MIXTURE DESIGN APPLIED TO CERAMICS MADE BY DRY MILLING PROCESS

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ABSTRACT

The dry milling process is an energy saving process. Lately, even porcelain tiles (gres porcellanato) are made via dry milling process. Besides this fact, some dry milling process industries in Brazil have problems regarding the quality of the ceramic tile produced. Ceramic compositions with high quality (low water absorption, high mechanical resistance and dimensional stability) can be made via dry milling process using statistical procedures. In this way, this work deals with statistical compositions of tiles made via dry milling process. Three clay minerals were used as raw materials. Experimental mixture design was used to formulate seven tile compositions using constrained mixture design and surface response analysis. The compositions were dry milled in eccentric jar mills (95% below 325 ASTM sieve). All compositions were pressed (300kgf/cm^2; 7% wt. moisture) in laboratory press and fired in an industrial roller kiln (1,150°C; 3min). Samples of each formulation were subjected to water absorption and flexural resistance tests and their linear shrinkage was determined. Also, thermal analysis was carried out to determine the sintering temperature of all seven formulations. The results were analyzed by surface response analysis. The results showed, as expected, great variation regarding the water absorption because the difficulties to flow the dried granules and to promote an adequate mold filling.

1. INTRODUCTION

The dry milling of ceramic pastes offers advantages in comparison with the wet milling process: reduced thermal energy cost; no need of processing additives; reduced maintenance; reduced environmental impact. The traditional dry milling process is associated with poor quality granules and a consequent poor quality compact. But increasing technologies applied to the dry milling process can produce granules with similar characteristics of the wet process [4]. High efficiency mills with pressing grinding rolls and granulators for very fine powders have stimulated the technology of dry milling process [3].

The technical improvement of the dry milling process is based on the reduction of the paste particle size, even smaller than the wet process, with high productivity. The very small particle size reduces the dimensions of the impurities contained in the raw materials so they cannot cause problems to the glaze layer. Also, thin particles have a very high specific surface promoting a better densification of the ceramic system. Therefore, it is possible to apply the dry milling to the single firing products [5].

A continuous granulation of the dry milled powder provides granules with shape and granularity similar to that of wet milling and spray-drying and the pressing phase have no problems [6]. Moreover, the higher compaction of the granules obtained via continuous granulation promotes a higher density of the green pressed compact and a minor firing contraction regarding wet milling and spray-drying. A minor contraction is very important to the production of a single firing dense product in order to maintain its dimensional stability. It is possible to reduce the linear contraction (or shrinkage as some authors prefer) by some percent units for gres products.

Also it is possible to reduce the segregation of non clay products in the dry pastes using a finer particle size. Soft and light materials like clays are separated from the harder and heavier materials like sands and feldspars during the conventional dry milling process [8]. If the particle size of the raw materials are smaller than 50μm to 60μm there is no segregation [7].

Regarding energy saving, the dry process strongly diminishes the thermal consumption. For single firing wall tiles ('monoporosa') a small amount of thermal energy is used in the mills to avoid make dirty the rollers by agglomerations formed by condensation of moisture from the raw materials [2].

Regarding environmental impact, the granulation using dry processes presents considerable advantages, such as the reduction of the hot emissions from the drying of the ceramic suspensions, reducing energy consumption and CO_2 emission. In this way the dry process can be applied without problems to the production of single firing products for walls or pavements. This paper is a study of a conventional dry milling process, common in Brazil, using clay mineral as the only raw material. A mixture design was used to study the influence of each raw material in the characteristics of the final product.

2. MATERIALS AND METHODS

Three minerals were used in this study: two clays (one feldspathic) and one argillite. The chemical analysis was determined by X-ray fluorescence (Philips PW2400, melted sample) and the phase (mineralogical) analysis by X-ray diffraction (Philips PW1830, CuKα, 0° to 75°, analysis with X'Pert HighScore software).

After raw material chemical and phase analysis a statistical design was used to study the influence of each mineral on the dry milling characteristics of the formed pastes. The chosen design was mixture design, suitable for the purpose of analysis [1]. As not all raw materials can be used as the major component in a ceramic paste, restrictions were imposed in the design (constrained limits). Using three factors (raw materials) at two levels (maximum and minimum amount in the paste) and one general centroid seven formulations were composed. The formulations were designated as V1 to V7, the last one as the centroid, table 1.

Minerals (wt. %)			
Formulations	Argillite	Clay	Feldspathic clay
V1	55%	10%	35%
V2	15%	50%	35%
V3	55%	30%	15%
V4	35%	50%	15%
V5	35%	10%	55%
V6	15%	30%	55%
V7	35%	30%	35%

Table 1. Mixture design for the analysis of dry milling process

The maximum and minimum limits used for argillite were 15% and 55% (mass fraction), respectively. The limits for the other minerals were 10% to 50% to the clay mineral and 15% to 5% to the feldspathic clay. The limits were established in function of the ordinary amount of each raw material in a typical dry milling tile paste and in function of their chemical and phase composition.

The raw materials were dried (110°C, 24h), fragmented (laboratory hammer mill), mixed according table 1 to form the compositions and stored. In sequence, each formulation was dry milled (laboratory ball mill, 5% residue in 325 mesh Tyler (44μm)) and mixed with 7% of water, forming a granulated paste. Each paste was compacted by uniaxial pressing (laboratory press, 300kgf/cm^2) in compacts with 50mm×100mm. The compacts were dried and fired in an industrial roller kiln at 1,150°C during 3min at maximum temperature, in a thermal cycle of 35 minutes. After firing the samples were tested to determine their linear contraction, water absorption and mechanical resistance by flexural test (Emic DL10000, 10mm/min).

The technique used to analyze the results was the multiple regression. The regression analysis consists to estimate the unknown parameters of the regression model or the adjustment of the data to the model and the validation of the model. The second step is used to study the adequacy of the chosen method to represent the response behaviour and the quality of the adjustment obtained.

If the validation result shows the model is not adequate the model must be modified and the parameters estimated again. Therefore the regression analysis is an iterative process, from the first adjustment to the attainment of a satisfactory model that can be used and adopted. The parameters model evaluation is fulfilled by the mean squares method. The method validation is made by evaluation techniques used to test and estimate the adequacy and adjustment of the used model, mainly the hypothesis regression test (F and t) and the R^2 estimation.

3. RESULTS AND DISCUSSION

The chemical and phase analysis of all raw materials are showed in table 2. Analyzing the results the argillite is a melting mineral due its content in alkalis, mainly magnesium, sodium and potassium oxides. Also its content in iron oxide permits eutectic formation at low temperatures. The argillite is formed by albite and clay minerals (muscovite and montmorillonite) and is contaminated with quartz and goethite.

Mineral (%)	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	LOI	Phases
Argillite	66.8	14.6	0.6	4.3	0.6	2.0	4.2	1.6	3.7	Q. Ab, Mu, Mo, G
Clay	60.8	17.7	0.8	9.7	0.0	0.7	2.4	0.0	6.6	Q, K, Mu, G
Feldspathic clay	66.0	14.2	0.6	5.4	0.8	2.8	3.3	0.9	4.8	Q, Mu, K, Ab, G, N
Q is quartz, Mu is muscovite, Mo is montmorillonite, K is kaolinite, G is goethite, Ab is albite and N is nontronite										

Table 2. Chemical and phase (mineralogical) analysis of the raw materials

The clay mineral is formed by kaolinite and muscovite and is contaminated with quartz and goethite. Finally, feldspathic clay is formed by clay minerals (muscovite, nontronite and kaolinite) and albite and is contaminated with quartz and goethite. All minerals analyzed contain a great amount of iron oxide in the goethite form.

All studied properties were determined for all compositions by means of analysis of variance (ANOVA) and the results plotted in response surfaces for the most adequate model. According table 3, analysis of variance for the water absorption measured for all seven formulations, the most suitable model is the linear model because the F test is more significant for it (F=1.11). The linear model for water absorption presents only 59% confidence and a very poor adjust (R^2=0,36).

ANOVA for water absorption	Main effects			Error			Confidence tests		
	SS	DF	MS	SS	DF	MS	F	p	R^2
Linear	1.12	2	0.56	2.03	4	0.51	1.11	0.41	0.36
Quadratic	1.22	3	0.41	0.81	1	0.81	0.50	0.75	0.74
Cubic	0.81	1	0.81	0	0	0			1.00
Total Adjusted	3.15	6	0.52						
SS means sum of squares, DF degree of freedom, MS mean square									

Table 3. Variance analysis for water absorption (wt. %)

The low confidence obtained for water absorption does not permit an analysis with high accuracy regarding this property. The lack of confidence can be caused by variations in the procedure used to prepare the samples: variations in particle size distribution, wetting and compaction can cause a great variation in the sample microstructure. It is a typical problem found in the dry milling process. The results from the ANOVA analysis were plotted in response surfaces, figure 1. Analyzing the response surface it is clear the effect of argillite in the water absorption of the system studied. This result occurs due the presence of albite in the argillite mineral.

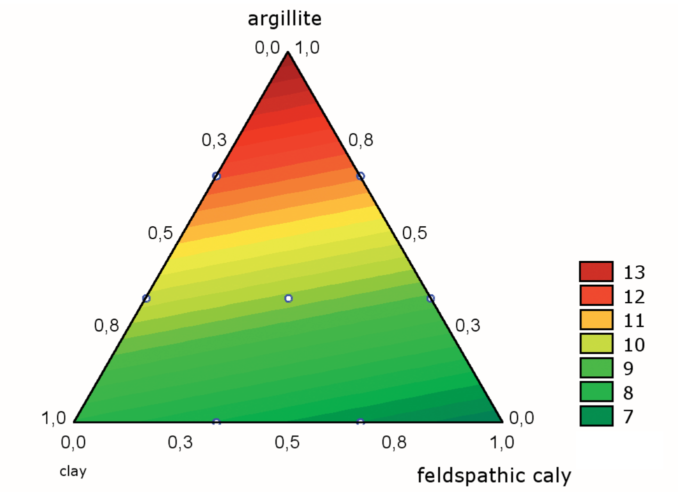

Figure 1. Response surface for water absorption of the studied system

Regarding the linear contraction (or shrinkage), the variance analysis shows the most suitable model also is the linear model (F=2.52) with 80% confidence but a poor fit (R^2=0,56). The same observations about sample preparation used to explain the variations in water absorption could be used here: problems in tile preparations inherent to the dry process. The response surface for linear contraction is plotted in figure 2.

ANOVA for linear contraction	Main effects			Error			Confidence tests		
	SS	DF	MS	SS	DF	MS	F	p	R^2
Linear	2.12	2	1.06	1.69	4	0.42	2.52	0.20	0.56
Quadratic	0.56	3	0.19	1.13	1	1.13	0.17	0.91	0.70
Cubic	1.13	1	1.13	0	0	0			
Total Adjusted	3.81	6	0.63						
SS means sum of squares, DF degree of freedom, MS mean square									

Table 4. Variance analysis for linear contraction (shrinkage) (%)

According figure 2 the argillite is the most influential mineral in the linear contraction of the studied system as expected because it contains melting minerals in its composition, specifically albite. On the other hand the feldspathic clay is the least influential mineral besides its content in albite. The amount of albite present in the feldspathic clay limits its plasticity but is not sufficient to cause densification during firing.

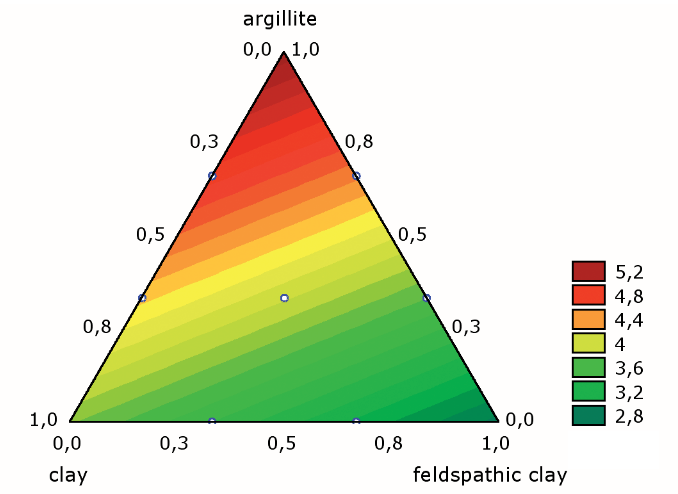

Figure 2. Response surface for linear contraction (shrinkage) of the studied system

Finally, regarding the mechanical resistance measured by the maximum load at rupture under flexural test (table 5), the analysis of variance had presented the best results: the confidence for the linear model (F=12.28) is 98%, showing the validity of the used model, with a satisfactory fit (R^2=0,86). The response surface for flexural resistance is plotted in figure 3.

ANOVA for load at rupture	Main effects			Error			Confidence tests		
	SS	DF	MS	SS	DF	MS	F	p	R^2
Linear	19.6	2	9.81	3.20	4	0.80	12.28	0.02	0.86
Quadratic	2.60	3	0.87	0.60	1	0.60	1.44	0.53	0.97
Cubic	0.60	1	0.60	0	0	0			
Total Adjusted	22.82	6	3.80						
SS means sum of squares, DF degree of freedom, MS mean square									

Table 5. Variance analysis for maximum load at rupture (flexural resistance) (kgf)

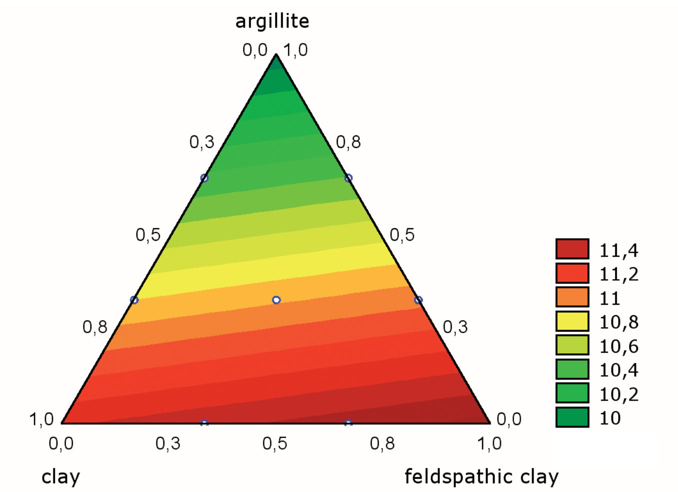

Figure 3. Response surface for the maximum load at rupture (flexural resistance) of the studied system

One more time the best results occur for the argillite mineral (figure 3), confirming its effect on the overall characteristics of the studied system. Probably the effect of argillite in promoting the best results densification is related to its content in albite and muscovite, minerals that can perform a strong densification by way of glass phase formation during sintering.

4. CONCLUSION

The use of mixture design in the study of ceramic formulations and the use of multiple regression and response surfaces is a powerful procedure in the evaluation of the individual effect of raw materials in the final properties of ceramic products. The strongest influence on the dry milled process among the raw materials studied was caused by the argillite, probably because its content in melting minerals like albite and muscovite.

This study could be improved with the analysis of processing parameters like particle size distribution, compaction pressure, granule size distribution, thermal behaviour and others.

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