullite crystals is, to a large extent, controlled by the fluidity of the local liquid matrix from which they precipitate and in which they grow, which itself is a function of temperature and composition [5]. Moreover, the phase peak intensities of mullite are observable in the CRM compositions, as indicated by XRD. The addition of MgO considerably increases the mullitisation of clays. It was observed that the Fe_2O_3 and TiO_2 content affects the kinetics and morphology of mullite formation [19, 20]. Therefore, by increasing the amount of clay 3 in the CRM2 composition, mullite crystals were clearly observed, as shown in the SEM images.

Conclusions

The effect of the alkaline-earth oxides MgO and CaO on the fast-firing behaviour of a single-fired wall tile body composition was investigated. It was found that magnesite had an appreciable effect on the sintering. The combined use of calcite with an appropriate amount of magnesite noticeably reduced the peak firing temperature as well. The developed compositions, however, presented better dimensional shrinkage. Taking this finding into account, implementing further modifications, such as to the firing conditions or the body composition, to obtain high dimensional stability (low linear shrinkage) is needed. Because magnesium oxide lowers the maturing temperature, reduces porosity and increases strength but shortens the firing cycle of the bodies, the defects can be eliminated due to the low degasification associated with low glaze maturation temperature, especially in thin and/or large-sized wall tiles to be manufactured.

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