



Effect of wollastonite addition on sintering of hard porcelain

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Abstract

Hard porcelain body with wollastonite additive was produced by the slip casting method using quartz, potassium feldspar and kaolin raw materials. Wollastonite powders were added to the porcelain formulation by replacing the potassium feldspar up to 5 wt% to explore its effect on the sintering behaviour and also technological properties of sintered end products. By means of rheological behaviour optimization of ceramic suspensions using several dispersants and sintering enhancement by wollastonite addition, hard porcelain of higher strength at lower firing temperature was obtained. By studying the effect of the additive concentration, on the firing temperatures of the hard porcelain, it is found that reducing firing temperature 25 °C without compromising its quality and thereby producing energy saving was achieved by 1 wt% wollastonite addition.

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1. Introduction

Porcelain is highly vitrified ceramic material produced from a body formulated by mixtures of clay, quartz and feldspar [1–4]. Porcelains typically have a triaxial formulation comprising about 50% clay, 25% flux and 25% filler. The clay acts as a binder for the other constituents in the green state, confers plasticity on the body for shaping and is usually kaolinite. The flux is a low melting phase that reacts with the other constituents and lowers the temperature of liquid formation in the system. This liquid permeates the microstructure leading to densification. Fluxes used commercially are alkali feldspars. The filler is reasonably stable at commercial firing temperatures and reduces distortion and shrinkage. Vitrification indicates a high degree of melting on firing which confers low (often < 0.5%) porosity and high (> 40%) glass contents on fired porcelains [4–6]. Porcelain microstructures are grain and bond type with large particles of filler (usually quartz) held together by a finer matrix, which is almost fully dense, composed by mullite crystals and a glassy phase [1–4].

Firing process is a heat treatment that gives sufficient strength to formed ceramic green body in-service condition. Activation energy is required for sintering process and it is transferred into heat energy; thereby, body temperature increased. Most of the reaction enthalpies required for sintering silicate ceramic products is between 25 and 550 kJ/kg [7]. Hard porcelain tableware ceramics have often fired in 1380–1450 °C [8]. This means that relatively high specific energy consumption and approximately 10–15 MJ is around for 1 kg porcelain in the fast firing conditions [7,9,10]. However, in practice, these values are the values 3–8 times as much as being more in industrial firing processes. In fact, only a fraction of the energy consumed in formation reactions for body the rest is devoted to the significant loss. Total cost share of energy in the production of ceramic products is enormous [7].

For keeping up competitive capability and high quality the porcelain industry needs new innovations which also require a change in firing process, sintering time, and energy cost. First improvements were achieved with introduction of the fast firing process in the past years. Here for example time for glost firing was reduced from 20 to 25 h (1965) to approximately 5 h (2000). Second improvements can be the change to the single firing technology which is rarely used at the moment for the

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Table 1
Chemical composition of raw materials.

Compositions (wt%)	Kaolin	K-feldspar	Quartz	Wollastonite
SiO ₂	47.00	66.33	99.04	52.37
Al ₂ O ₃	37.00	17.80	0.52	0.36
Fe ₂ O ₃	0.45	0.11	0.03	0.21
TiO ₂	0.50	0.03	0.02	0.01
CaO	0.30	0.18	0.02	45.80
MgO	0.20	0.28	0.02	0.36
Na ₂ O	0.20	2.83	0.10	0.24
K ₂ O	0.80	11.90	0.02	0.06
LOI*	13.55	0.54	0.21	0.59

LOI*: loss on ignition.

production of tableware. Another promising idea to decrease energy demand is the reduction of temperature during glost firing. A reduction of energy consumption implies a decline of energy cost and a lower environmental pollution because of less CO₂ emission. An innovative way of reduction of firing temperature can be reached by addition fluxing agents for higher reactivity [11].

Optimizing the use of flux has been increasingly intensified in the ceramic industry, due to the large reduction in energy costs provided. However, instability in non-crystalline phases formed by the flux, developed during the firing process of the ceramic material will directly influence the final properties of different ceramic materials produced industrially [12]. Glassy phase determines the temperature and the firing range of ceramics formulated with silicate raw materials. Glassy phase control is a key factor to reduce firing temperature, which means a direct reduction in cost associated with the fuel. Realizing this aspect, whenever possible, industry chooses to use strong fluxes [13]. A great quantity of a glassy ingredient in the raw materials promotes liquid phase formation at a lower temperature. This resultant glassy phase has a higher reactivity in body sintering, glaze firing and frit melting, which allows a reduction of the processing temperature. Fully crystallized alkali containing raw materials (feldspars and pegmatites) have a lower fusibility due to the higher energy threshold for crystal network destruction. In respect of reactivity on heating, the fine fibred microcrystal quartz varieties are preferred because of their specific surface [14].

Wollastonite (CaSiO₃) is an important material in fine ceramics, and the tile and cement industries. A host of favourable properties such as low shrinkage, good strength, lack of volatile constituents, body permeability, fluxing characteristics, whiteness, and acicular shape render wollastonite useful in several ceramic and other applications [15]. Use of wollastonite is desired for rapid heating and cooling without cracking or warping. Other sources of CaO, such as limestone, enhance loss on ignition. Besides, wollastonite is interesting to use in white porcelain due to its very low level of colorants oxides, such as Fe₂O₃, FeO, and TiO₂ [13]. Wollastonite can be used in the production of porcelains as a CaO source. The high content of CaO decreases the liquid phase viscosity of the porcelain at high temperatures, which makes it particularly easy to generate shape distortion of the porcelain bodies [16]. Some studies

have been devoted to the creation of low firing porcelain and to reduce energy consumption [17,18]. In these studies, it was observed that addition of additives such as wollastonite to porcelain can reduce the firing temperature of the triaxial body to a great extent and also increase bending strength which was attributed to relatively advantageous microstructure [16,18].

This study presents the initial results on the use of wollastonite, in partial substitution of feldspar, for hard porcelain production. Thus, different ceramic compositions were formulated based on a wollastonite, quartz, potassium feldspar and kaolin raw materials. Samples were fired at temperatures of 1250, 1275 and 1300 °C to determine the influence of wollastonite additions on sintering temperature and post-firing properties of hard porcelain.

2. Experimental procedure

The raw materials used in the present investigation were kaolin ($d_{50}=9.822 \mu\text{m}$ and specific surface area $11.804 \text{ m}^2/\text{g}$), quartz ($d_{50}=25.690 \mu\text{m}$ and specific surface area $0.588 \text{ m}^2/\text{g}$), potassium feldspar ($d_{50}=18.434 \mu\text{m}$ and specific surface area $0.961 \text{ m}^2/\text{g}$) and wollastonite ($d_{50}=14.992 \mu\text{m}$ and specific surface area $1 \text{ m}^2/\text{g}$) provided by Ceramic Companies in Turkey. The chemical composition of raw materials, as determined by X-ray fluorescence (XRF) is shown in Table 1.

A standard composition for hard porcelain production was prepared by mixing 50 wt% kaolin, 25 wt% potassium feldspar and, 25 wt% quartz. Typically, potassium feldspar is used as fluxing agent in the industrial manufacture of hard porcelain stoneware. However, in the present study, wollastonite was chosen as another fluxing agent partially replacing potassium feldspar since fully crystallized alkali containing raw materials such as feldspars have a lower fusibility due to the higher energy threshold for crystal network destruction. Five additional body mixes were formulated on the basis of a standard composition. The major additive to the mixtures was wollastonite powder where the added amounts were 0, 1, 2, 3, 4 and 5 wt%. The prepared powder mixtures are encoded as W_0 , W_1 , W_2 , W_3 , W_4 and W_5 where, W stands for wollastonite while '0, 1, 2, 3, 4 and 5' stand for wt% wollastonite. The batch compositions of bodies with additives are given in Table 2. The suspensions of W_0 , W_1 , W_2 , W_3 , W_4 and W_5 were prepared so that each solution had solid loading levels given in Table 2, and favourable dispersant, determined as a result of rheological studies on the standard composition, was added to achieve a good dispersion of ceramic particles in aqueous solution.

The homogenisation and the rheological behaviour of the suspensions has been shown to play a significant role on the slip casting processing, and in turn, on the microstructure and

Table 2
Compositions of powder mixtures.

Compositions (wt%)	W_0	W_1	W_2	W_3	W_4	W_5
Kaolin	50	50	50	50	50	50
Quartz	25	25	25	25	25	25
Potassium feldspar	25	24	23	22	21	20
Wollastonite	0	1	2	3	4	5

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