USE OF THERMALLY TREATED BENTONITIC CLAY IN CERAMIC TILE FORMULATION

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ABSTRACT

In the wet formulation of ceramic bodies, the use of bentonitic clays is limited because in the milling stage, the polar nature of these clays limits the solids concentration and generates rheological problems (deflocculation problems) in the suspension. This is why although this clay has an appropriate chemical composition for the forming of ceramic bodies, it is little used. The present study describes the use of a thermally pre-treated calcium bentonite for the formulation of porous white ceramic wall tile bodies, processed by the wet method. The bentonite content in the formulation is 40-45 % by weight. In thermal dilatometric analysis (TDA) a stability area $\Delta l/l_0 \cong 0$ *was observed between 1000 and 1100 ºC, with a sintering start temperature of 850 ºC. The sintering kinetics studied by TDA confirm the dependence of the stability range on the peak firing temperature and isothermal treatment time, a stage characterised by the reaction of CaO with the glassy matrix, from which anorthite and calcium albite crystals segregated, identified by XRD. The results of the sintering kinetics study, as well as the XRD and SEM analyses, indicate that this material sinters in a reactive liquid phase. This sintering mechanism differs from the mechanism conventionally used in the ceramic industry. With this formulation it is feasible to obtain porous ceramic tiles which, after production, display no dimensional changes due to hydration of some of the formed phases.*

1. INTRODUCTION

Despite bentonites having an appropriate chemical composition, their use is limited in the ceramic floor and wall tile industry according to Díaz et al.[1]; these so-called special clays are not widely used in the ceramic sector and their most significant application is as suspending agents (in very low concentrations) or as rheological modifiers. In industrial processes, the solids concentration for suspensions obtained by milling or mixing clays needs to be 60 % or more, with a view to reducing costs in the drying stage and decreasing shrinkage of the pieces formed by pressing, extrusion, slip casting, or on a potter's lathe, which is why the use of bentonite type clays has always been limited. When bentonitic clays are used in the production of craftware in the field of the pottery, the paste that is prepared for forming o throwing has the appropriate plasticity for hand moulding. However, due to the high water content, serious problems of cracking appear during drying as a result of excessive shrinkage. Bentonites are therefore mainly used in the formulation of ceramic bodies as suspension stabilising agents in quantities of 2-3 % at most. Brescani et al.[2] used montmorillonite clay to increase the densification of ceramic bodies, and the maximum content of this clay that they managed to use in the formulation was 15 %, though at these concentrations they reported important problems in the rheological properties of the slurry in processing.

The typical ceramic body formulations for porous tiles are generally made up of: kaolin, silica, fillers (feldspathic sands), and $CaCO_3$, while the formation of crystalline phases occurs during the vitrification process, by CaO reaction with the amorphous silica or the metakaolinite that develops from the kaolinite decomposition reaction. The crystals that form are Anorthite, Gehlenite, Albite, and Wollastonite, as well as mullite and amorphous silica by thermal decomposition of the kaolinite, in accordance with reactions 1 and 2, shown below. All these phases form during the different vitrification process stages of the ceramic body[3,4].

Kaolinite decomposition

$$Kaolinite_{(Al_2Si_2O_5(OH)_4)} \xrightarrow[T>550°C]{} Metakaolinite_{(Al_2Si_2O_5)} \xrightarrow[T>960°C]{} Mullite_{(Al_{4.5}Si_{1.5}O_{9.75})} + Silica_{(SiO_2)}$$

(1)

Crystallisation reaction

$$SiO_2 + Al_2O_3 + CaO \xrightarrow[T>920°C]{} Anorthite_{(CaAl_2Si_2O_8)} + Wollastonite_{(CaSiO_3)} + Gehlenite_{(Ca_2Al(AlSi)O_7)}$$

(2)

The crystallisation process depends on the degree of homogenisation of the materials, as well as on firing temperature and time, and on calcium carbonate particle size – the smaller this particle size, the more reactive it will be to enable more complete crystallisation[3].

Because the reactions depend on many variables and some of these limit the advance of crystallisation, it is difficult for this process fully to unfold, which is why at firing end, quantities of unreacted silica, other amorphous phases, and even CaO are obtained, which are hydratable phases that give rise to the problem of moisture expansion in the fired products[4]. Hydratable phase formation can be reduced by increasing firing temperature or time, or using a formulation that promotes crystalline phase formation by alternate sintering mechanisms, achievable by using clays that contribute a reactive liquid phase.

In accordance with Aguilar et al.[5], it is possible to decrease or to eliminate the undesirable characteristics of bentonites for the formulation of ceramic bodies by thermal treatment before the clay is incorporated into the formulation. Of the different pre-treatments for the clay that are presented in the patent, one was selected that consisted of heating the bentonite up to 700 °C, and holding that temperature for 5 minutes, since it is the heating with the lowest energy demand. This paper describes the formulation of a porous white tile body, prepared with 12 % $CaCO_3$ by weight, 40 % thermally pre-treated bentonite TX (designated BTX), while the rest consisted of ball clay, silica and feldspathic sand. The study determined the main technical characteristics of this tile, as well as the influence of the crystallisation processes on sintering kinetics (vitrification).

2. EXPERIMENTAL

A porous white tile formulation was prepared by wet milling. The suspension was dried and the dry solid was powdered until it passed through a 500 µm sieve. This material was wetted to a moisture content of 5% by weight. The powder was used to form samples measuring 5 x 10 x 0.7 cm with a Nannetti Model Mignon-SSEA laboratory hydraulic press by uniaxial pressing, applying a unit load of 300 kg/cm^2.

Table 1 details the mineralogical and chemical composition of bentonite TX and the feldspathic sand, while Table 2 presents the formulation of the porous white tile (RPBTX). Milling was conducted in 1 l alumina jars and an eccentric mill, using a charge of 500 g solids and 370 g water; sodium polyacrylate (0.4 g) was used as an additive and the alumina ball charge was 580 g. The milling time was 15 minutes in all cases.

MINERALOGICALSPECIES	FELDSPATHIC SAND	CLAY BTX
	(wt%)	(wt%)
Quartz	47	5
Orthoclase	23	0
Oligoclase	13	0
Calcium montmorillonite -15A	8.3	77
Calcite	0.9	12
Hematite	0.8	0
LOI	7	6
Total	100	100

Table 1. Mineralogical composition of the feldspathic sand and bentonite BTX,

RPBTX FORMULA	
MATERIAL	(wt%)
BTX (treated at 700ºC)	40
Bentonite Texas	5
Feldspathic sand	28
Ball clay	17
Silica	10
Total	100

Table 2. Formulation of the RPBTX tile.

2.1. FIRING OF LABORATORY TEST PIECES

In order to study the development of vitrification, green test pieces were fired in a Nabertherm model LS 12/13 laboratory kiln, which was programmed with the firing curve described in Figure 1. The treatments referenced R_1, R_2, R_3, and R_4 were conducted without isothermal treatment and correspond to temperatures of 900, 950, 1000, and 1050 ºC respectively. The test pieces referenced RP_5 were fired at 1115 ºC with 6-minute isothermal treatment. The points in Figure 1 represent each treatment. The resulting test pieces were used in the SEM and XRD analyses to study the composition of the liquid phase and crystalline phase formation. Their bulk density (DAP) and linear shrinkage (LS) were also determined.

2.2. THERMAL DILATOMETRIC ANALYSIS AND SINTERING STUDY

Thermal dilatometric analysis (TDA) was carried out with green and fired samples measuring 3 x 3 x 12 mm by a double-beam optical dilatometer (Expert System Model Misura ODHT 1400-80), at different heating rates (see Table 3) to a temperature of 1200 ºC with different isotherms. The coefficient of linear expansion a of the RP5 test pieces was determined, based on the measurement parameters of the instrument.

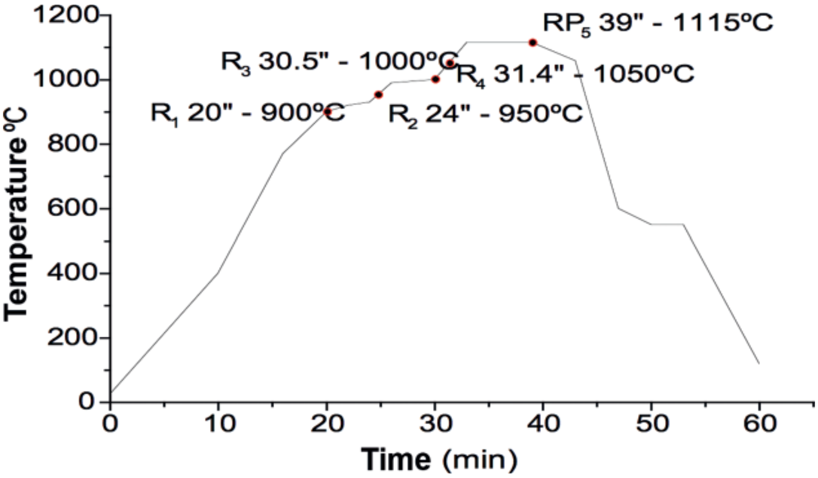


Figure 1. Heating curve of the laboratory kiln for firing the green test pieces. The points indicate the different thermal treatments at which samples were obtained for XRD and SEM analysis

The sintering rate behaviour was determined by TDA at three temperatures: 1050, 1100, and 1115ºC, designated T_1, T_2, and T_3 respectively, with isothermal treatment for 10 min. Table 3 gives the heating programme used in the dilatometer.

THERMAL PROGRAMME	INITIAL TEMP.	STAGE 1		STAGE 2		STAGE 3		
	(°C)	r_1 (°C/min)	T_1 (°C)	r_1 (°C/min)	T_1 (°C)	r_1 (°C/min)	T_1 (°C)	t_3 (min)
T1	22 ± 2	45	900	9.5	1000	16.6	1050	10
T2	22 ± 2	45	900	9.5	1000	33. 3	1100	10
T3	22 ± 2	45	900	9.5	1000	38.3	1115	10

r_x, Heating rate to reach temperature T_x
t_x, Time of the sample at temperature T_x; in Stages 1 and 2 t_x is zero

Table 3. Programme of the TDA temperature cycle for the study of the sintering rate

2.3. X-RAY DIFFRACTION

X-ray diffraction (XRD) analyses were performed of the samples referenced RPBTX, R_1, R_2, R_3, R_4, and RP_5, which were milled, put through a 60 µm mesh sieve, and pressed manually in a standard sample holder. The analyses were performed at ambient temperature (22 ± 2 ºC) with a Philips model X´Pert diffractometer, scanning at an angle of 5-65º (2θ), with a secondary graphite monochromator, scintillation detector (0.2 mm divergent slit, 2 mm receiving slit, 0.6 mm scatter slit, 40 kV, 30 mA) with Bragg-Brentano geometry. The detection step was 0.05º (2θ) in spinner mode, with a count time of 10 (s/step).

2.4. SCANNING ELECTRON MICROSCOPY (SEM)

The samples referenced R1, R2, R3, R4, and RP5 were cut into square sections of 20 x 20 mm, which were polished by traditional metallographic preparation techniques. For the microstructural observation, the samples were duly polished and attacked for 3 minutes with a 5 vol% HF solution. To avoid the charge during exposure to the electron beam, a thin gold foil was deposited on the surfaces to be analysed. The observations were performed in a Jeol JSM-5800LV scanning electron microscope coupled to an EDAX microanalysis instrument.

Finally, bending strength, shrinkage, bulk density, moisture expansion and water absorption were determined of test pieces measuring 50 x 100 mm, obtained by uniaxial pressing, according to the relevant standards.

3. RESULTS AND DISCUSSION

The technical characteristics of the porous tile are given in Table 4. The density of the slurry is low compared with the values used for industrial production (1.650-1.700 $g{\cdot}cm^{-3}$). Considering that the RPBTX formulation contains 45% bentonite and that a fluid suspension is obtained with a viscosity of 1000 cps, this is a promising result for the possible industrial application of this type of tile. The other parameters reported in Table 4 are within acceptable parameters for industrial processing.

The TDA analysis at a low rate allows determination of the range of area $(\frac{\Delta l}{l_0} \to o)$ formation. Three main points stand out in the curve of Figure 2a: a) sintering temperature at 850 ºC, which matches the bentonite sintering temperature; b) change of slope in the ratio $(\text{Shrinkage\%}/_{\text{Temperature}})$ at 950ºC, related to the crystalline phase formation process, which presents a sufficient magnitude to counteract the sintering process (correlated with the shrinkage %); and c) from 990 ºC on, the start of area $(\frac{\Delta l}{l_0} \to o)$ known as the stability range, up to 1100 ºC. Therefore, in the temperature range (990-1100 ºC) the material displays no appreciable dimensional changes.

Characteristics of the Slurry, milling in one-litre Jars		Technical characteristics of tile RPBTX (1115 ºC)	
** Viscosity 1(cp)	900	Shrinkage $_{dry}$ (%)	0.34
Density (g/cm^3)	1.600	** Shrinkage $_{fired}$ (%)	1.52
** Residue on 75µm sieve	3.7	* MR $_{dry}$ (N·mm^{-2})	2.58
		* MR $_{fired}$ (N·mm^{-2})	20
		** DAP $_{dry}$ (g·cm^{-3})	1.785
		** DAP $_{fired}$ (g·cm^{-3})	1.776
		*** Water Absorption (%)	16.35
		**** Moisture expansion (mm/m)	0.28
		Coefficient of linear expansion $\alpha_{20\text{-}400^{\circ}C}$(ºC^{-1})	59 x10^{-7}

* MR Modulus of Rupture, Standard UNE-EN ISO 10545-4.

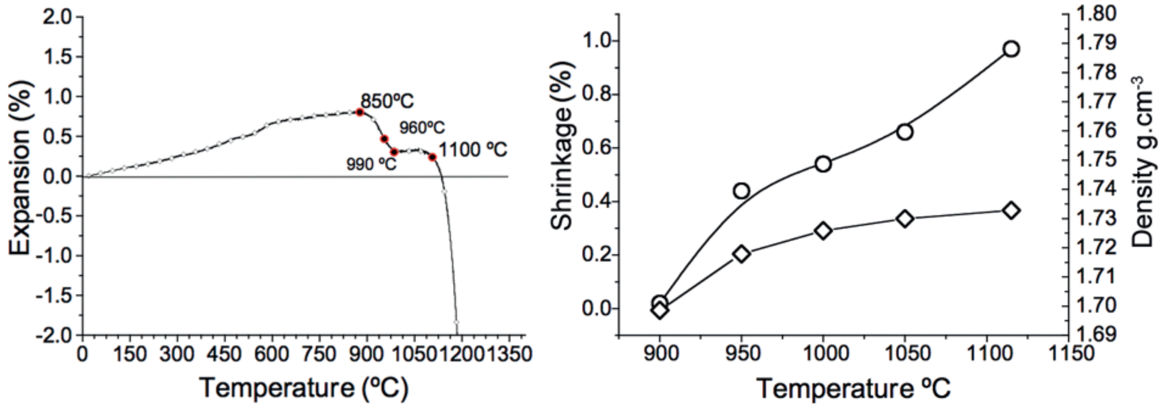
** E-3C Viscosity of a suspension; E-4 Residue on sieve; E-8B Mercury displacement method[6].

*** Water absorption, Standard UNE-EN-ISO 10545-3

**** Moisture expansion, Standard UNE-EN-ISO 10545-10 (test pieces of 5x10x0.7 cm fired at 1115 ºC), all measurements were made on the 10 cm side.

Table 4. Technical characteristics of the porous white tile with clay BTX, milling and firing results.

Since in industrial firing processes, the so-called preheating zone displays heating rates in the range of 30-45 ºC·min^{-1}, the firing curve shown in Figure 1 was applied to the firing of green test pieces. Figure 2b presents the plots of the density and shrinkage variables versus temperature for treatments R_1, R_2, R_3, R_4, and RP_5. Above 1000 ºC a reduction is observed in the slope of the bulk density curve (DAP); in the shrinkage curve, the smaller slope appears in the temperature range (950-1100 ºC). These two characteristics are correlated with the stability range detected in the TDA analysis in Figure 2a.



a) b)

Figure 2. a) TDA showing the behaviour of the green RPBTX body.
b) Development of density (◊) and shrinkage (o) in regard to the firing temperature of treatments R_1, R_2, R_3, R_4, and RP_5.

To determine the appropriate heating rate and sintering temperature for the development of the stability range, the tests described in Table 3 were conducted with treatments T_1, T_2, and T_3. Figures 3a-b show the plots of the shrinkage curves as a function of time and temperature.

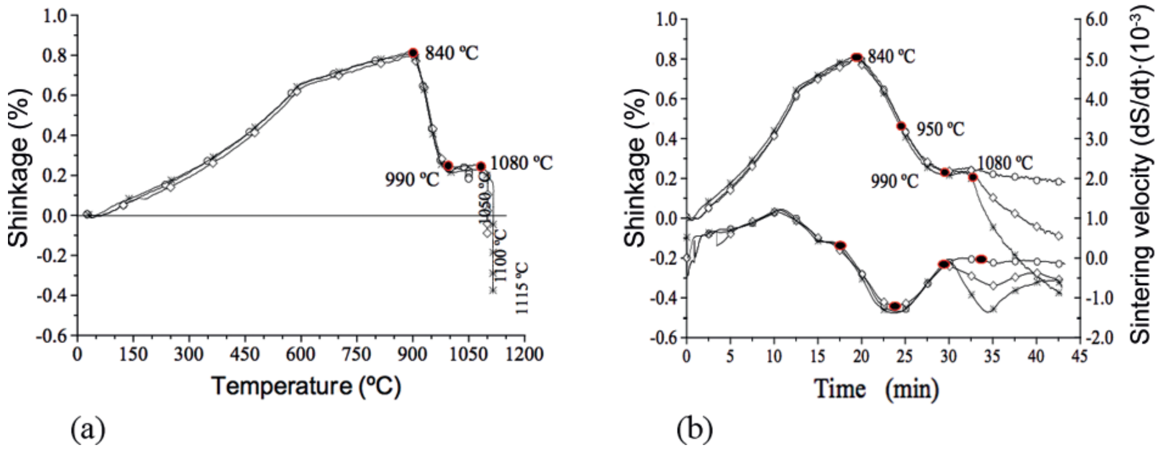


Figure 3. Effect of thermal treatment temperature and time on the crystallisation and sintering process, a) TDA temperature vs. Shrinkage % of treatments T1(o), T2(◊), and T3(∗), b) Curves of sintering time vs. Shrinkage (S) % and first derivative of the sintering curve for treatments T1(o), T2(◊), and T3(∗).

Since the sintering process is short owing to the increase in glassy phase viscosity and rise in the crystalline phase content in the glassy phase, the crystallisation process is therefore determining in the formation of the stability range, while the temperature and time variables govern the crystallisation process[7,8]. Figure 3a shows that sintering becomes active above 840 ºC. For treatments T$_2$ and T$_3$, Figure 3b shows that the sintering rate increases exponentially as a function of temperature up to the range 990-1080 ºC, this being the range in which sintering halts. Above 1080 °C sintering becomes active again and decreases exponentially according to the temperature value of the constant temperature stage. The foregoing allows the crystallisation process to be considered sufficiently extensive to counteract sintering in the temperature range 990 to 1080 ºC.

The same sintering behaviour is observed for treatment T$_1$ as for treatments T$_2$ and T$_3$ up to 990 ºC (see Figures 3 (a) and (b)); however, unlike these, in the treatment T$_1$ the sintering rate tends to zero from 990ºC to the end of the isothermal treatment.

The behaviour of the sintering curves in Figures 3 (a) and (b) can be explained by the formation of crystalline phases during firing of the tile body. Figure 4 displays the XRD patterns that allow identification of the mineralogical species of the test pieces sintered with treatments R$_1$, R$_2$, R$_3$, R$_4$, and RP$_5$. In treatment R$_1$(900°C), the formation of anorthite and albite crystalline phases is detected, while in the treatments at high temperature (R$_3$, R$_4$ and RP$_5$), a larger quantity of anorthite and smaller quantity of albite phase crystallise. In all the treatments conducted, particularly to be noted is the absence of mullite, gehlenite, or wollastonite formation. Anorthite and albite are plagioclases (calcium and sodium aluminosilicates), which form a continuous compositional series between sodium and calcium, in this case forming by reaction of calcium oxide (CaO) with the products resulting from clay mineral vitrification during firing.

Since the mineralogical composition displayed no mullite phase in any of the test treatments and the bentonite provides abundant liquid phase above 840 ºC (sintering start) which can incorporate the metakaolinite into its glassy phase, it may be stated that the sintering mechanism is a reactive liquid phase mechanism, since it involves dissolution in the liquid phase of the solids present and precipitation or growth of new crystalline phases or of crystalline phases that already existed in the initial composition[7]. See reaction 3.

Crystallisation process by precipitation in the glassy phase

$$\textit{Bentonite} + \textit{CaO} \xrightarrow[T>850°C]{} \textit{glassy liquid phase} \xrightarrow[T>950°C]{} \textit{Anorthite} + \textit{Albite crystal precipitation} \quad (3)$$

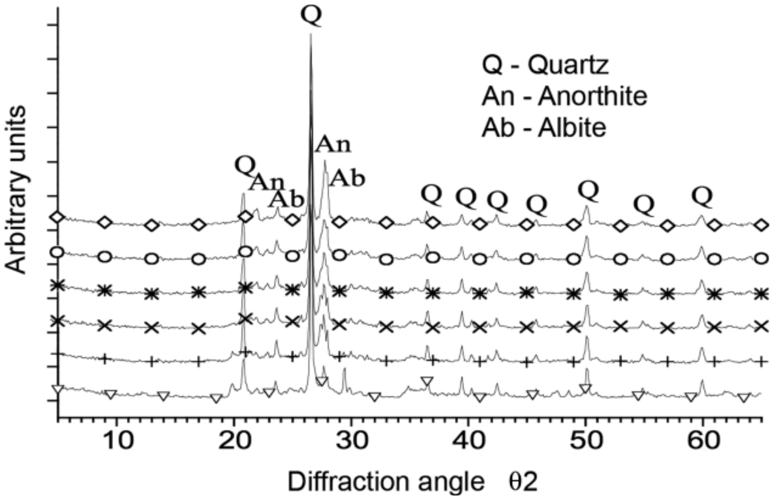


Figure 4. Diffraction patterns of green RPBTX test pieces (∇), R_1 (900 °C) (+), R_2 (950 °C) (x), R_3 (1000 °C) (*), R_4 (1050 °C) (o), and RP_5 (1115 °C) (◊).

With a view to corroborating the sintering mechanism, SEM micrographs were taken of treatments R_1, R_2, R_3, R_4, and RP_5, and EDAX microanalysis was performed of the R_4 treatment test piece. The images obtained are shown in Figure 5.

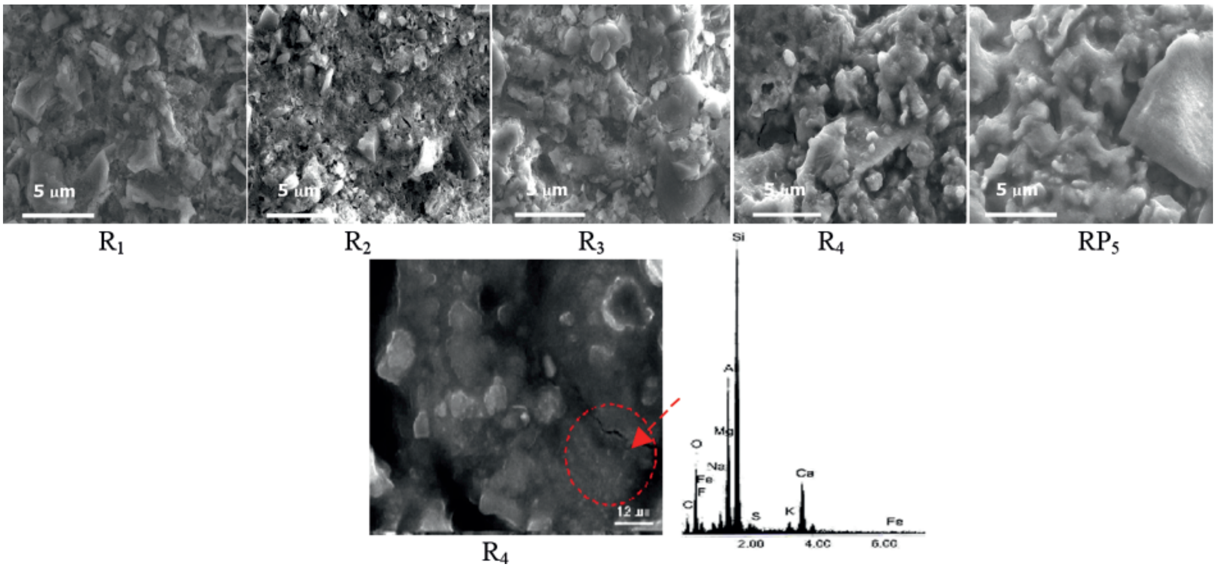


Figure 5. SEM micrographs of the fired test pieces, attacked with HF, obtained from the R_1, R_2, R_3, R_4, and RP_5 treatments.

Since the acid attack dissolves the glassy matrix, the SEM micrographs of the R_1 and R_2 treatments display the originally polished surface in relief and the particles appear not to be joined by means of glassy phase; however, the presence of liquid phase is evident in treatments R_3, R_4, and RP_5, where the particles are observed to be immersed in the glassy phase. The chemical composition of this glassy phase was determined for treatment R_4, which showed that it was mainly rich in calcium, with some sodium, while small crystals of 1-2 µm are also noted immersed in the glassy phase, confirming that the sintering process has developed in reactive liquid phase.

4. CONCLUSIONS

From the viewpoint of industrial parameters, the use of formulations with thermally treated bentonite is feasible, particularly if these types of formulations are focused on dry route processes. However, the results obtained by the wet route are also promising for application in this type of process.

With the studied formulation, through the sintering process and crystallisation, the stability range can be controlled in the temperature range 1000-1100 ºC, and dimensionally stable tiles can be obtained, which is a fundamental requirement for porous tiles.

With the use of thermally pre-treated bentonite, the firing of these types of formulations can be carried out at lower temperatures than those used at present in industrial processes, with the entailing energy savings.

The sintering process is carried out in reactive liquid phase, which allows materials to be produced without the so-called hydratable phases because the firing yields a vitreous product and the obtained moisture expansion values conform to the relevant UNE-EN-ISO standard.

The use of thermally treated bentonite gives rise to recrystallisation processes in which only appreciable quantities of Albite and Anorthite phases are obtained, which precipitate from the glassy phase formed by dissolution of the clays in the formulation.

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