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Simultaneous optimization of linear firing shrinkage and water absorption of triaxial ceramic bodies using experiments design

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Abstract

In the development and manufacture stages of floor and wall ceramic tiles, firing shrinkage and water absorption are basically determined by the combination of raw materials and frequently used as quality control parameters. This configures the ideal scenario to apply the techniques of experiments design, often used in various other areas, to model those properties of such ceramics bodies. In the present study, 10 formulations of three different raw materials, namely a clay mixture, potash feldspar and quartz (triaxial compositions) were selected and used in the experiments design. Those formulations were processed under conditions similar to those used in the ceramics industry: powder preparation (wet grinding, drying, granulation and humidification), green body preparation (pressing and drying), firing (at 1170 °C) and characterization. With the experimental results, regression models were calculated, relating linear firing shrinkage and water absorption with composition. After statistical analysis and verification experiments, the significance and validity of the models were confirmed. The regression models can then be used to select the best combination of those three raw materials to produce a ceramic body with specified properties.

Keywords: A. Firing; A. Mixing; D. Traditional ceramics; Experiments design

1. Introduction

The design of mixture experiments configures a special case in response surface methodologies using mathematical and statistical techniques [1,2]. The basic assumption is that there is a given mixture property which depends solely on the fractions (x_i, summing up to unity) of specific components, or ingredients, of the mixture, and not on the amount of the mixture (i.e. the property is not extensive); thus, the changes in (or the response of) the property is entirely determined by the proportions of those components. To this aim, it is necessary first to select the appropriate mixtures from which 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.

In a system with q variables (or components), there will be $(q - 1)$ independent composition variables x_i, and the geometric description of the factor space containing the q components consists of all points on or inside the boundaries (vertices, edges, faces, etc.) of a regular $(q-1)$-dimensional simplex. The response function f can be expressed in its canonical form as a low degree polynomial (typically, first or second degree):

$$\text{Linear} \quad f = \sum_{i=1}^{q} \beta_i x_i \tag{1}$$

$$\text{Second degree} \quad f = \sum_{i=1}^{q} \beta_i x_i + \sum \sum_{i<j}^{q} \beta_{ij} x_i x_j \tag{2}$$

This polynomial equation has to be evaluated over a number N of points 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. Then, a laboratory study consisting of N experiments $(N > q)$ has to be carried out and the values of the property on those selected N lattice points evaluated.

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A regression equation, such as Eq. (1) or Eq. (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.

When some or all the compositions x_i are restricted by either 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), which is frequently the case, the concept of pseudo-component [1,2] can be used to define another simplex of new components (pseudo-components) present in the proportions $x_i{}'$ and to which the $\{q, m\}$ simplex lattice is applied. 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 determined.

In the industrial processing of ceramic bodies such as floor and wall tiles, due to the sensitivity to raw materials and/or processing changes and the simplicity of their laboratory determination [3–5], linear firing shrinkage and water absorption are frequently used as quality and process control parameters in the development and manufacture stages. Under constant processing conditions, both properties are basically determined by the combination (or mixture) of raw materials and can, therefore, be modeled using the optimization methodology specific to the design of mixture experiments. Such procedure is common practice in the chemical industry [6–8] and is becoming popular in the field of glasses and ceramics [9–11]. It has proven, in all cases reported, to lead to greater efficiency and confidence in the results obtained, and to be less demanding in time and both material and human resources.

In the particular case of ceramic mixtures, there are three major components or ingredients (triaxial mixtures) to be considered, given the distinctive roles they play during ceramic processing: a plastic component (clays), a fluxing component (feldspar) and an inert component (quartz). Thus, an equilateral triangle can be used ($q = 3$) 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).

This work describes the use of the design of mixture experiments methodology to calculate a regression model relating the linear firing shrinkage and water absorption of ceramic bodies, with the proportions of clay, feldspar and quartz present, under constant processing conditions (wet grinding, moisture content, compaction pressure, firing schedule). 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). The crystalline phases present were identified by X-ray diffraction (XRD) and quantified by rational analysis [12]. A mixture of the two clays (23.0 wt.% of clay A + 77.0 wt.% of clay B) was used throughout the work.

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

The selected mixtures were wet processed, following the conventional wall and floor tile industrial procedure: wet grinding (residue left in a 325-mesh sieve below 1 wt.%), drying, moisturizing (6.5 ± 0.2 wt.%, dry basis), granulation and uniaxial pressing (Micropressa Gabbrielli, 10 ton hydraulic press).

To determine the linear firing shrinkage, 10 flat test pieces (50 mm × 8 mm × 5 mm, using 4.0 g of material per test piece) were prepared from each mixture; water absorption was determined on five cylindrical test pieces from each mixture ($20 \times 10\,mm^3$, using 4.5 g of material per test piece). The compaction pressure, in both cases, was 47 MPa. After compaction, the test pieces were oven-dried at $110 \pm 5\,^{\circ}C$ until constant weight, fired at 1170 °C for 1 h (heating at 3 °C/min up to 600 °C, and at 5 °C/min from 600 to 1170 °C), and naturally cooled.

The linear shrinkage was calculated from the change in length (measured with Mitutoyo callipers with a resolution of 0.05 mm), upon firing, of the flat test pieces. Water absorption was determined via boiling in water for 2 h, using a digital scale Precisa XB 4200 C with a resolution of 0.01 g. For each mixture, the property final value was taken as the average of all test pieces evaluated (10 for linear shrinkage, 5 for water absorption).

Those values were then used to iteratively calculate the coefficients of a regression equation such as Eq. (1) or Eq. (2), until a statistically relevant model and response surface was obtained, relating the firing shrinkage and water absorption 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. The $\{3, 2\}$ augmented simplex-lattice mixture compositions and models for linear firing shrinkage and water absorption

The distinctive roles that clays, feldspar and quartz play during ceramic processing were used to establish the lower bound limits of 20 wt.% of clay, 15 wt.% of feldspar and

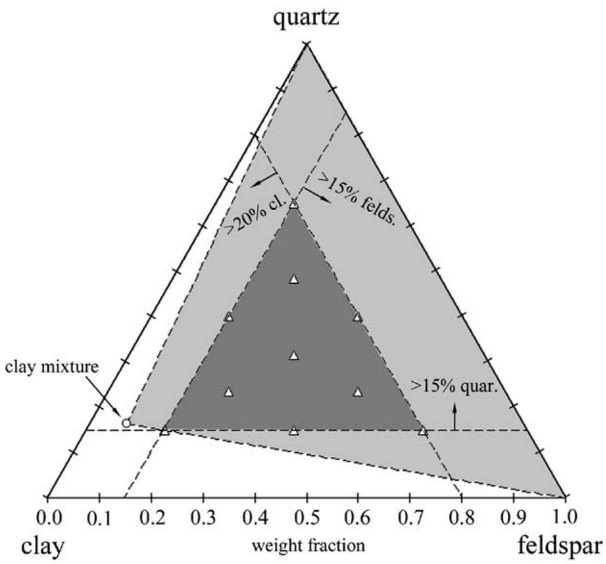

Fig. 1. The ternary system clay–quartz–feldspar (independent components), showing the raw materials triangle, the restricted pseudo-components triangle and simplex points, and the intersection area containing all compositions that fulfill those restrictions.

15 wt.% of quartz, and create a restricted composition triangle of pseudo-components (Fig. 1) on which a {3, 2} simplex lattice (six 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).

Bearing that in mind, the quartz sand and the potash feldspar were considered to be pure, whereas the clay mixture (Table 1) was divided into its alumino-silicate fraction (kaolinite + muscovite + montmorillonite), feldspar fraction and quartz fraction (i.e. a point inside the composition triangle). Fig. 1 shows that the pseudo-components triangle lies inside the raw materials triangle, which means that all the resulting 10 mixtures can be prepared. Table 2 presents the compositions of those 10 mixtures (M_i, $i = 1, 2, \ldots, 10$) in terms of the independent components, and the measured values for linear firing shrinkage and water absorption.

Having a measured value for the response properties at specific coordinates (Table 2), a regression equation can be sought for each property. For both, a second-degree polynomial, such as Eq. (2), was found to be statistically the most adequate, with a significance level of 2%:

$$\text{Linear firing shrinkage} = 21.52x_1 + 12.72x_2 - 0.95x_3 - 27.24x_1x_2 - 29.31x_1x_3 + 23.01x_2x_3 \quad (3)$$

Table 2
Composition of design mixtures and corresponding measured values of linear firing shrinkage and water absorption

Design mixture	Weight fractions			Linear firing shrinkage (%)	Water absorption (%)
	Clay	Feldspar	Quartz		
1	0.700	0.150	0.150	11.35 ± 0.08	0.54 ± 0.06
2	0.200	0.650	0.150	10.24 ± 0.15	0.00 ± 0.00
3	0.200	0.150	0.650	3.32 ± 0.10	12.78 ± 0.20
4	0.450	0.400	0.150	9.17 ± 0.08	0.00 ± 0.00
5	0.450	0.150	0.400	5.64 ± 0.10	4.90 ± 0.22
6	0.200	0.400	0.400	8.38 ± 0.11	1.35 ± 0.22
7	0.367	0.317	0.316	7.46 ± 0.06	1.84 ± 0.13
8	0.533	0.233	0.234	8.48 ± 0.07	1.45 ± 0.11
9	0.283	0.483	0.234	8.84 ± 0.05	0.00 ± 0.00
10	0.283	0.233	0.484	4.92 ± 0.05	7.32 ± 0.32

Table 3
Major statistical properties relevant for variance analysis

Response property	*P*-value	R^2	R^2_A
Water absorption	0.0195	0.9866	0.9699
Linear firing shrinkage	0.0040	0.9941	0.9866

$$\text{Water absorption} = -2.17x_1 + 4.69x_2 + 34.98x_3 - 0.49x_1x_2 - 21.11x_1x_3 - 73.95x_2x_3 \quad (4)$$

In Eqs. (3) and (4), x_1 is the clay fraction, x_2 is the feldspar fraction and x_3 is the quartz fraction (i.e. independent component fractions). Table 3 gives the major statistical properties of the regressions, using the nomenclature commonly found in the relevant texts (*P*-value, coefficient of multiple determination, R^2, and adjusted coefficient of multiple determination, R^2_A, for a second-degree polynomial).

Eqs. (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). Eqs. (5) and (6) are the final result:

$$\text{Linear firing shrinkage} = 28.13X_1 + 10.67X_2 - 5.52X_3 - 35.61X_1X_2 - 38.32X_1X_3 + 31.58X_2X_3 + 2.59X_2^2 + 6.22X_3^2 \quad (5)$$

$$\text{Water absorption} = -3.16X_1 + 4.57X_2 + 35.33X_3 + 0.42X_1X_2 - 26.68X_1X_3 - 71.21X_2X_3 - 0.03X_2^2 + 4.33X_3^2 \quad (6)$$

Table 1
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

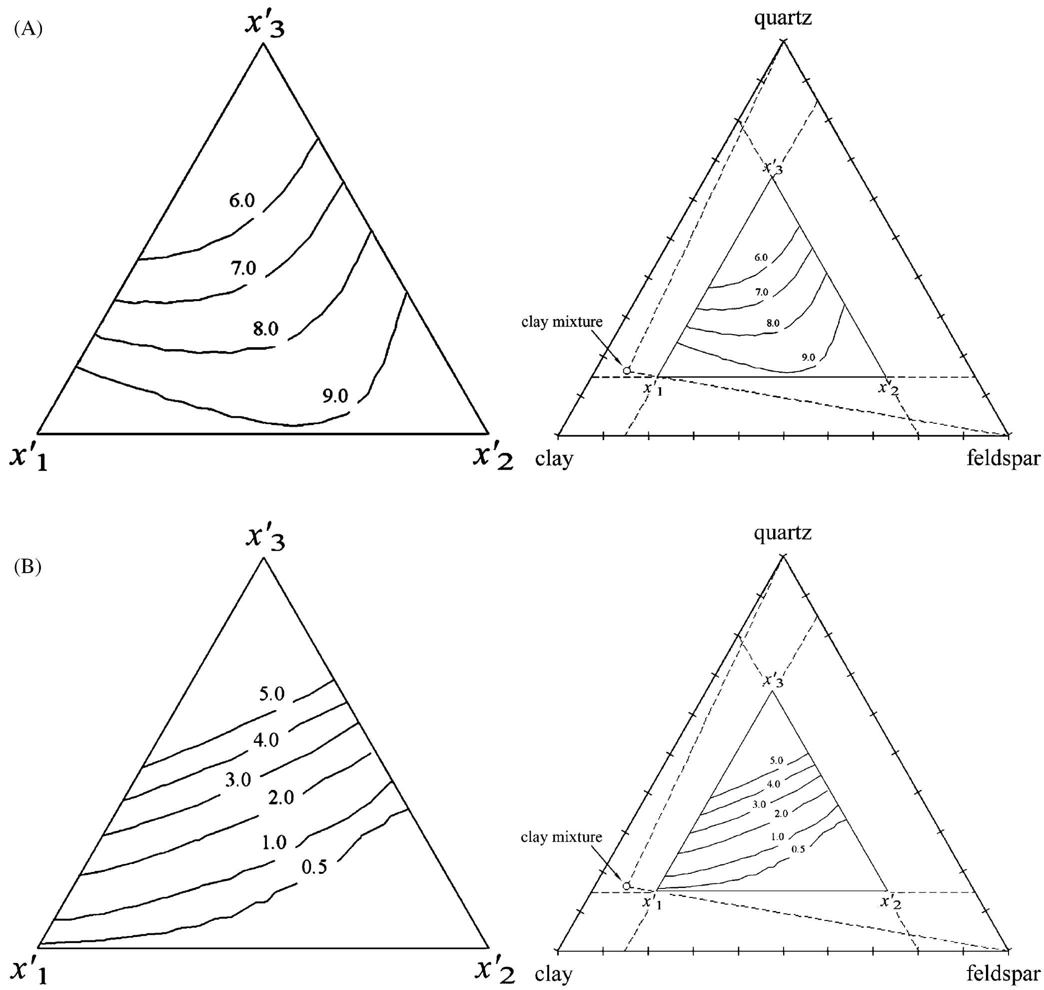

Fig. 2. Constant contour plots, expressed in terms of pseudo-components (see diagram on the right for composition location): (A) linear firing shrinkage vs. composition; and (B) water absorption vs. composition.

3.2. Contour plots

Fig. 2 shows the projection of the calculated response surfaces (in pseudo-components) onto the composition triangle, as constant property contours (contour plots).

Fig. 2A is the constant contour plot for the linear firing shrinkage. It can be seen that the feldspar (x_2') has the strongest effect on the property, followed by the clay. Nevertheless, low firing shrinkage values (e.g. below 7.0%) can be reached within a reasonably forgiving composition area, corresponding to feldspar contents below 30 wt.% and quartz contents above 35 wt.% (as independent components). The lowest firing shrinkage value (∼3.32%) was found for the composition with 20 wt.% clay, 15 wt.% feldspar and 65 wt.% quartz (composition 3, in Table 2).

Fig. 2B is the constant contour plot for the water absorption. In this case, it can be seen that water absorption is mostly controlled by the ratio feldspar/quartz and low values (e.g. below 2.0%) can be reached for feldspar/quartz ratios above ∼1.0, for clay contents up to 65 wt.% (again, as independent components). The lowest water absorption values (virtually zero) were found for compositions with high feldspar content and low quartz content (compositions 2, 4 and 9, in Table 2).

3.3. Response trace plots

The effect of each raw material can be best visualized 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 the fraction of one of the components is changed while the proportion between the other two is kept constant).

In this case, the reference composition used was 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 component varies from zero to unity while the fractions of the other pseudo-components,

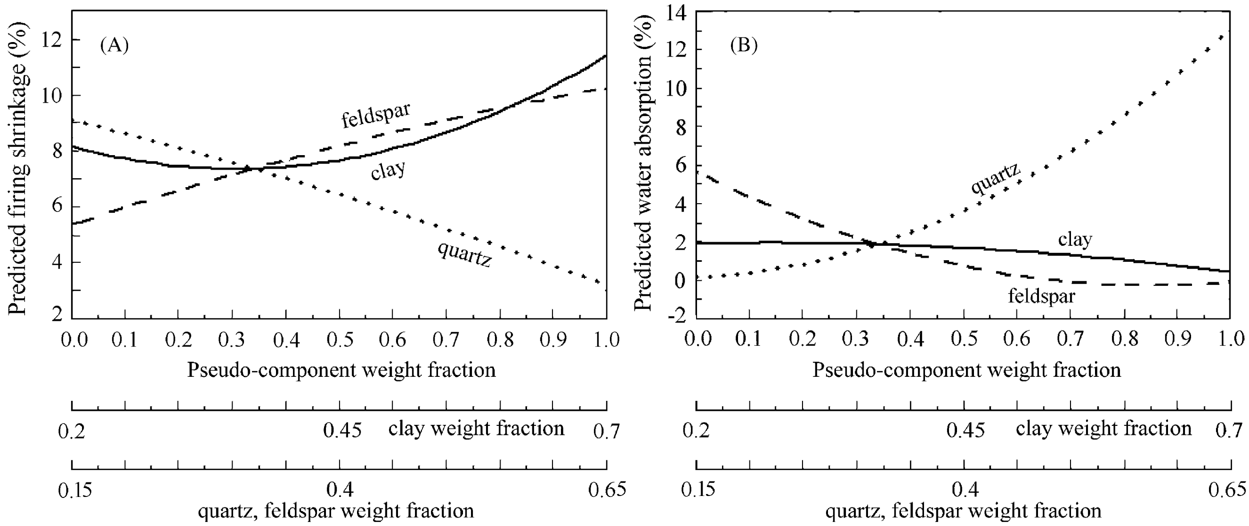

Fig. 3. Predicted property trace plots (the composition moves away from the simplex centroid along lines that go through the simplex apex): (A) firing shrinkage, and (B) water absorption.

present in equal amounts, vary from 0.5 to 0. Fig. 3 shows the response trace plots of linear firing shrinkage and water absorption for each component. There are two auxiliary axes in Fig. 3, to help in the conversion of weight fractions from pseudo-components into components.

Fig. 3A shows that the firing shrinkage varies almost linearly with quartz and feldspar contents in the composition, increasing with the feldspar while decreasing when the quartz content increases. On the contrary, the clay content can vary between ~25 and ~45% (read on the clay axis) without introducing significant changes in the shrinkage value (only when the clay content exceeds 45 wt.% its effect on the firing shrinkage becomes important). For instance, the clay fraction that minimizes the firing shrinkage is ~0.35 (read from the relevant trace plot on the clay axis), which corresponds to a pseudo-clay fraction of 0.30 (read on the pseudo-component axis); thus, the fractions of the other two pseudo-components are 0.35. These values are used to obtain the corresponding components fractions on the relevant component axis: quartz 0.325 (starting from 0.35) and feldspar 0.325 (starting from 0.35).

Fig. 3B shows that the water absorption is more sensitive to changes in quartz and feldspar contents in the composition than firing shrinkage was (decreases with the feldspar and increases when the quartz content increases). On the contrary, the clay content can vary between ~20 and ~50% (0–0.6 pseudo-clay fractions, respectively) without introducing significant changes in the water absorption value (only when the clay content exceeds 50 wt.% its effect on the water absorption becomes important).

3.4. Applicability, subjected to restrictions in processing and product specification

Assuming that the raw materials studied in this work were to be used in the production of stoneware floor tiles, hence in the AI (extruded) or BI (pressed) groups specified by the European standard EN 87 [13] (water absorption below 3.0%) or the Brazilian standard ABNT 13818 [14] (water absorption between 0.5 and 3.0%), the intersection of Fig. 2A and B could be used to select an adequate mixture composition. In this case, the water absorption values must meet the final product specifications and the linear firing shrinkage is used as restricting parameter during processing. Fig. 4 shows the intersection of Fig. 2A and B and highlights the composition area, within which 5.0% ≤ firing shrinkage ≤ 9.0% and 0.5% ≤ water absorption ≤ 3.0%.

Within the shaded area of Fig. 4, mixtures 6 and 8 (Table 2) were selected to test the applicability of the

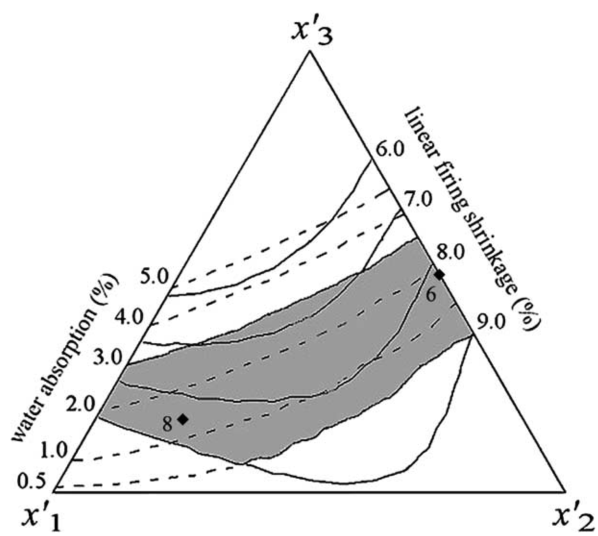

Fig. 4. Intersection of the linear firing shrinkage and water absorption surfaces, expressed in terms of pseudo-components. The shaded area is the composition range suitable for stoneware floor tiles, within which 0.5% ≤ water absorption ≤ 3.0% and 5.0% ≤ firing shrinkage ≤ 9.0%.

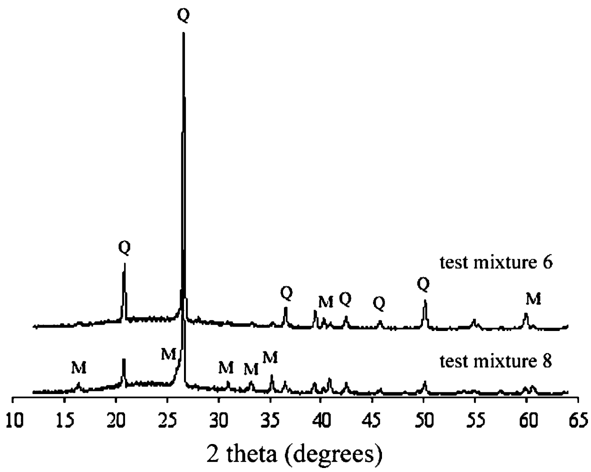

Fig. 5. X-Ray diffraction patterns obtained for fired compositions within the shaded area of Fig. 4: (A) test mixture 6; and (B) test mixture 8 (refer to Table 2 for mixture composition and properties).

mathematical models. The two test compositions were prepared as described earlier and fired at 1170 °C. Fig. 5 shows the corresponding X-ray diffraction patterns.

Although quite apart in terms of composition, the two mixtures present close values of both firing shrinkage and water absorption, both within the specified range of values for the properties. Those values show the dominant effect of the feldspar/quartz ratio on the water absorption and the synergetic effect of feldspar and clay on the firing shrinkage. In both, quartz is the major crystalline phase and the mullite content tends to increase with the clay mineral content in the starting mixture. This suggests the possibility of tailoring the proportions of crystalline phases that might promote a third property (e.g. mechanical strength) without compromising the former two.

4. Conclusions

The design of mixture experiments and the use of response surface methodologies enabled the calculation of regression models relating linear firing shrinkage and water absorption with composition, which can then be used to select the best combination of three given raw materials (clay mixture, potash feldspar and quartz) to produce, under constant processing conditions, a ceramic body with specified properties. Furthermore, the use of intersecting surfaces shows that, for the particular raw materials under consideration, there is a rather forgiving composition range within which it is possible to simultaneously specify the values of two different properties.

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