Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Application of grits waste as a renewable carbonate material in manufacturing wall tiles

F.B. Siqueira, J.N.F. Holanda*

Laboratory of Advanced Materials/GMCer, State University of Northern Fluminense, Campos dos Goytacazes, RJ 28013-602, Brazil

ARTICLE INFO

Keywords:
A. Firing
B. Porosity
E. Structural applications
Grits waste

ABSTRACT

This work focuses on the reuse of grits waste, from cellulose industry, as a raw material to replace traditional carbonate material in ceramic wall tiles. Wall tile formulations bearing up to 15 wt% of the grits waste were prepared for replacement of calcareous. The tile manufacturing route consisted of dry powder granulation, uniaxial pressing, and firing at temperatures ranging from 1100 °C to 1180 °C by using a fast-firing cycle. The wall tile specimens were tested to determine their physical and mechanical properties (linear shrinkage, water absorption, apparent porosity, apparent density, breaking strength, and flexural strength). The firing behavior, phase transformations, and microstructure were evaluated by dilatometry, XRD, and SEM. The results showed that the fired wall tile specimens are composed of anorthite and quartz, as major mineral phases, and mullite as a minor phase. It was found that the grits waste had a positive influence on the properties and microstructure of the wall tile specimens. The results also revealed that the grits waste from cellulose industry could be used as a total replacement of traditional calcareous material in wall tile formulations.

1. Introduction

Cellulose is a biomass produced on a large scale in many parts of the world. Brazil is currently the fourth worldwide producer of cellulose, behind the United States, China, and Canada. However, the cellulose industry produces huge amounts of by-products worldwide, including grits waste derived from the liquor causticizing step [1–3]. In Brazil, for example, the cellulose industry yields approximately 690,000 t per year of grits waste. The grits waste is environmentally classified to be a non-inert solid waste material (class IIA) [4], potentially pollutant. At the present, most of the grits waste produced is commonly disposed of in private solid waste sites without any pretreatment. However, such waste management method presents economic and environmental disadvantages. This fact evidences the need to the use of grits waste in added-value products as an option that meets current needs in terms of sustainable development.

At present, there is an increasing interest in the valorization of solid waste materials worldwide. Previous works [5–10] have reported the potential of replacing non-renewable ceramic raw materials by different types of solid wastes in the manufacture of ceramic tile materials. As a rule, this valorization approach is more favorable, from the technical, economic and environmental point of view, when there are similarities between the chemical and mineralogical compositions of solid wastes and conventional ceramic raw materials.

Wall tiles are porous ceramic products with very high open porosity suitable for indoor coverage and decorative work. They are characterized by excellent dimensional stability, good adherence, low hydratability, and low weight per square meter [11,12]. Wall tile formulations are mainly composed of non-renewable ceramic raw materials, such as kaolinitic and illitic clays, carbonates, quartz, feldspars, and talc in variable amounts [12,13]. The wall tiles are fired in industrial single-layer roller kilns using single fast-firing cycles (< 60 min) at peak temperatures between 1080 and 1150 °C. On firing, the main components of the wall tile formulations (clay/carbonate material/quartz) react to form calcium-based crystalline phases, such as calcium aluminosilicates and calcium silicates. Such crystalline phases formed upon firing are of paramount importance for the technical properties and performance of ceramic wall tiles.

It is well known that, in ceramic wall tiles, the carbonate material plays an important role as a fluxing agent during firing. In particular, the carbonate material influences the whole wall tile properties, such as degree of whiteness, shrinkage on firing, water absorption capacity (open porosity), firing temperature range, thermal expansion coefficient, and moisture expansion [12]. The wall tile formulations are characterized by the presence of appreciable amount of carbonate material, whose recommended amount usually ranges from 10 to 16 wt

* Corresponding author.
E-mail address: holanda@uenf.br (J.N.F. Holanda).

https://doi.org/10.1016/j.ceramint.2018.07.203
Received 12 May 2018; Received in revised form 5 July 2018; Accepted 23 July 2018

Table 1
The proportions of the blends for the wall tile formulations (wt%).

Formulation	Kaolin	Quartz	Calcareous	Grits waste
MF0	70	15	15	0
MF5	70	15	10	5
MF10	70	15	5	10
MF15	70	15	0	15

% [11]. Since the grits waste from the cellulose industry is mainly composed of calcium carbonate in the form of calcite ($CaCO_3$) [4,14], then it is very important to investigate its use as a renewable carbonate material for manufacturing ceramic wall tiles. For our best knowledge, the use of grits waste from cellulose industry in manufacturing ceramic wall tiles has not been investigated yet. Thus, the grits waste has important benefits that could be reclaimed as a low-cost renewable carbonate material in ceramic wall tile formulations.

The use of grits waste from cellulose industry as a renewable carbonate material for manufacturing wall tiles is reported, with special emphasis on the formulation characteristics, their effects on the densification behavior, technical properties, and microstructural evolution of the fired specimens.

2. Experimental procedure

Wall tile compositions were formulated (Table 1) using mixtures of kaolin, quartz, calcareous, and grits waste. The standard wall tile composition used as a reference consisted of 70 wt% kaolin, 15 wt% calcareous, and 15 wt% quartz [15]. In this study, the grits waste additions were up to 15 wt% in gradual replacement of calcareous (traditional carbonate material), while the kaolin and quartz were maintained constant. Commercial kaolin, calcareous, and quartz were used. The grits waste was obtained from a cellulose plant located in southeastern of Brazil (Espírito Santo State). Table 2 gives the chemical compositions and loss on ignition of the raw materials. Table 3 displays the mineral phases of the raw materials.

The raw materials were dried at 110 °C for 24 h, dry grounded separately in a ball mill, and then passed through a 200 mesh (< 75 µm) sieve. The wall tile powders (Table 1) were prepared by the dry-process, in which the dry-ground raw materials are mixed and homogenized with finely nebulized water to agglomerate the particles into granules.

X-ray diffraction measurements were carried out on the wall tile crystalline phases using a Shimadzu XRD7000 diffractometer with Cu-Kα radiation, working at 40 kV, 40 mA, and scanning speed of 1.5° (2θ)/min. The dilatometric analysis was performed on green wall tile pellets with a Netzsch DIL 402 C dilatometer in the range of 25 – 1050 °C using a heating rate of 10 °C/min under air atmosphere. The granule size distribution was determined via sieving procedure. The plasticity of the wall tile powders was obtained using the Atterberg method. The real density was measured employing the pycnometer method. The Hausner ratio was calculated as the ratio of tap density to apparent density of the granulated tile powders. The residue of 63 µm sieve has been also determined.

Table 2
Chemical compositions of the raw materials (wt%).

Oxides	Kaolin	Quartz	Calcareous	Grits waste
SiO_2	49.70	98.98	4.03	–
Al_2O_3	33.74	0.41	–	–
CaO	0.30	0.01	65.27	68.67
MgO	0.06	0.01	4.68	–
K_2O	1.97	0.18	1.01	1.04
Na_2O	0.52	0.13	–	–
Fe_2O_3	0.22	0.02	0.53	–
SO_3	–	–	0.44	1.06
TiO_2	0.01	–	–	–
SrO	–	–	–	0.15
LoI$^+$	13.48	0.26	24.04	29.08

LoI$^+$ – loss on ignition.

Table 3
Crystalline phases identified in the raw materials.

Raw materials	Crystalline phases
Kaolin	Kaolinite ($Al_2O_3.2SiO_2{\cdot}2H_2O$), quartz ($SiO_2$), and muscovite ($(K,Na)(Al,Mg,Fe)_2(Si_{3.1},Al_{0.9})O_{10}(OH)_2$)
Quartz	Quartz (SiO_2)
Calcareous	Calcite ($CaCO_3$), dolomite ($Ca,Mg(CO_3)_2$), and quartz (SiO_2)
Grits waste	Calcite ($CaCO_3$), portlandite ($Ca(OH)_2$), and pirssonite ($CaNa_2(CO_3)_2{\cdot}2H_2O$)

The granulated wall tile powders were moistened with 7 wt% water, uniaxially pressed at 50 MPa to produce rectangular tiles (11.50 cm × 2.52 cm), and then dried at 110 °C for 24 h. Finally, the green wall tile specimens (five test specimens for each composition) were fast-fired between 1100 °C and 1180 °C with a soaking time of 5 min in a laboratory fast-firing kiln. The whole fast-firing-cooling cycle lasted less than 60 min to simulate industrial fast-firing process.

Linear shrinkage values upon drying and firing have been determined from the length variation of the rectangular specimens according to ASTM C 326-09. Water absorption, apparent density, and apparent porosity were established by using the Archimedes method according to ASTM C 373 14a/2014. The breaking strength and flexural strength of the rectangular specimens were determined by a three-point bending test at a constant loading rate of 0.5 mm/min, according to ISO 10545-4, using a universal mechanical testing machine (Instron, model 1125).

The mineral phase analysis after fast-firing cycle was done by X-ray diffraction (Shimadzu, XRD 7000 diffractometer) using Cu-Kα radiation, 2θ (5–70 °). SEM analysis was carried out on the fractured surface of fired wall tile specimens by scanning electron microscopy (Shimadzu, SEM SSX-550) at 15 kV after gold-coating surfaces.

3. Results and discussion

Fig. 1 shows the XRD patterns of the green wall tile formulations. It can be observed that the formulations presented kaolinite ($Al_2O_3.2SiO_2{\cdot}2H_2O$), quartz ($SiO_2$), and calcite ($CaCO_3$) as the main mineral phases, and muscovite ($KAl_2Si_3AlO_{13}(OH)_2$) as a minor phase. However, the mineral composition of the wall tile formulations presents small but important differences. In the reference wall tile formulation (MF0 formulation), characteristic peaks of dolomite ($CaMg(CO_3)_2$) were also detected (Fig. 1a) while in the wall tile formulation bearing grits waste (MF15 formulation), peaks of pirssonite ($CaCO_3.Na_2CO_3{\cdot}2H_2O$) and portlandite ($Ca(OH)_2$) were observed (Fig. 1b). This finding agrees with the chemical and mineralogical compositions of the raw materials as shown in Table 2 and Table 3. Thus, the replacement of calcareous with grits waste is expected to influence the technological properties and microstructure of wall tile materials.

Fig. 2 presents the granule size distribution of the wall tile powders prepared by the dry process. There was only a small difference in the granule size distribution of the wall tile powders. For all wall tile powders, the majority of the granules were concentrated in the size range of 150–250 µm in agreement with ceramic tile powders produced by the dry process [16].

Table 4 presents important technological parameters of the wall tile powders. It was clear that the variation of real density of the wall tile formulations was small (2.51–2.52 g/cm^3) when the calcareous was replaced by grits waste. In fact, the real density reflects their mineral compositions (Fig. 1). The residue retained on a sieve of 63 µm was in the range of 1–3 wt%, which is adequate for producing ceramic tile materials [13]. Thus, the primary particles of the wall tile powders had high degree of grinding, being compatible with industrial wall tile