

FLUXING AGENTS FOR PORCELAIN TILES PRODUCED BY THE DRY ROUTE

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ABSTRACT

Fluxing agents are particularly important in porcelain tile compositions because this type of ceramic tile requires high volumes of vitreous phases during firing to eliminate open porosity. The volume and viscosity of the vitreous phases that form during firing control the densification process and thus determine the firing temperature and pyroplastic deformation.

The fluxing agents commonly employed in porcelain tile compositions are feldspars, phyllites (used in Brazil) and nephelines. These raw materials are water-insoluble, which makes them particularly suitable for compositions of traditional porcelain tile produced by the wet route. However, a large group of water-soluble raw materials also have a good potential to act as fluxing agents and could be used in dry route processes.

In this context, the purpose of this work was to determine the fluxing potential of water-soluble or partially water-soluble raw materials in a porcelain tile composition. The effectiveness of several borates, i.e., colemanite, ulexite, hydroboracite, as well as sodium carbonate, was tested in a comparative study.

The results of this study indicate that small additions of these fluxing agents suffice to greatly reduce the firing temperature without causing high pyroplastic deformation of the bodies. The best results were obtained in compositions containing hydroboracite.

This finding is especially relevant for the creation of alternative compositions of porcelain tiles produced by the dry route. Dry route processing is currently the focus of a great deal of interest due to environmental and economic issues.

1. INTRODUCTION

Today, an essential requirement for the economic feasibility of ceramic bodies prepared by the wet route is the formation of aqueous suspensions of low viscosity and high solids concentrations [1]. The low viscosity of such suspensions plays an important role in ensuring proper discharge from mills, transportation to storage tanks, and the subsequent spray-drying stage. In this context, deflocculants should act as agents that promote particle dispersion in suspensions [2], enabling the obtainment of suspensions of low viscosity with low proportions of water and thus reducing the energy-related costs of water evaporation in the spray-drying stage of these suspensions.

In view of the requirements for suspensions prepared from clay paste processed by the wet route, it is essential that these compositions exhibit rheological behaviours that are compatible with the aforementioned requirements. In this context, several highly plastic clays normally have only a limited use in ceramic body compositions destined for this process [3], since some minerals are known for not easily forming stable suspensions with high solids concentrations and low viscosities. Moreover, the raw materials used in the formulation of ceramic bodies for wet route processing are limited to those consisting of minerals that are water-insoluble at room temperature, since their dissolution – even if partial – can affect the balance of particle surface charges and impair the rheological properties of the suspensions [4].

In recent years, several studies [5] have been conducted to evaluate the feasibility of manufacturing porcelain tiles by the dry route. Dry route processing, which involves lower energy consumption and lower volumes of water, can be considered an important alternative for the production of porcelain tiles in the near future, particularly in view of the environmental protocols that have been adopted in the last few years.

In dry route porcelain tile manufacturing, the rheological behaviour in suspension is no longer a fundamental requirement for the ceramic body formulation employed, since its preparation does not involve the formation of suspensions. This difference may allow for the use of highly plastic clays and of minerals that are somewhat soluble in water in ceramic body compositions destined specifically for this fabrication route. Considering this possibility, the purpose of this study was to evaluate the potential use of some fusible raw materials in porcelain tile compositions destined for wet route processing, in view of the limitations imposed by their rheological behaviours.

Fluxing agents [7] play a fundamental role in porcelain clay pastes due to the need to obtain low porosities in the finished product. Low porosity is achieved through the formation of high volumes of liquid phases during firing, which result from the progressive melting of the fusible minerals used in the composition of the ceramic body. Thus, fluxing agents, which are determinants in defining the product's firing temperature and are responsible for the pyroplastic deformation

[8] the ceramic body undergoes during firing, strongly affect the microstructural characteristics of the resulting porcelain tiles.

The fluxing agents traditionally used in ceramic tiles prepared by the wet route are feldspars [9]. Phyllites [10] (the fluxing agents typically used in Brazil) and nephelines can also be used in porcelain tiles in place of feldspar. Borates, in turn, may be highly interesting alternatives for use in porcelain tiles, since B_2O_3 allows for the formation of glassy phases with low viscosity at low temperatures. Although initiatives [11] have focused on their use in ceramic bodies destined for wet route processing, the use of borates in formulations of these bodies should be limited, in view of their partial solubility in water.

2. MATERIALS AND METHODS

To carry out this study, samples were collected of the raw materials of an industrial paste used for the fabrication of glazed porcelain tiles by the wet route. The raw materials were used in the proportions of the formulation of the paste to create a composition referenced "AT Porcelain Body." This paste was first characterized chemically and mineralogically by X-ray fluorescence and X-ray diffraction analyses.

Samples were also collected of the fluxing agents tested in this study, namely sodium carbonate, hydroboracite, ulexite and colemanite. These raw materials were selected due to their potential to act as fluxing agents during firing, as indicated by the chemical elements that make up their compositions – B_2O_3 , Na_2O , CaO and MgO . The selected borates offer economic advantages over boric acid and hydrated sodium borates. Their chemical compositions were initially determined by X-ray fluorescence to confirm the chemical elements they contained and their proportions.

To evaluate the potential of these raw materials as fluxing agents, they were added in fixed amounts to the porcelain body selected for this stage of the study. Table I presents the compositions of the tested bodies.

Raw materials	STD	B	H	U	C
AT Porcelain body	100.0	97.5	97.5	97.5	97.5
Sodium carbonate (%)	-	2.5	-	-	-
Hydroboracite (%)	-	-	2.5	-	-
Ulexite (%)	-	-	-	2.5	-
Colemanite (%)	-	-	-	-	2.5

Table I – Compositions of the tested bodies

All the bodies were dry-ground in a laboratory-scale hammer mill, followed by dry-grinding in a mortar and in a laboratory ball mill. Grinding was performed until all the bodies passed entirely through an ABNT #230 sieve (63 μm mesh holes). After grinding, all the bodies were granulated in laboratory sieves with the addition of 6.5% of moisture, forcing the passage of the resulting agglomerates through sieves with 1.0 mm diameter openings. The granulated bodies were allowed to rest for 24 hours to homogenize the added moisture, after which they were pressed into test specimens.

The test specimens, with approximate dimensions of 60x20x6 mm, were pressed uniaxially in a hydraulic laboratory press under a fixed compaction pressure of 380 kgf/cm². The resulting test specimens were characterized based on the following analyses: apparent density after drying, flexural modulus of rupture after drying, linear drying shrinkage, gresification curves after firing at four different temperatures in cycles with a total duration of 45 minutes and a 5-min hold time at the maximum firing temperature, flexural modulus of rupture after firing, reflectance spectrophotometry of colour coordinates, pyroplasticity indices and coefficients of linear thermal expansion.

3. RESULTS AND DISCUSSION

Table II describes the chemical compositions of the porcelain body and the fusible raw materials selected for this study. Table III shows the mineralogical composition of the AT porcelain body estimated from the results of the chemical and mineralogical analyses.

The results indicate that the chemical composition of the AT body is typical of the glazed porcelain bodies currently utilized in Brazil, which have relatively lower Fe₂O₃ and TiO₂ contents than red ceramic fired tiles. As can be seen, the oxides of the alkaline elements (Na₂O and K₂O) show very similar weight contents. A rational analysis indicates similar contents of albite and muscovite mica, which are the minerals that contain the aforementioned oxides. The high content of muscovite mica is probably attributable to the use of phyllite [10], which has been widely employed as a fusible raw material in Brazilian glazed porcelain tiles as an alternative to reduce the content of feldspars, which are less abundant in the south of the country.

In addition to the presence of kaolinite and quartz, the rational analysis also indicates the existence of auxiliary fluxing agents in the body, represented by the presence of talc and dolomite in estimated contents of less than 3.0%.

Oxides	AT Porcelain body	Sodium carbonate	Hydroboracite	Ulexite	Colemanite
L.O.I. (%)	5.59	40.52	26.61	6.57	25.68
SiO ₂ (%)	68.02	0.01	5.98	7.22	9.69
Al ₂ O ₃ (%)	17.72	-	1.04	1.43	2.18
Fe ₂ O ₃ (%)	1.24	0.03	0.68	0.67	0.76
TiO ₂ (%)	0.42	-	0.12	0.23	0.14
CaO (%)	1.05	-	14.18	12.07	22.11
MgO (%)	1.50	-	9.46	0.70	2.11
Na ₂ O (%)	2.20	58.23	-	16.80	0.40
K ₂ O (%)	2.02	0.01	0.27	0.46	0.53
MnO (%)	-	-	-	-	0.01
P ₂ O ₅ (%)	0.02	-	-	0.05	0.07
B ₂ O ₃ (%)	-	-	41.59	53.52	35.97

Table II – Chemical compositions of the AT porcelain body and fusible raw materials

Minerals	AT body
Kaolinite (%)	19.0
Quartz (%)	37.1
Albite (%)	18.6
Muscovite mica (%)	17.1
Dolomite (%)	3.5
Talc (%)	2.4
Others (%)	2.3

Table III – Estimated mineralogical composition of the AT porcelain body

The chemical analysis of the fluxing agents indicates that the raw materials selected exhibit high purity, since their chemical compositions are very similar to their chemical formulas. It should be noted that the purity of sodium carbonate is higher than that of borates, which are usually contaminated with 5% to 10% of SiO₂. Another point to be highlighted is the presence of chromophoric elements (Fe₂O₃ and TiO₂) in borates, which may affect the firing colour of the bodies, although the contents of these elements fall entirely within the acceptable limits for glazed porcelain bodies.

Table IV lists the characteristics of the bodies prior to firing. None of the bodies except the one containing sodium carbonate (body B) display significant changes in their apparent density and flexural modulus of rupture after drying

when compared to the STD body. The body containing sodium carbonate showed a significantly higher apparent density and flexural modulus of rupture than the other bodies. This result has to do with the binding effect of sodium carbonate in ceramic tile bodies. According to the literature [12], this type of binder forms solid bridges between particles through crystallization, and can promote increases of up to 50% in the mechanical strength of unfired ceramic clay bodies when added in the proportion of 0.5% to a ceramic body.

With regard to drying shrinkage, the added borates led to small increments in the magnitude of shrinkage of the bodies in comparison to the STD body. The presence of sodium carbonate in body B significantly increased the body's firing shrinkage, which was attributed to the solubilization of this raw material in the water used in the granulation step.

Bodies	Apparent density (g/cm ³)	Flexural modulus of rupture (MPa)	Drying shrinkage (%)
STD	1.94 ± 0.02	2.8 ± 0.2	0.11 ± 0.01
B	2.01 ± 0.02	6.6 ± 0.7	0.22 ± 0.01
H	1.93 ± 0.03	3.3 ± 0.6	0.15 ± 0.02
U	1.93 ± 0.02	2.9 ± 0.3	0.14 ± 0.02
C	1.96 ± 0.02	3.0 ± 0.3	0.14 ± 0.01

Table IV – Characteristics of the test specimens of the bodies prior to firing

The behaviour of the bodies during firing can be evaluated based on the gre-sification diagrams shown in Figures 1 and 2, which indicate the effects of firing temperature on the bodies' linear shrinkage and water absorption.

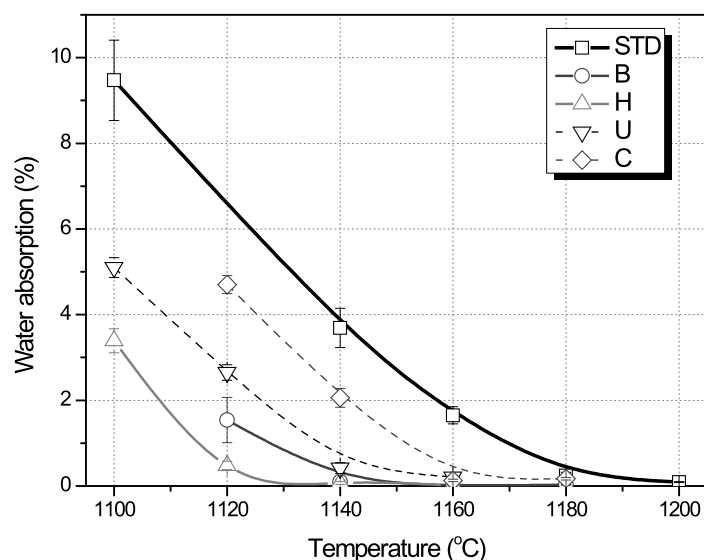


Figure 1 – Effects of firing temperature on the water absorption of the STD, B, H, U and C bodies.

The gresification diagrams indicate that all the tested fluxing agents were effective in reducing the firing temperature of the STD body, since the bodies to which they were added reached their maximum densification temperatures after firing at significantly lower temperatures than that of the STD body. These results are extremely interesting, since the increase in the fusibility of the body may enable the use of lower firing temperatures and/or of faster firing cycles in the fabrication of porcelain tiles by the dry route.

Special emphasis should be given to the results obtained with body H – containing hydroboracite as fluxing agent. This body presented maximum densification after firing at 1140°C, which represents a reduction of 40°C in the firing temperature needed to reach the maximum densification of the STD body. The body containing ulexite as fluxing agent also presented very high fusibility, probably due to the combined presence of sodium and boron. The greater melting effect of hydroboracite than that of the other borates is probably due to the higher effective participation of boron in this raw material and its lower SiO₂ content, considering the proportions of the elements during firing (no loss on ignition).

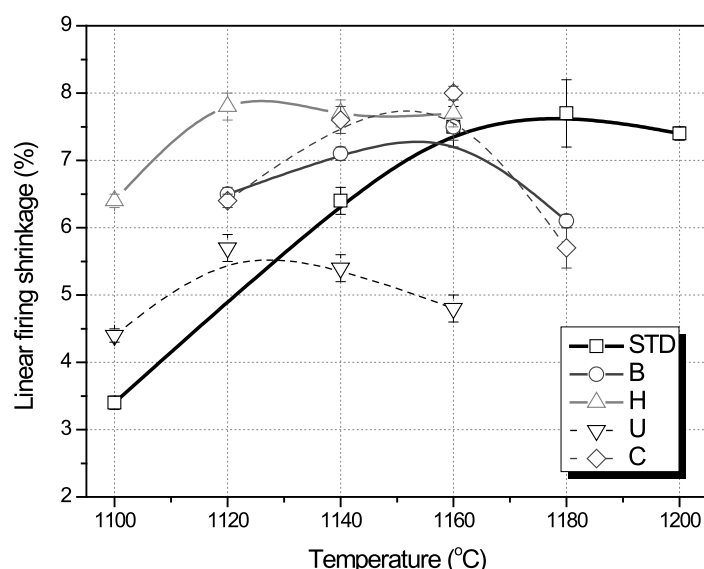


Figure 2 – Effects of firing temperature on the linear firing shrinkage of the STD, B, H, U and C bodies

In the case of the test specimens containing sodium carbonate, the formation of a thin vitrified layer was observed on their surface. This phenomenon is likely attributable to the complete solubilization of sodium carbonate in the granulation water. During the drying of test specimens, sodium carbonate is transported by water to the surface of the bodies and, after the water evaporates, the sodium carbonate crystallizes on the surface. This phenomenon renders the use of sodium carbonate as a fluxing agent in this type of body practically unfeasible, at least in the content tested, since it leads to significant heterogeneity of the fired bodies.

In addition to reducing the maximum densification temperature of the bodies, the analysis of the gresification curves indicates that the firing ranges of the bodies

containing the tested fluxing agents were shorter than that of the STD body. This finding was confirmed by the shapes of the linear shrinkage curves as a function of the firing temperature, which reveal larger dimensional changes in the bodies containing the tested fluxing agents in response to minor changes in temperature at around the maximum densification temperature of the bodies.

It should be pointed out that similar results have been reported previously in the specialized literature [11], where studies of the same nature were conducted on a porcelain body fabricated by the wet route. However, borates should be used very cautiously in bodies destined for this type of processing, since the rheological properties of suspensions are directly affected by their presence, starting at very low added contents.

Table V lists the maximum densification temperatures of the bodies, as well as their properties (modulus of rupture, pyroplasticity index, coefficient of thermal expansion, and the colour coordinates that indicate the firing colour) after firing at these temperatures.

The results reveal the existence of significant differences in the flexural modulus of rupture of the fired bodies at their respective maximum densification temperatures. With the exception of body B, all the bodies containing added fluxing agents presented lower rupture moduli than the STD body. These results are due to the probable heterogeneous densification of these compositions, which presented a slight increase in the firing temperatures required to attain zero water absorption. In the case of the body containing hydroboracite, it was found that the mechanical strength, evaluated from its flexural modulus of rupture, was even slightly higher than that of the STD body.

Bodies		STD	B	H	U	C
Max. densification temp. (°C)		1180	1160	1140	1140	1160
Flexural modulus of rupture (MPa)		64.7 ± 1.7	32.7 ± 3.0	72.6 ± 1.9	42.7 ± 0.7	51.2 ± 2.3
Pyroplasticity index (cm ⁻¹)		7.8 × 10 ⁻⁵	13.0 × 10 ⁻⁵	8.3 × 10 ⁻⁵	8.7 × 10 ⁻⁵	9.8 × 10 ⁻⁵
α_{25-325} (°C ⁻¹)		68.4 × 10 ⁻⁷	77.8 × 10 ⁻⁷	66.8 × 10 ⁻⁷	66.2 × 10 ⁻⁷	66.9 × 10 ⁻⁷
Colour coordinates	L*	60.7	58.7	62.6	64.1	62.3
	a*	2.1	3.8	3.6	4.2	2.6
	b*	12.2	15.8	12.7	14.1	11.9

Table V – Characteristics of the STD, B, H, U and C bodies after firing at their respective maximum densification temperatures

As for the results of the pyroplasticity indices, it was found that, in general, the addition of energetic fluxing agents tends to increase the susceptibility to deformation of the STD body. This is due to the decrease in viscosity of the glassy

phases that are formed, which exhibit greater fluidity at high temperatures, thus favouring the deformation of the test specimens. The presence of boron, allied to the alkaline and alkaline earth elements contributed by the fluxing agents employed, are responsible for this phenomenon in the bodies in question, in view of the known effects of these elements on the viscosity of glasses [13].

With regard to the thermal expansion coefficient, the effects of the addition of the borates under study on the STD body were but minor, causing only slight decreases, probably due to the decrease in the thermal expansion of the glassy phases formed in response to the presence of boron. In the case of the body containing sodium carbonate, the presence of a high concentration of sodium in the glassy phases that were formed was undoubtedly responsible for the increase in the thermal expansion coefficient of the product. The literature describes sodium as a lattice modifier which has marked effects on the properties of glasses due to its atomic radius [13].

Lastly, the analysis of the firing colour of the samples indicates that the bodies containing the fluxing agents under study generally presented slightly whiter, yellowish and reddish colours. This is due to the use of lower firing temperatures to obtain the maximum densification of the bodies, and is consistent with the effects of the firing temperature on the colour coordinates of ceramic tile bodies described in the literature [1].

The overall results point to considerable advantages in the use of hydroboracite as a fluxing agent in porcelain bodies produced by the dry route. Hydroboracite causes practically no change in the behaviour of the body before firing and accelerates the densification of the product significantly during firing, allowing for substantially lower firing temperatures. Moreover, it makes the body only slightly more susceptible to pyroplastic deformation, without affecting the other properties of the finished product.

As mentioned earlier, this fluxing agent can be used in bodies prepared by the dry route without the restrictions imposed by the rheological behaviour of suspensions, as is the case of bodies prepared by the wet route. The dosage of this borate in formulations of porcelain bodies destined for dry-route processes should be chosen taking into account its energetic melting effect, with precautions in terms of the amount of its addition regarding only the reduction of the firing range and the increase in pyroplastic deformation it may confer on the bodies.

4. CONCLUSIONS

The following conclusions can be drawn based on the overall results obtained:

- The use of the dry route process for the manufacture of glazed porcelain tiles may allow for the incorporation of a series of raw materials that are currently

not used in spray-dried bodies for the development of porcelain tile formulations.

- Borates can be utilized successfully in the manufacture of porcelain tiles by the dry route, since they act as energetic fluxing agents during firing, allowing for significantly lower firing temperatures even when added in small amounts.
- In general, the presence of borates in the glazed porcelain bodies studied here had only a minor effect on the properties of green bodies. During firing, in addition to reducing the firing temperature, they can shorten the firing range and augment the tendency for pyroplastic deformation of the bodies.
- The use of sodium carbonate in the contents tested in this study is not recommended, since it presents high solubility in the water used for granulation of the body, resulting in heterogeneous bodies.
- The best results were obtained with the addition of hydroboracite in the porcelain bodies under study, due to its melting behaviour and the greater homogeneity of the resulting bodies.
- Considering the mixture limitations of dry-route processes, an important point to keep in mind is the homogeneity of these fluxing agents in porcelain bodies, since their heterogeneity may preclude the use of these raw materials.

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