

PON ref 78-FAST SINGLE FIRING APPLIED TO CLAY ROOF TILES

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This work aimed to obtain clay roof tiles using the fast single firing process. Four clay samples were characterized by chemical (XRF), mineralogical (XRD) and particle size (laser diffraction) analyses and mixture design was used for the formulation of eight compositions. The compositions were dried, homogenized with 15% moisture and processed in a laboratory extruder. After drying (110°C, 24h), the formulations were fired in a laboratory roller kiln (1,050°C, 55min) and then characterized (water absorption and flexural resistance, according ISO standards). The temperature of maximum sintering rate of each formulation was determined by optical dilatometry (10°C/min) and the mineralogical composition by XRD. Analysis of variance (ANOVA) was used to show the effect of chemical and mineralogical composition of each clay mineral on the properties of the final compositions. The study shows the possibility of obtaining clay roof tiles at firing cycles as fast as 55min with 7%wt water absorption.

Keywords: clay ceramics, fast single firing, sintering, microstructure, mixture design.

1. Introduction:

Clay products, after drying, are subjected to firing in tunnel furnaces during several hours (up to 48h) at temperatures ranging from 850°C (bricks) to 1200°C (ceramic tubes). After drying, the ceramic products have a specific content of residual water, depending on the efficiency of the process. The mass fraction of residual water is then eliminated in the furnace at temperatures close to 110°C [1-3].

The reactions that take place in clay products during firing are different, depending on clay mineralogy. The first phenomenon that occurs in the furnace is the elimination of residual water, a physical phenomenon, and the ceramic products undergo a loss weight without retraction because the water trapped in the pores is eliminated. From 200°C to 300°C takes place the dehydration of the montmorillonite mineral. At higher temperatures, 250°C to 300°C, takes place the release of hydroxyl from the hydroxides (such as aluminum hydroxide), and from 400°C to 500°C, the removal of the crystallization water of several clay minerals occurs. From 450°C to 650°C starts the clay minerals decomposition, with water release as vapor (chemically combined in kaolinite, a fundamental constituent of clay, containing silica and alumina) [2,3].

Those reactions are all endothermic, absorbing energy. However, there are also exothermic reactions, with energy release, due to combustion of organic substances naturally present (or added) in the raw materials. At temperatures around 570°C occurs the transformation of α -quartz to β -quartz, accompanied by significant expansion (during the cooling at this temperature, contraction occurs) [1-5].

If clay contains carbonates, around 550°C to 600°C they begin to dissociate. First of all magnesium carbonate dissociates, and at higher temperatures, around 800°C, calcium carbonate dissociates, a more abundant mineral. It should be stated that these reactions are influenced by heating rate and carbonate dissociation releases CO₂ and absorbs heat. All reactions are time dependent and heat distribution takes time to be uniform in each ceramic piece. Above 700°C takes place chemical reactions among silica and alumina and the flux elements, with the formation of complex aluminosilicates, resulting in hardness, strength and physical and chemical stability of the ceramic products [1,6,7].

Close to 800°C takes place the maximum expansion of the clay product. At this temperature it is possible to establish a shoulder more or less broad on the firing or sintering dilatometric curves, encompassing a temperature range up to 900°C or 950°C, when starts the sintering shrinkage and, therefore, the mineralogical transformations occur. The mineral illite undergoes shrinkage after an expansion peak around 800°C. In sequence, the clay product undergoes a sudden and fast shrinkage in a very short temperature range, often linked to the presence of carbonates in the illite mineral, leading to an expansion at higher temperatures and resulting in the characteristic inflection point around 920°C in a thermogram curve [1,3].

After reaching the maximum firing temperature, which for bricks is 1,000°C, the product begins to shrink and the fuel flow must be cut. The product continues to shrink and releases heat into the oven's atmosphere, in contrast with the preheating and the initial stages of firing. It is very interesting to determine the different reactions and dimensional changes that take place in different temperature ranges, especially in the contraction (shrinking) phase [1,4-6].

All these reactions are well known in the conventional technique of firing in slow cycle tunnel furnaces, which in some cases can last up to 24 hours of sintering only, not mentioning the heating and cooling steps [7]. Thus, the objective of this study was to assess the raw material influence on the sinterability and properties like water absorption and flexural strength of clay roof tiles subjected to rapid single firing cycles using a laboratory roller kiln.

2. Experimental procedure:

Four clays were selected for the study. The clays were characterized by X-ray diffraction (Phillips, CuK α ($\lambda=1.5418\text{\AA}$), operating at 30kV and 15mA, 2θ from 0° to 70°, 0.05° step size and 1s of residence time) and X-ray fluorescence (Phillips, CuK α ($\lambda=1.5418\text{\AA}$)). After characterization, the clays were dried (90°C, 24h) and mixed according a mixture experimental design using four factors with restrictions, resulting in eight formulations, Table 1.

After drying the clays were mixed in an eccentric mill (300mL, high alumina) according the mixture design formulations (Table 1) and then were extruded in a laboratory extruder (samples with 3cm \times 1cm \times 10cm) with 15%wt moisture; after extrusion the compositions were dried (110°C, 24h). Samples of each composition were also prepared for optical dilatometry (Misura, 10°C/min, 20°C to 1,200°C). Finally, 10 samples of each composition were fired in a laboratory electric roller kiln (1,050°C maximum temperature, 55min cycle).

After firing, the fired samples were subjected to water absorption and mechanical strength (Emic, 1mm/min) tests (according ISO 10545).

3. Results and discussion:

Chemical and phase analyses are shown in Table 1. A higher alkali and Fe₂O₃ content indicates which clay is more melting, and the silica and alumina content means the clay is more refractory. Therefore, clay M probably presents a more fluxing (melting) behavior due the alkali content (8.1%wt); clay 3L and clay VD are similar in alkali content (2.4 and 3.1%wt, respectively), but the alumina content for clay 3L is higher (19.8%wt). Finally, clay SA appears to be more refractory due the lower alkali content (1.5%wt) and higher silica content (72.2%wt).

Table 1. Chemical and mineral composition of clays

Clay	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	LOI	Phases
SA	72.2	14.4	1.3	3.3	0.4	0.9	0.2	0.0	7.2	Q, C, A, R
3L	60.8	19.8	1.0	8.2	0.6	1.7	0.1	0.1	8.1	Q, C, I, H
VD	67.8	15.3	1.3	5.8	0.7	1.5	0.9	0.1	7.1	Q, C, M
M	55.8	19.5	0.8	9.0	2.8	4.7	0.6	0.4	6.6	Q, C, I, Cl, R

Where: LOI=Loss on ignition, Q=Quartz, C=Kaolinite, A=Anatase, R=Rutile, I=Illite, H=Hematite, Cl=Clinochlore, M=Microcline.

Regarding the clay minerals, all clays exhibit quartz and kaolinite in their composition, both refractory minerals. Clays 3L and M contain the mineral illite in its composition, which gives plasticity and is beneficial to the extrusion process, but this property was not determined in this work. Clay 3L also exhibits hematite, which gives a strong reddish color to the product. Because clay

3L does not contain the highest amount of iron oxide in its composition, probably the Fe₂O₃ is forming the illite or clinocllore minerals in clay M, or even an amorphous phase in clays SA and VD. Clay VD is formed by microcline and clay M by clinocllore, a clay mineral composed by Mg and Fe.

From the raw materials analysis a mixture design with 4 variables was developed, being the SA, 3L, VD and M clays the design factors. The mixture design was performed with restrictions in the formulation, resulting in 7 vertices and a central point, Table 2.

Table 2. Mixture experimental design (4 factors, with restrictions)

Formulation (%)	SA	VD	M	3L	T _{sinter} (°C)	WAbs (%)	σ _c (kgf/cm ²)
1V	0.4	0.0	0.0	0.6	1,091	7.8	165.3
2V	0.4	0.2	0.0	0.4	1,092	10.1	233.1
3V	0.4	0.0	0.2	0.4	1,073	7.3	256.4
4V	0.0	0.2	0.2	0.6	1,064	8.7	185.8
5V	0.4	0.2	0.2	0.2	1,053	9.7	354.7
6V	0.2	0.2	0.0	0.6	1,089	10.6	238.2
7V	0.2	0.0	0.2	0.6	1,083	6.3	208.4
8C	0.3	0.1	0.1	0.5	1,075	7.2	226.7

Where: V=vertices; C=central point; T_{sinter}= temperature of maximum sintering rate; WAbs=water absorption; and σ_c=compressive strength.

The results for the temperature of maximum sintering rate are shown in Table 3 and the contour curve is shown on Figure 1. For the chosen design, mixture design with four factors and restrictions, only the linear model can be analyzed: The results show great statistical reliability (96%, p=0.04) and good fitting to the ideal model (R²=86%).

Table 3. Analysis of variance for the temperature of maximum sintering rate

Model	SS _{effect}	Y _{effect}	MS _{effect}	SS _{error}	Y _{error}	MS _{error}	F test	p test	R ²
Linear	1,168	3	389.2	196.5	4	49.1	7.9	0.04	0.86
Total	1,364	7	194.9						

Where: SS=Sum of squares; γ=Degrees of freedom; MS=Mean squares.

The contour curve of Figure 1 clearly shows the effect of clay M in reducing the firing temperature, measured by the temperature of maximum sintering rate, obtained by optical dilatometry: Clay M tends to reduce the maximum sintering rate below 1,010°C. The chemical composition of clay M justifies its behavior (Table 1). However, these temperatures are much higher than those normally used in ceramic furnaces for clay products.

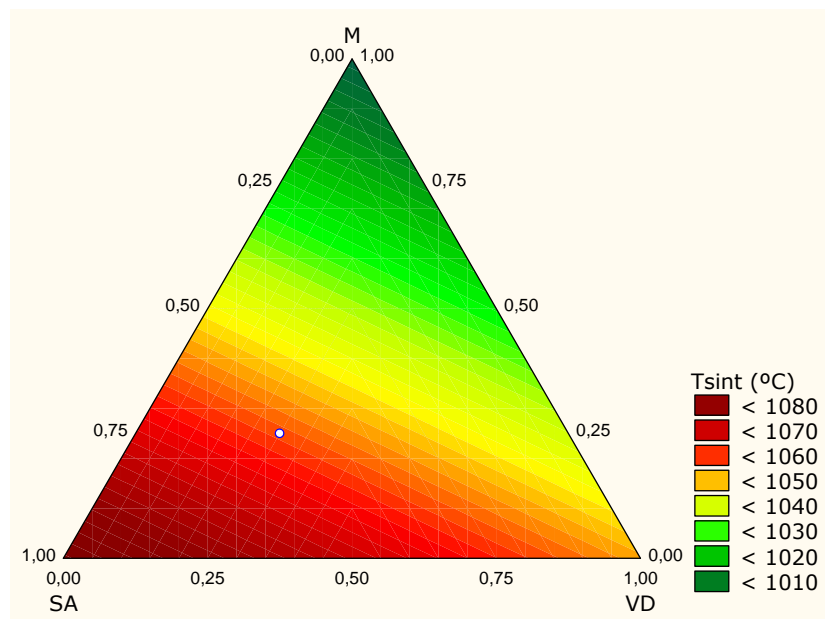


Figure 1. Contour lines for the temperature of maximum sintering rate, linear model

Regarding the water absorption, Table 4, the results show low reliability (60%, $p=0.40$) and a poor fitting to the ideal model ($R^2=48\%$). But this feature is not surprising, since the water absorption is one of the most variable characteristics of the ceramic products.

Table 4. Analysis of variance for water absorption

Model	SS _{effect}	Y _{effect}	MS _{effect}	SS _{error}	Y _{error}	MS _{error}	F test	p test	R ²
Linear	10.7	3	3.55	11.4	4	2.86	1.24	0.40	0.48
Total	22.1	7	3.15						

Where: SS=Sum of squares; γ =Degrees of freedom; MS=Mean squares.

The contour curve of Figure 2 shows the effect of clay VD in reducing the water absorption, observing the low reliability of the results. Despite clay M is the most effective for the sintering rate, Figure 1, apparently clay VD is the one that most reduces the water absorption, at least to a temperature of 1,050°C, used for testing. Probably the action of clay M is evident only at temperatures around 1,200°C.

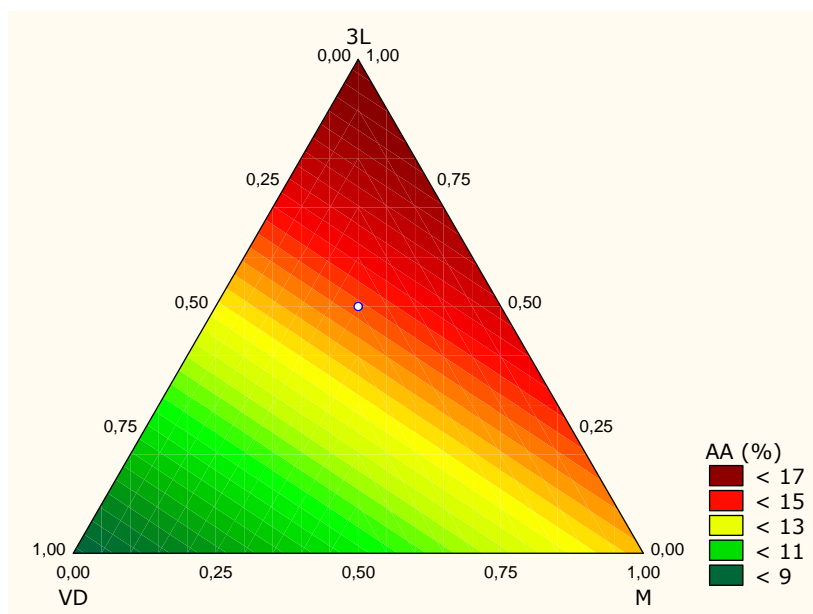


Figure 2. Contour lines for the water absorption, linear model

Finally, for mechanical strength, Table 5, the reliability of the results is again high (95%, $p=0.05$) and the fitting to the ideal model is good ($R^2=83\%$).

Table 5. Analysis of variance for the mechanical strength

Model	SS _{effect}	Y _{effect}	MS _{effect}	SS _{error}	Y _{error}	MS _{error}	F test	p test	R ²
Linear	19,011	3	6,337	3,827	4	957	6.62	0.05	0.83
Total	22,839	7	3,263						

Where: SS=Sum of squares; γ =Degrees of freedom; MS=Mean squares.

The contour curve of Figure 3 shows again the effect of clay VD in mechanical strength, noting that this property was also determined at 1,050°C, temperature used in this study to reduce the firing cycle. The same considerations that were made for the water absorption should be made to the compressive strength, i.e., the effect of clay VD on densification of the samples even at lower temperatures (<1,000°C).

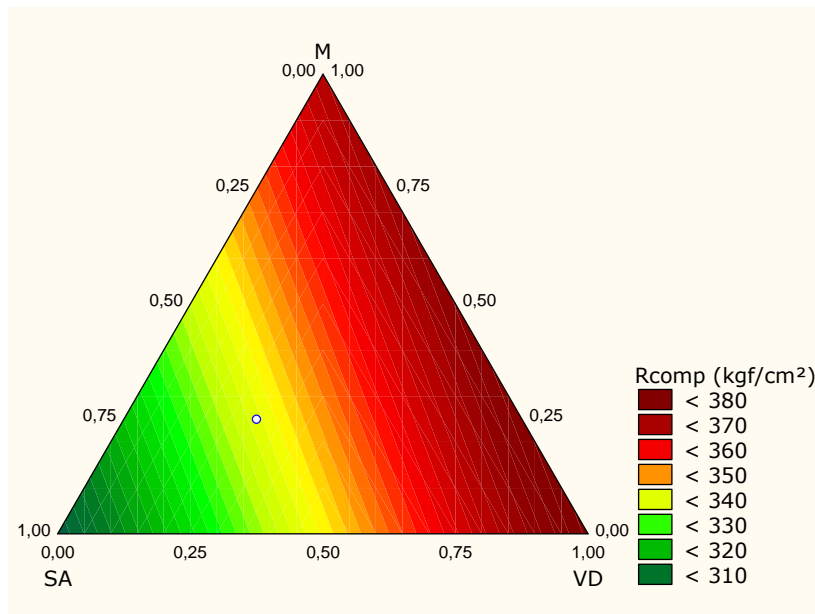


Figure 3. Contour lines for resistance to compression

4. Conclusion

The results show the effect of chemical and mineralogical composition of the studied clays on the physical-mechanical properties of the final compositions. The kaolinitic compositions were more refractory, with low compression strength and higher water absorption. By increasing the fraction of illite and microcline, fluxing phases, the compositions sintered at lower temperatures, becoming more resistant and less porous. The crystalline phases present in the clay before firing are fundamental to the development of ceramics after firing, since they directly affect both the conformation of the samples and the final microstructure. The microstructural characterization of the fired samples is ongoing, but the use of fast single firing to clay ceramics is totally viable, since the study was conducted at 55 minutes cycle.

5. References

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