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Optimising mechanical strength and bulk density of dry ceramic bodies through mixture design

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In industrial practice, it is desirable to be able to predict, in an expeditious way, what the effects of a change in raw materials or the proportions thereof might be in the various processing steps towards the final product. When the property of interest is basically determined by the combination (or mixture) of raw materials, an optimisation methodology specific to the design of mixture experiments can be successfully used. In the present study, dry bending strength and bulk density were selected as the properties to model, given the simplicity of their experimental determination and because they are frequently used as quality control parameter in the development and manufacture stages of floor and wall ceramic tiles. Ten formulations of three raw materials (a clay mixture, potash feldspar and quartz sand) were processed in the laboratory under fixed conditions, similar to those used in the ceramics industry, and characterised. The use of this methodology enabled the calculation of valid regression models (equations) relating dry bending strength and bulk density with the contents, in the starting mixture, of the particular raw materials used.

Keywords: Experiments design; Regression models; Ceramic tiles.

Optimización de la resistencia mecánica y densidad de cerámicas en verde a través del diseño de mezclas

En el trabajo industrial es deseable poder predecir de manera efectiva, los efectos que los cambios en las materias primas o en sus proporciones pueden ejercer sobre las variables del proceso y como estos afectan al producto final. Cuando la propiedad de interés depende preferentemente de la mezcla de las materias primas, una metodología específica de optimización para el diseño de los experimentos de mezclas puede ser empleada con éxito. En este trabajo, la resistencia mecánica en seco y la densidad se emplearon como los parámetros de control en el desarrollo y producción de azulejos cerámicos para pavimento y revestimiento. Diez formulaciones a partir de tres materias primas (una mezcla de arcilla, feldespato potásico y arena de cuarzo) fueron procesadas en el laboratorio bajo condiciones fijas que son similares a las empleadas en la industria cerámica y finalmente se procedió a su caracterización. El empleo de esta metodología permite el cálculo de modelos de regresión (ecuaciones) relacionando la resistencia mecánica y la densidad con el contenido en la mezcla de partida de las materias primas.

Palabras clave: diseño experimental; modelos de regresión; azulejos cerámicos.

1. INTRODUCTION

In industrial practice, it is desirable to be able to predict, in an expeditious way, what the effects of a change in raw materials or the proportions thereof might be in the various processing steps towards the final product. But the means to do that are not usually available and, instead, a number of key properties are regularly evaluated and used as quality and process control parameters. This is the case of dry mechanical strength and bulk density for ceramic floor and wall tiles, because low resistance to handling before firing, even when the fired body fulfils the specified characteristics of the desired product, can be enough reason to reject a given composition. Both properties are simple to evaluate in the laboratory (resistance to rupture in bending and immersion in mercury) and basically depend on the raw materials contents, as long as processing parameters are kept unchanged [1-3].

This is the basic assumption in the use of mathematical and statistical techniques to design mixture experiments and calculate a property response surface [4-5]. Its application to ceramic products such as floor and wall tiles would mean that, for a given set of raw materials and processing conditions, an equation could be sought for each property (response surface), relating that property with the raw materials contents in the starting mixture. Such methodology has seen applications in a variety of fields, not only in materials formulation and processing research, but also in industrial processes [6-14].

Therefore, those properties can be modelled using statistically planned experiments and the response surface methodologies. To this aim, it is necessary first to select the appropriate (independent) components and then the mixtures from whose properties the response surface might be calculated; having the response surface, a prediction of the property value can be obtained for any mixture, from the changes in the proportions of its components.

There are three major types of components or ingredients (triaxial mixtures) to be considered in ceramic mixtures, given the distinctive roles they play during ceramic processing: plastic components (clays), fluxing components (feldspar) and inert components (quartz). Thus, an equilateral triangle can be used to represent the composition of any such ceramic mixture and a property axis can then be used, perpendicular to the triangle plane, to represent the response surface function (property prism).

The property response, *f*, can be expressed in its canonical form as a low degree polynomial (typically, first or second degree) [4-5], in terms of the weight fractions, x_i, of the three components (summing up to unity):

First degree:

$$f = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 \tag{1}$$

Second degree:

$$f = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 \tag{2}$$

Such a polynomial equation has to be evaluated over a number *N* of points (greater than the number of components) so that it can represent the response surface over the entire region and it is only natural that a regular array of uniformly spaced points (*i.e.* a lattice) is used. This lattice is referred to as a {*q*, *m*} simplex lattice, *m* being the spacing parameter in the lattice and *q* the number of components. Then, a laboratory study consisting of *N* experiments has to be carried out and the values of the property on those selected *N* lattice points evaluated.

A regression equation, such as equations (1) or (2), is then fitted to those experimental values and the model is considered valid only when the differences between the experimental and the calculated values (error) are uncorrelated and randomly distributed with a zero mean value and a common variance.

The distinctive roles that clays, feldspar and quartz play in ceramic processing also impose restrictions on their contents in the mixture and lower bound composition limits must be used [13-14]. When some or all the compositions x_i are restricted by a lower bound (and/or an upper bound), *i.e.* the component fraction is not allowed to vary from 0 to 1.0 and only a sub-region of the original simplex is of interest, the concept of pseudo-component can be used to create a restricted composition triangle and define another simplex of new components (pseudo-components) present in the proportions x_i' to which the {*q*, *m*} simplex lattice is applied [4-5]. The fractions x_i' are first calculated from the original x_i (by $x_i' = (x_i - L_i)/(1-L)$, where L_i is the lower bound for the ith component and $L<1$ is the sum of all the lower bounds) and, once the regression equation is obtained, they are reverted back to the original components, so that the mixture can be prepared and the property experimentally evaluated.

This work describes the use of the design of mixture experiments and response surface methodologies to express the dry bending modulus of rupture (DMoR) and dry bulk density (DBD) of ceramic compositions processed under constant conditions, as a function of the proportions of the clay, feldspar and quartz present in the mixture of raw materials. This involves fitting of mathematical equations, such as equations (1) and (2), to the experimental results (*i.e.* measured modulus of rupture and bulk density) to get the entire response surface, and the statistical analysis and validation of the model (variance and residue behaviour). The model so obtained can then be used to select the best combination of those three raw materials to produce a ceramic body with specified properties.

2. EXPERIMENTAL PROCEDURE

The raw materials used were two clays (A and B), potash feldspar (99.5 wt.% microcline) and quartz sand (99.5 wt.% α-quartz), all supplied by *Colorminas* (Criciúma, SC, Brazil). The chemical composition of the clays was determined by X-Ray Fluorescence (XRF, Philips PW 2400). The crystalline phases present were identified by X-Ray Diffraction (XRD, Philips X'PERT) and quantified by rational analysis [15].

A {3,2} centroid simplex-lattice design, augmented with interior points, was used to define the mixtures of these raw materials that should be investigated.

The selected mixtures were wet processed, following the conventional wall and floor tile industrial procedure: wet grinding (less than 1 wt.% residue left in a 325 mesh sieve), drying, moisturizing (6.5±0.2 wt.%, dry basis), granulation and uniaxial pressing at 47 MPa (*Gabbrielli CE* 10 ton hydraulic press, 50 x 8 x 5 mm^3 test pieces). After compaction, the test pieces were oven dried at 110±5 ºC until constant weight and naturally cooled.

The mechanical strength of dried test pieces was determined as the modulus of rupture (DMoR) in three-point bending tests, using a digital Shimadzu AUTOGRAPH AG-25TA test machine, with a 0.5 mm/min cross-head speed until rupture. For each mixture, the test result was taken as the average of the DMoR of ten test pieces.

The bulk density of dried test pieces (DBD) was determined using Archimedes' liquid displacement method, by immersion in Hg. For each mixture, the test result was taken as the average of the DBD of five test pieces.

TABLE 1. CHEMICAL COMPOSITION (WT.%) OF CLAYS A AND B, AS OBTAINED BY XRF

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	MnO	P_2O_5	LoI
Clay A	69.41	18.51	2.20	0.82	0.05	0.08	2.91	0.73	0.01	0.14	5.15
Clay B	51.61	32.57	1.04	1.59	1.48	0.89	1.57	0.08	0.03	0.12	9.02

TABLE 2. MINERALOGICAL COMPOSITION OF CLAYS A AND B AND THEIR MIXTURE.

Minerals (wt.%)	Kaolinite	Muscovite	Montmorillonite	Quartz	Microcline	Other
Clay A	40.23	9.91	—	47.46	—	2.40
Clay B	72.67	—	10.31	6.61	9.31	1.10
Clay mixture	65.21	2.28	7.94	16.01	7.17	1.40

Each set of values was then used to iteratively calculate the coefficients of a regression equation such as Eq.s (1) or (2), until a statistically relevant model and response surface was obtained, relating the dry bending modulus of rupture and dry bulk density with the weight fractions of clay, feldspar and quartz present in the mixtures (the calculations were carried out with *STATISTICA* — StatSoft Inc., 2000).

3. RESULTS AND DISCUSSION

3.1. Mixture compositions and models for DMoR and DBD

Table 1 shows the chemical analysis results (XRF) obtained for the two clays. Table 2 shows the mineralogical constitution of the individual clays and of the mixture of 23 wt% clay A + 77 wt% clay B, which was used throughout the work.

Bearing in mind the selected independent components and the raw materials compositions, the quartz sand and the potash feldspar were considered to be pure, whereas the clay mixture (Table 2) was divided into its plastic fraction (kaolinite + muscovite + montmorillonite), feldspar fraction and quartz fraction (*i.e.* a point inside the composition triangle).

The chosen processing conditions require that lower bound composition limits are used, which were 20 wt.% of clay, 15 wt.% of feldspar and 15 wt.% of quartz. Thus, a restricted composition triangle of pseudo-components was created (Figure 1), on which a {3,2} simplex lattice (6 points) was set. To these original six points, a central point was first added (centroid simplex), followed by three more (augmented {3,2} simplex lattice).

Figure 1 shows that the pseudo-components triangle lies inside the raw materials triangle, which means that all the resulting ten mixtures can be prepared. Table 3 presents the compositions of those ten mixtures in terms of the independent components, and the experimentally determined values for dry modulus of rupture (DMoR) and dry bulk density (DBD).

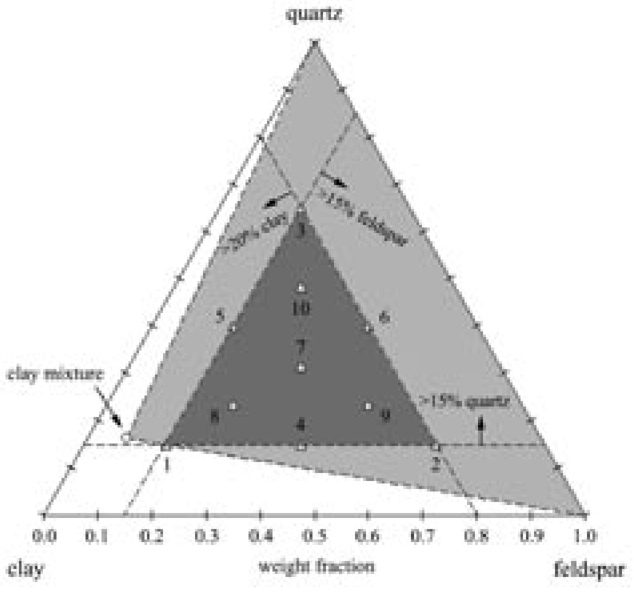

Figure 1. The ternary system clay-quartz-feldspar (independent components), showing: the raw materials triangle, the restricted pseudo-components triangle and simplex points, and the intersection area containing all compositions that fulfil those restrictions

Having a measured value for the property response at specific coordinates (Table 3), a regression equation can be sought for each property. Both linear and second degree regressions were evaluated, subjected to a significance level of 2%. Tables 4 and 5 give the various statistical properties of the regressions for DMoR and DBD, using the nomenclature commonly found in the relevant texts [4-5].

Using the p-value approach to hypothesis testing (*i.e.* p-value ≤ significance level), Tables 4 and 5 show that the linear models do not reach the stipulated significance value. The second degree model is statistically significant at that level in both cases and the corresponding coefficients of multiple determination, R^2, show that the models present small variability.

The final equations, relating the DMoR and DBD with the proportions of the independent components, are:

$$\mathrm{DMoR} = -2.19\,x_1 - 2.20\,x_2 - 2.34\,x_3 + 18.76\,x_1x_2 + 21.69\,x_1x_3 + 0.89\,x_2x_3 \qquad (3)$$

$$\mathrm{DBD} = 1.43\,x_1 + 1.36\,x_2 + 1.38\,x_3 + 1.85\,x_1x_2 + 2.09\,x_1x_3 + 0.37\,x_2x_3 \qquad (4)$$

In equations (3) and (4), x_1 is the clay fraction, x_2 is the feldspar fraction and x_3 is the quartz fraction. Eq.s (3) and (4) can be further rearranged to relate each property with the weight fractions of the original raw materials (X_1 = clay mixture, X_2 = feldspar and X_3 = quartz). Equations (5) and (6) are the final result:

$$\mathrm{DMoR} = -2.86\,X_1 - 1.99\,X_2 - 1.88\,X_3 + 24.53\,X_1X_2 + 28.36\,X_1X_3 - 5.15\,X_2X_3 - \\ - 1.78\,X_2^2 - 4.61\,X_3^2 \qquad (5)$$

$$\mathrm{DBD} = 1.87\,X_1 + 1.22\,X_2 + 1.08\,X_3 + 2.42\,X_1X_2 + 2.73\,X_1X_3 - 0.22\,X_2X_3 - \\ - 0.18\,X_2^2 - 0.44\,X_3^2 \qquad (6)$$

TABLE 3. MIXTURE COMPOSITIONS AND CORRESPONDING MEASURED VALUES OF DMOR AND DBD.

Design mixture	Weight fractions			DMoR	DBD
	Clay	Feldspar	Quartz	(MPa)	(g.cm^{-3})
1	0.700	0.150	0.150	1.97±0.30	1.83±0.02
2	0.200	0.650	0.150	1.08±0.11	1.71±0.01
3	0.200	0.150	0.650	1.14±0.15	1.75±0.01
4	0.450	0.400	0.150	2.79±0.44	1.90±0.02
5	0.450	0.150	0.400	2.92±0.52	1.94±0.03
6	0.200	0.400	0.400	1.28±0.22	1.77±0.02
7	0.367	0.317	0.316	2.54±0.23	1.86±0.01
8	0.533	0.233	0.234	3.04±0.38	1.91±0.02
9	0.283	0.483	0.234	1.43±0.33	1.83±0.02
10	0.283	0.233	0.484	2.10±0.18	1.82±0.02

TABLE 4. ANALYSIS OF VARIANCE FOR SIGNIFICANCE OF THE REGRESSION MODELS FOR DMOR *

Model	SSR	df	MSR	SSE	df	MSE	F-test	p-value	R^2	R^2_A
Linear	2.3911	2	1.1955	2.8844	7	0.4121	2.9014	0.1209	0.4532	0.2970
Second degree	2.5873	3	0.8624	0.2971	4	0.0743	11.6111	0.0192	0.9437	0.8733
Residual	0.2971	4	0.0743							
Total	5.2755	9								

* SSR: regression sum of squares; df: degrees of freedom; MSR: regression mean squares; SSE: error sum of squares; MSE: error mean squares; R^2: coefficient of multiple determination; R^2_A: adjusted R^2.

TABLE 5. ANALYSIS OF VARIANCE FOR SIGNIFICANCE OF THE REGRESSION MODELS FOR DBD *.

Model	SSR	df	MSR	SSE	df	MSE	F-test	p-value	R^2	R^2_A
Linear	0.0220	2	0.0110	0.0267	7	0.0038	2.8854	0.1219	0.4519	0.2953
Second degree	0.0249	3	0.0083	0.0019	4	0.0005	17.8462	0.0088	0.9619	0.9143
Residual	0.0019	4	0.0005							
Total	0.0488	9								

* as in Table. 4

The fact that the models obtained are statistically significant at the specified level does not mean that they are valid. Figure 2 (a) is a plot of the DMoR raw residuals (*i.e.* difference between the experimentally determined value and the calculated estimate) as a function of the predicted DMoR values, and shows that the errors can be considered randomly distributed around a zero mean value, hence are uncorrelated, which suggests a common constant variance for all the DMoR values. Figure 2 (b) shows that a straight line can be considered to relate the residuals with the expected normal values, meaning that the distribution is normal [4-5]. Thus, the model can be considered adequate and a good estimate of the DMoR can be obtained using Eq. (3).

A similar reasoning applies to Figure 3 (a) and (b). Again, the errors can be considered randomly distributed around a zero mean value (hence are uncorrelated) and the distribution is normal. Thus, a good estimate of the DBD can be obtained, using Eq. (4).

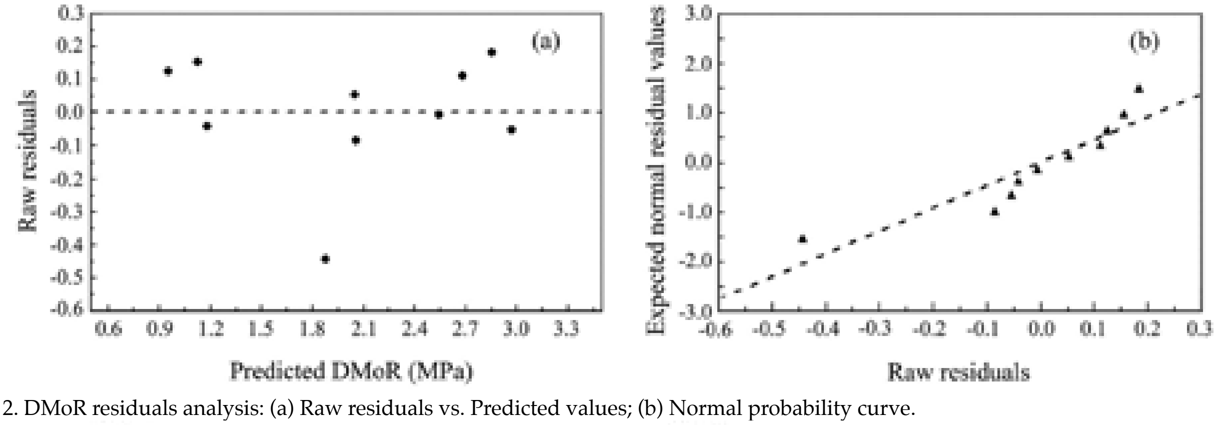

Figure 2. DMoR residuals analysis: (a) Raw residuals vs. Predicted values; (b) Normal probability curve.

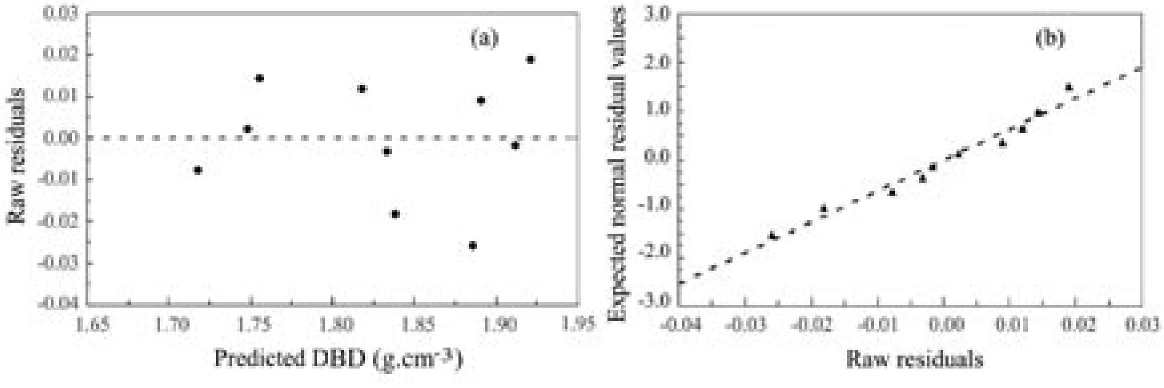

Figure 3. DBD residuals analysis: (a) Raw residuals vs. Predicted values; (b) Normal probability curve.

3.2. Contour plots

Figure 4 shows the projection of the calculated response surfaces (in pseudo-components) onto the composition triangle, as constant property contours (contour plots).

It can be seen from Figure 4 (A) that the highest dry bending strength (DMoR ≥ 2.65 MPa) is reached within a reasonably wide composition area, for clay contents of 38-57 wt.% (~50-75 wt.% original raw clay mixture), whatever the feldspar and quartz contents. It is interesting to note that high DMoR values correspond to high contents of plastic material. This can probably be explained by a particle packing effect, since both quartz and feldspar contain larger particles, and the presence of montmorillonite in the clay, which will have a dominant role as a green body binder.

Figure 4 (B) shows that the highest dry bulk density (DBD ≥ 1.89 g.cm^{-3}) is reached for the same composition range as the DMoR. The fact that this is not surprising, as is well known in the industrial practice that both properties are similarly affected by the same processing parameters [3], provides an extra validation for the proposed models.

3.3. Response trace plots

The effect of each raw material can be best visualised when response trace plots are constructed. The response trace is a plot of the estimated property values as the composition, expressed as pseudo-component weight fraction, moves away from a reference point, along lines that go through each apex in turn (*i.e.* it is a vertical section through the property prism in which

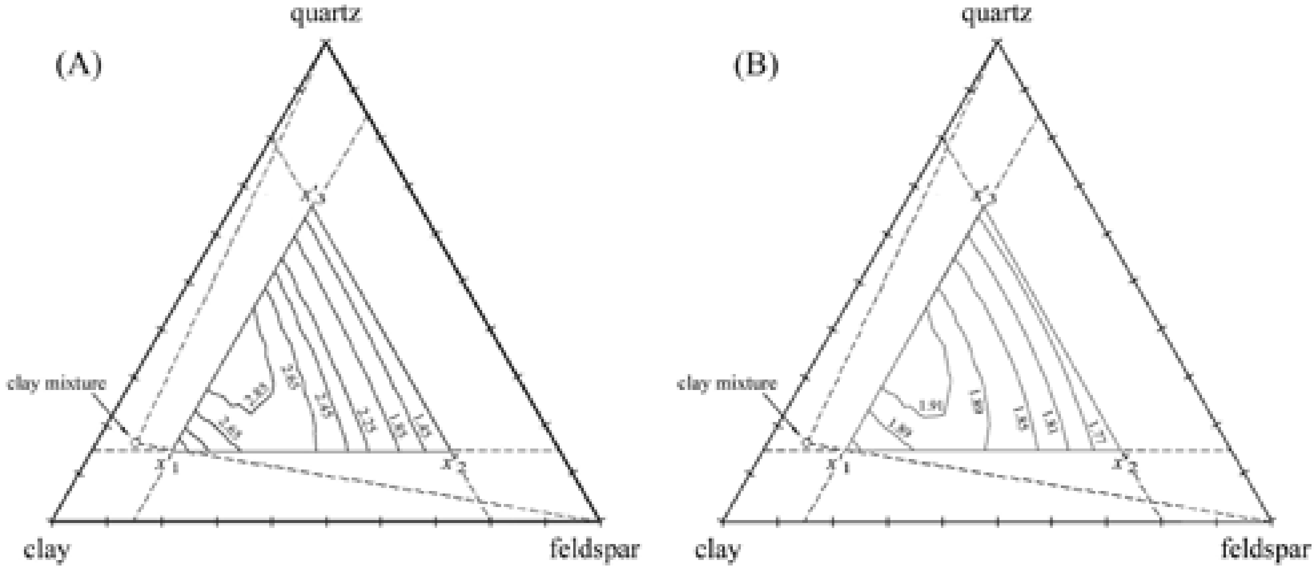

Figure 4. Constant contour plots, expressed in terms of pseudo-components: (A) dry modulus of rupture vs. composition; and (B) dry bulk density vs. composition.

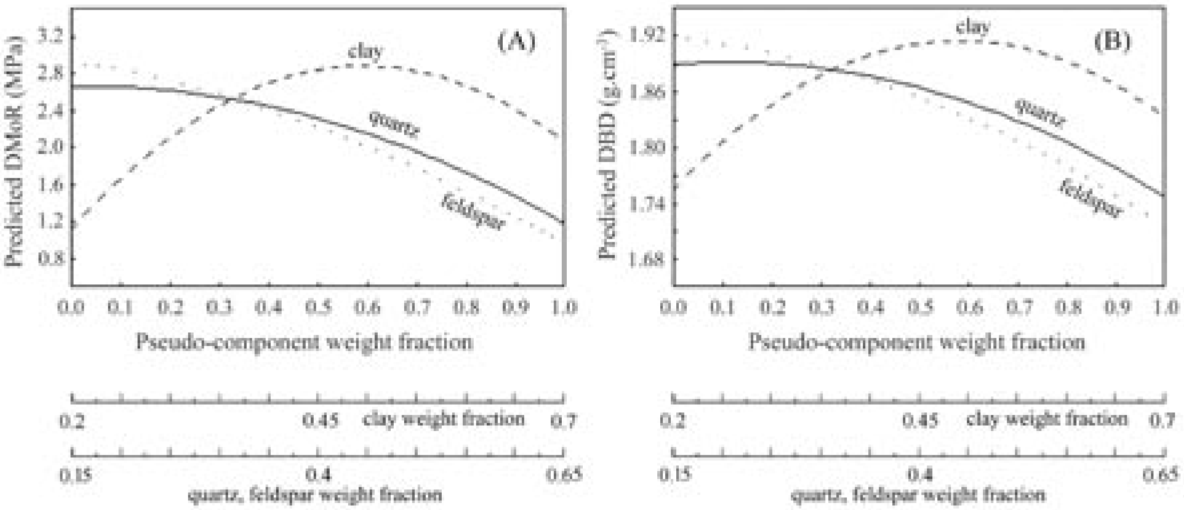

Figure 5. Predicted property trace plots: (A) dry modulus of rupture, and (B) dry bulk density.

the fraction of one of the pseudo-components is changed while the proportion between the other two is kept constant).

In this case, the reference composition is the simplex centroid, which corresponds to 36.6 % clay, 31.7 % feldspar and 31.7 % quartz (by weight). Thus, the response trace for each pseudo-component shows the property values as the weight fraction of that pseudo-component varies from zero to unity while the fractions of the other pseudo-components, present in equal amounts, vary from 0.5 to zero. Figure 5 shows the response trace plots of estimated DMoR and DBD for each pseudo-component. There are two auxiliary axes in Figure 5, to help in the conversion of weight fractions from pseudo-components into components.

Figure 5 shows that the dry bending strength and dry bulk density tend to decrease when the quartz and feldspar contents increase, although they both can tolerate contents as high as ~20 wt.% of the two pseudo-components without much change (hence, 25 wt.% of quartz or feldspar, read from the relevant trace plot on the quartz / feldspar axis). On the other hand, both properties show a clear maximum (2.90 MPa and 1.92 $g.cm^{-3}$) for pseudo-clay weight fractions of ~0.60 (or ~50 wt.% clay, read from the relevant trace plot on the clay axis).

The trace plots also show the implications of the changes, purposeful or accidental, in the raw materials proportions: while clay contents on both sides of the maximum (*i.e.* both lower and higher than ~50 wt.%) have a similar effect on the properties, to keep the properties as high as possible it is safer to work on the quartz- and feldspar-poor side (contents lower than 25 wt.% are slightly beneficial to both properties).

4. CONCLUSIONS

The use of the design of mixture experiments methodology to model the dry bending modulus of rupture (DMoR) and dry bulk density (DBD) of triaxial ceramic compositions, prepared with the same three raw materials under constant processing conditions, proved to be coherent: second degree equations were found to significantly relate the DMoR and DBD with the starting proportions of the particular raw materials considered (*viz.* clay mixture, feldspar and quartz).

The constant contour and response trace plots obtained show that, with the particular raw materials and processing conditions used, high DMoR and DBD values correspond to reasonably high contents of plastic materials (~50-75 wt.% original raw clay mixture) and that the dry bending strength and dry bulk density are particularly sensitive to the changes in the clay content. The results obtained also show how the two properties are related and behave similarly as the mixture composition changes. This fact is well known in the industrial practice, which provides an extra validation for the proposed models. The mathematical models also show the implications of the changes, purposeful or accidental, in the raw materials proportions.

Still, for the three raw materials and processing conditions used, even within the high DMoR and DBD region, the values do not reach the level usually recommended by the floor and wall tile industries (dry bending strength ≥ 3.0 MPa and dry bulk density ≥ 2.0 $g.cm^{-3}$).

These results throw a strong light onto the role of the hidden variables (*i.e.* those that were kept constant throughout the work). Particle size distribution and particle packing on one hand, and processing conditions on the other, seem to be especially relevant and their effect will be investigated in future works.

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