# MIXTURE DESIGN AS A TOOL FOR DESIGNING PORCELAIN CERAMIC TILES TO PREVENT PYROPLASTICITY

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## 1. ABSTRACT

The porcelain tile is a noble ceramic covering, standing out in the market due to its great resemblance to natural stones. It shows an almost zero water absorption and its beauty and practicality has become attractive to the consumer market. The production of a covering with so many special characteristics requires the use of carefully selected raw materials. However, although it is produced very carefully, there are still problems affecting the porcelain tiles, such as pyroplasticity, characterised as a shape shift that occurs due to the formation of an excess of liquid phase during the sintering of the material. Therefore, this study aimed to discover the causes of pyroplasticity in a porcelain tile composition from the individual behaviour of the raw materials, using the mixture design procedure as a method to experimentally minimise their effects on the porcelain tile production. Each raw material was characterised by its physicochemical properties (chemical analysis by X-ray fluorescence, phases by X-ray diffraction and thermal by dilatometry) and, from the results of this characterisation, 19 compositions were obtained. After firing, the compositions were characterised by their linear shrinkage, water absorption, mechanical resistance by three-point bending, variation of tonality and, finally, pyroplasticity, with the results undergoing an analysis of variance and response surface curves. The results showed that the feldspar is the raw material responsible for the pyroplasticity among the minerals used in this study, due to the presence of lithium oxide in its composition.

## 2. INTRODUCTION

The porcelain tile is a noble ceramic covering, standing out in the market due to its great resemblance to natural stones. The almost zero water absorption and the beauty and practicality of the porcelain tile has become attractive to the consumer market [1].

Although the porcelain tile had been originally produced to be a non-enamelled covering, nowadays there are commercially enamelled and non-enamelled surfaces. The non-enamelled porcelain tiles show special characteristics such as high resistance to abrasion, surface resistance to acids and alkalis, impermeability, resistance to ice, uniformity of colours, easy maintenance and numerous possibilities of compositions. When polished, it shows surfaces that are always closer to marbles and granites. Enamelled porcelain tiles follow the requirements of the products used in residences, whose surface aesthetics prevail over the tenacity of the product [2,3].

The manufacture of enamelled porcelain tiles is intended to add various decorative shapes and effects to the product, without losing its characteristics such as low water absorption (<0.5%), high mechanical strength (close to 45 MPa) and high durability [1].

Although there are technological innovations in the production of porcelain tiles, problems that aesthetically damage the product still exist, such as dimensional variations and shape deviations that are basic requirements for the quality of the porcelain tiles [4,5].

One of these very common deviations, found mainly in products made from highly vitrified pastes such as porcelain and stoneware, is pyroplasticity or pyroplastic deformation, defined as a de-characterisation of the product form that occurs during firing. The production of a covering with so many special characteristics requires the use of carefully selected raw materials.

The literature shows few studies in the ceramic area aiming at the reduction of pyroplasticity. These studies cover the analysis of all steps of the porcelain tile production process, its current formulation and tests with possible raw materials that will replace the raw materials responsible for the pyroplasticity [6,7].

The composition of pastes for the manufacture of ceramic products is a very important research stage involving numerous laboratory tests until a paste suitable for industrial production is developed. When the stage of development and characterisation of a composition is carried out carelessly, without any statistical control, even if a paste composition of good quality is obtained in the laboratory scale, the knowledge of the effect that the variation of some raw material will have in the final product will hardly be obtained.

Among the many typologies of ceramic tiles, the porcelain tile stands out because of its technical properties and its resemblance to natural stones. Porcelain pastes, when compared to traditional paste compositions, are made with a lower proportion of clay materials and with increased non-plastic materials such as feldspars [6,7].

As a result of the modernisation of the ceramic tile production, from the traditional slow firing process, where each raw material acts in a series of reactions that result in the total modification of the components and the formation of new compounds, until the fast firing, where all raw materials almost always manifest in the final product their unique characteristics in the final firing temperature, there was a

strong reduction of the kaolin content, which in the current cycles behaves as a refractory material with high porosity at the end of the firing cycle [2,8,9].

As feldspar and plastic clays are raw materials with a fluxing behaviour, quartz is always present and its quantity can vary depending on the degree of purity of the raw material, it is also possible to introduce energetic fluxes in small quantities such as talc and wollastonite, among others.

On the other hand, the elaboration of a composition for white porcelain tiles decorated with soluble salts requires the paste to be extremely white to emphasize the chromatic tonalities. In this case, raw materials such as zirconium silicate and alumina are added which, regardless of their refractory characteristics, means only a slight touch-up in the composition has to be made [10,11].

Considering those compositions where the presence of fluxing materials is predominant, it is possible to obtain a low porosity and thus a water absorption of less than 0.5% at firing temperatures around 1200 °C in firing cycles of 45 to 60 minutes. It must be pointed out that some ceramic companies in Brazil produce porcelain tiles at firing cycles of only 30 minutes.

Therefore, this study aimed to discover the causes of pyroplasticity in a porcelain tile composition from the individual behaviour of the raw materials using as a methodology the experimental design of mixtures to minimise their effects on porcelain tile production.

## 3. MATERIALS AND METHODS

One clay, two kaolins, one potassium feldspar and one albite were used as raw materials. Each raw material was characterised to determine its physicochemical characteristics, i.e., chemical (by X-ray fluorescence), mineral (by X-ray diffraction) and thermal (by dilatometry) analyses, and, from the results of this characterisation, 19 formulations were obtained according to a mixture design with constrained limits and one overall centroid. The constrains were (mass %):15-25 of clay, 20-25 of kaolin 1, 10-15 of kaolin 2, 5-15 of albite and 30-40 of potassium feldspar. The constrains were established according to the usual percentages of these raw materials in the composition of a Brazilian industrial porcelain tile manufacturer. No quartz was used in the composition.

The chemical analyses were performed on fused beads by X-ray fluorescence using a WDS type wavelength dispersion spectrometer (Philips PW2400).

Phase analyses were performed with dried samples by X-ray diffraction (Philips PW 1830).The phases were identified using the X'Pert HighScore (Philips) application, with $CuK_{\alpha}$ incident radiation (1.5418Å), operating at 30kV and 15mA, with a 2θ interval between 0 ° and 75 °, 0.05 ° step and time of 1s.

The dilatometry was performed using a Netzsch 409 apparatus (10 °C/min, under air).

The compositions were grinded in ball mills with high alumina balls and 52 mass % of water. The grinding time was 45 minutes for all compositions. After grinding, the suspensions were oven dried at 110 °C, disintegrated in mortar and sieved into 40 ABNT mesh (425 µm).

After sieving, the powders were mixed with 7% water (by mass).Compacts with 120 mm × 25 mm and approximately 20 g were made in a hydraulic press with a specific pressure of 50 MPa. In sequence, they were oven dried at 110 °C for 24 hours and then fired in a roller kiln at 1200 °C of maximum temperature in a firing cycle of 43 minutes.

The fired samples were characterised in terms of linear shrinkage, water absorption, mechanical resistance (by the three point-bending method), variation of tonality and, finally, pyroplasticity, with the results undergoing an analysis of variance and response surfaces.

The density of the samples was determined by buoyancy in water. The linear shrinkage was determined using a caliper. The water absorption was determined by boiling in water (2 h).The tonality variation was measured using a spectrophotometer (Byk-Gardner with integration sphere, 400-700 nm range, 2 nm resolution).The bending strength was determined by the three point-bending method. Finally, the pyroplasticity index was determined by the measure of the maximum bending height of a specimen fired at the top of two refractory supports.

## 4. RESULTS AND DISCUSSION

Table 1 shows the chemical analysis and mineralogical composition of the raw materials used in this work. The most refractory raw materials are kaolin 1 and 2, due to the high content of alumina and low content of fluxes ($Na_2O$, $K_2O$, CaO and MgO, in ascending order). Kaolin 1 presents ~17 wt% of alumina and ~0.9 wt% of total flux, while kaolin 2 shows ~21 wt% of alumina and ~1.6 of% fluxes. The mineralogical analysis of these raw materials confirms its characteristics: kaolin 1 is formed only by quartz and kaolinite, refractory raw materials, while kaolin 2 is formed by quartz, kaolinite, mullite and ilite, probably in small quantities.

Regarding the clay, this mineral is rich in alumina (~27 wt%) and is formed by fluxes (~6.1 wt%) and iron oxide (1.4 wt%), which can form low melting point eutectics with the other oxides; this mineral is formed by quartz and kaolinite, as well as feldspathic raw materials such as albite and microcline, and probably lower smectite contents.

As a function of the amounts of silica (~78 wt%) and alumina (~16 wt%) regarding the alkalis (~3.8 wt%), the feldspar would have a mildly fluxing character, but the spodumene phase was identified in its mineralogical composition, with strong fluxing effect; it is formed by albite and microcline, being contaminated by quartz and muscovite.

Finally, the albite presents large amounts of sodium oxide (~9.5 wt%), being contaminated with quartz and calcite. A quantitative analysis of the mineralogical phases present in the raw materials was not performed, as it was not the objective of this work.

| RM (wt%) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | PF | Phases |
|---|---|---|---|---|---|---|---|---|---|
| Kaolin 1 | 74.3 | 17.4 | 0.77 | 0.02 | 0.15 | 0.54 | 0.18 | 6.65 | Q, K |
| Clay | 55.4 | 27 | 1.4 | 2.6 | 1.4 | 1.1 | 1.1 | 10.2 | Q, K, A, Mi, S |
| Kaolin 2 | 68.3 | 21 | 1.2 | 0.01 | 0.31 | 1.3 | 0.1 | 7.7 | Q, K, M, I |
| Feldspar | 78.2 | 16 | 0.94 | 0.3 | 0.03 | 2.0 | 1.5 | 0.4 | Q, A, Mi, M, Sp |
| Albite | 75.2 | 11.8 | 0.62 | 1.3 | 0.38 | 0.53 | 9.5 | 1.1 | Q, A, Ca |

*Where Q is the quartz phase, K is the kaolinite phase, A is albite, Mi is microcline, S is smectite, M is muscovite, I is illite, Sp is spodumene, Ca is calcite.*
***Table 1**.Chemical and mineralogical analysis of the raw materials*

Regarding the dilatometric behaviour of the samples, figure 1 shows the dilatometry of the raw materials used in the study. The albite and feldspar exhibit a uniform expansion up to 524 °C; at 573 °C. An expansion occurs due to the polymorphic transformation of the quartz-alpha to the quartz-beta, followed by a dimensional stability. At 824 °C, both samples distinguish their behaviour, the albite remains stable until 1024 °C and after this its retraction begins, whereas the feldspar undergoes a small retraction, expands again from 1024 °C and its retraction occurs at 1124 °C.

The clay and kaolin 1 showed similar behaviour throughout the analysis, with small peaks of retraction from 924 °C, definitively retracting at 1130 °C, but it is worth mentioning that the retraction of kaolin 1 is greater than that of clay. Kaolin 2 shows a uniform expansion until 924 °C, point at which the beginning of its retraction occurs.

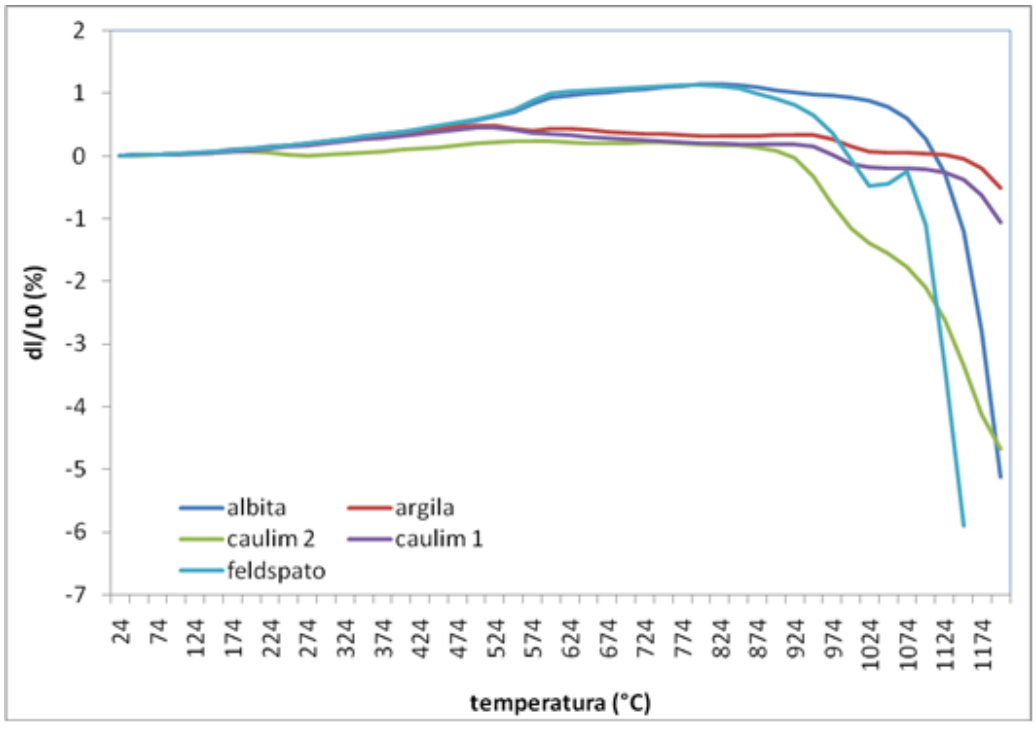


***Figure 1.**Dilatometric curves for the raw materials*

Table 2 shows the results of apparent density, linear shrinkage, modulus of bending strength, water absorption, pyroplasticity index and difference of tonality for the mixture design used in this study.

| | Kaolin 1 | Clay | Kaolin 2 | Feldspar | Albite | D (%) | LS (%) | WA (%) | BS (MPa) | DE | PI ($\times 10^{-5}$ $cm^{-4}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| M1 | 20 | 25 | 10 | 30 | 15 | 2.33 | 9.18 | 1.4 | 49 | 0 | 3.5 |
| M2 | 25 | 25 | 10 | 30 | 10 | 2.04 | 8.36 | 2.36 | 44 | 3.29 | 3.55 |
| M3 | 25 | 15 | 15 | 30 | 15 | 2.49 | 8.28 | 5.65 | 43 | 5.6 | 3.93 |
| M4 | 20 | 25 | 15 | 30 | 10 | 2.3 | 8.49 | 2.36 | 48 | 3.11 | 3.53 |
| M5 | 25 | 25 | 15 | 30 | 5 | 2.28 | 8.43 | 2.59 | 43 | 4.38 | 4.56 |
| M6 | 20 | 15 | 10 | 40 | 15 | 2.29 | 9.43 | 2.07 | 51 | 2.41 | 4.43 |
| M7 | 25 | 15 | 10 | 40 | 10 | 2.3 | 9.13 | 1.07 | 51 | 1.73 | 4.95 |
| M8 | 20 | 25 | 10 | 40 | 5 | 2.31 | 8.47 | 0.9 | 43 | 0.99 | 4.93 |
| M9 | 20 | 15 | 15 | 40 | 10 | 2.28 | 9 | 2.99 | 51 | 3.98 | 4.7 |
| M10 | 25 | 15 | 15 | 40 | 5 | 2.25 | 8.69 | 4.58 | 43 | 5.81 | 4.49 |
| M11 | 25 | 25 | 10 | 35 | 5 | 2.3 | 9.07 | 2.38 | 50 | 2.93 | 4.09 |
| M12 | 25 | 20 | 10 | 40 | 5 | 2.28 | 8.64 | 4.23 | 50 | 2.69 | 4.16 |
| M13 | 20 | 25 | 15 | 35 | 5 | 2.29 | 8.52 | 2.84 | 51 | 2.47 | 4.77 |
| M14 | 20 | 20 | 15 | 40 | 5 | 2.3 | 8.76 | 1.88 | 57 | 3.24 | 4.72 |
| M15 | 25 | 20 | 10 | 30 | 15 | 2.23 | 8.46 | 3.18 | 44 | 4.65 | 4.06 |
| M16 | 25 | 15 | 10 | 35 | 15 | 2.24 | 8.96 | 2.97 | 48 | 4.04 | 5.08 |
| M17 | 20 | 20 | 15 | 30 | 15 | 2.3 | 8.92 | 2.87 | 51 | 3.76 | 4.0 |
| M18 | 20 | 15 | 15 | 35 | 15 | 2.26 | 8.83 | 3.18 | 46 | 5.23 | 4.22 |
| M19 | 22.5 | 20 | 12.5 | 35 | 10 | 2.28 | 9.49 | 2.66 | 45 | 3.67 | 4.66 |

***Table 2.****Mixture design with constraints and results for apparent density, linear shrinkage, bending strength, water absorption, pyroplasticity and tonality variation*

The analysis of variance (ANOVA) for the apparent density after firing showed that there is no statistical significance for the results, since the p-test showed a very low value for the statistical reliability, only 29%.Therefore, this property will not be analysed.

The analysis of variance for the linear shrinkage shows a reasonable reliability of the results: the p-value, which shows the reliability of the system, is 0.12 for the linear function, pointing out a reliability of the results of 88%, statistically acceptable for the analysis of the effect of the raw materials on the linear shrinkage of the specimens. From the data of the ANOVA (analysis of variance), the results for the linear shrinkage were represented graphically as level curves, figure 2.

The graphs show that the minerals that most influence the linear shrinkage during firing (sintering) are albite and feldspar, with a tendency to shrinkage greater than 9%.It should be noted that the fitting of the results to the linear model, given by the $R^2$ factor, is not good ($R^2$ = 0.39).The lowest shrinkage was caused by both kaolins alone. Analysing the chemical and phase (mineralogical) composition of the raw materials, the albite and the feldspar present the highest concentrations of fluxing oxides. These results show the strong densification action of the melting oxides $Na_2O$, $K_2O$, CaO and MgO on the studied system.

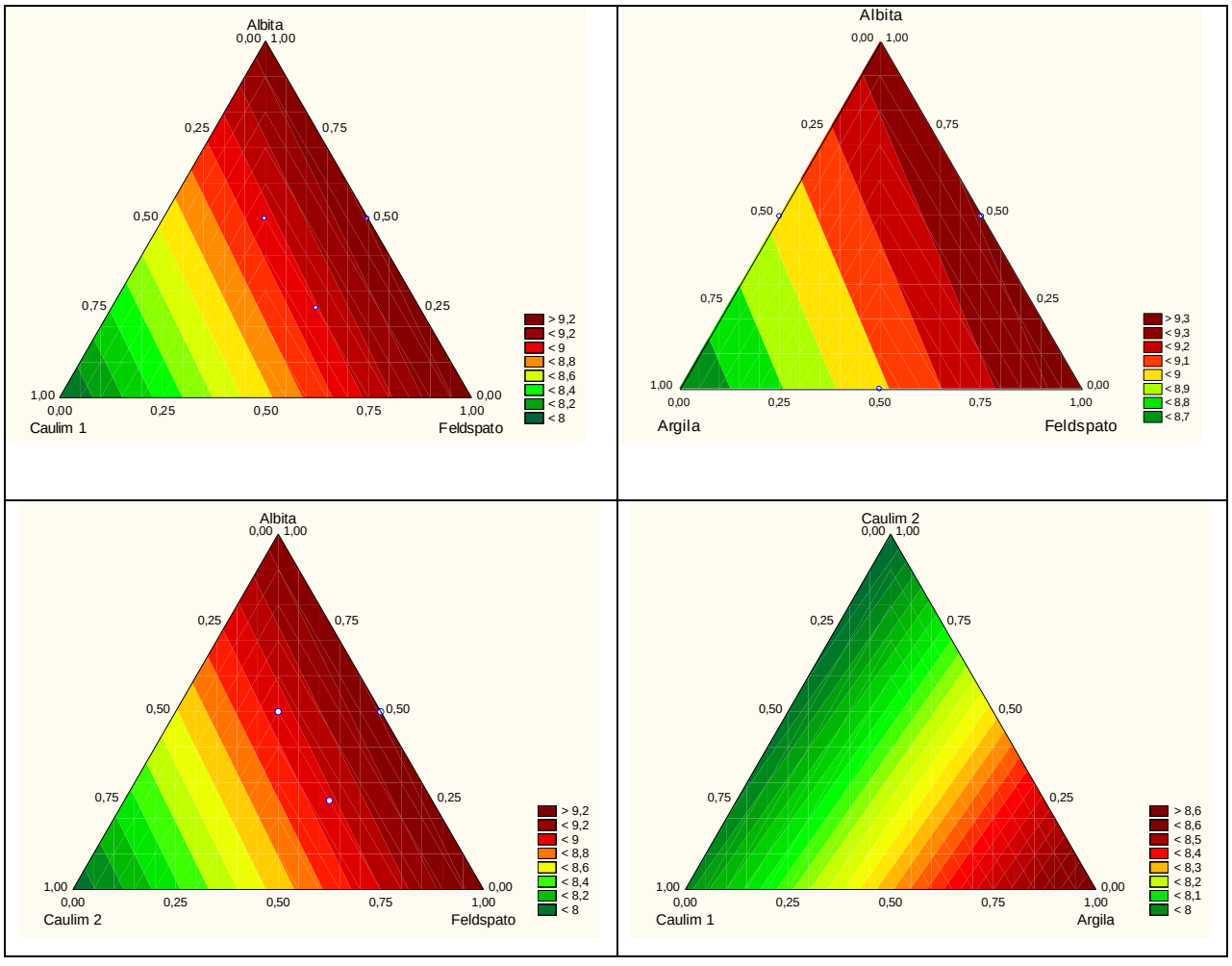


***Figure 2.****Response surfaces for the linear shrinkage after firing*

The analysis of variance for the water absorption shows that the most significant model is the linear one. The p-value is 0.01, indicating a reliability of 99% for the results. From the data of the ANOVA (analysis of variance), the results for water absorption are represented graphically as response surfaces, figure 3.The adjustment of the observed values to the linear model is $R^2 = 0.59$, being only reasonable.

Clay, feldspar and albite are the minerals that most contribute to the decrease of water absorption. Due to the presence of feldspathic phases, such as albite and microcline, as well as spodumene, this causes a higher densification through sintering with viscous liquid phase and consequent decrease of water absorption by reduction of open and communicating porosity.

The kaolins, as more refractory materials, had little effect on the reduction of the water absorption of the studied system.

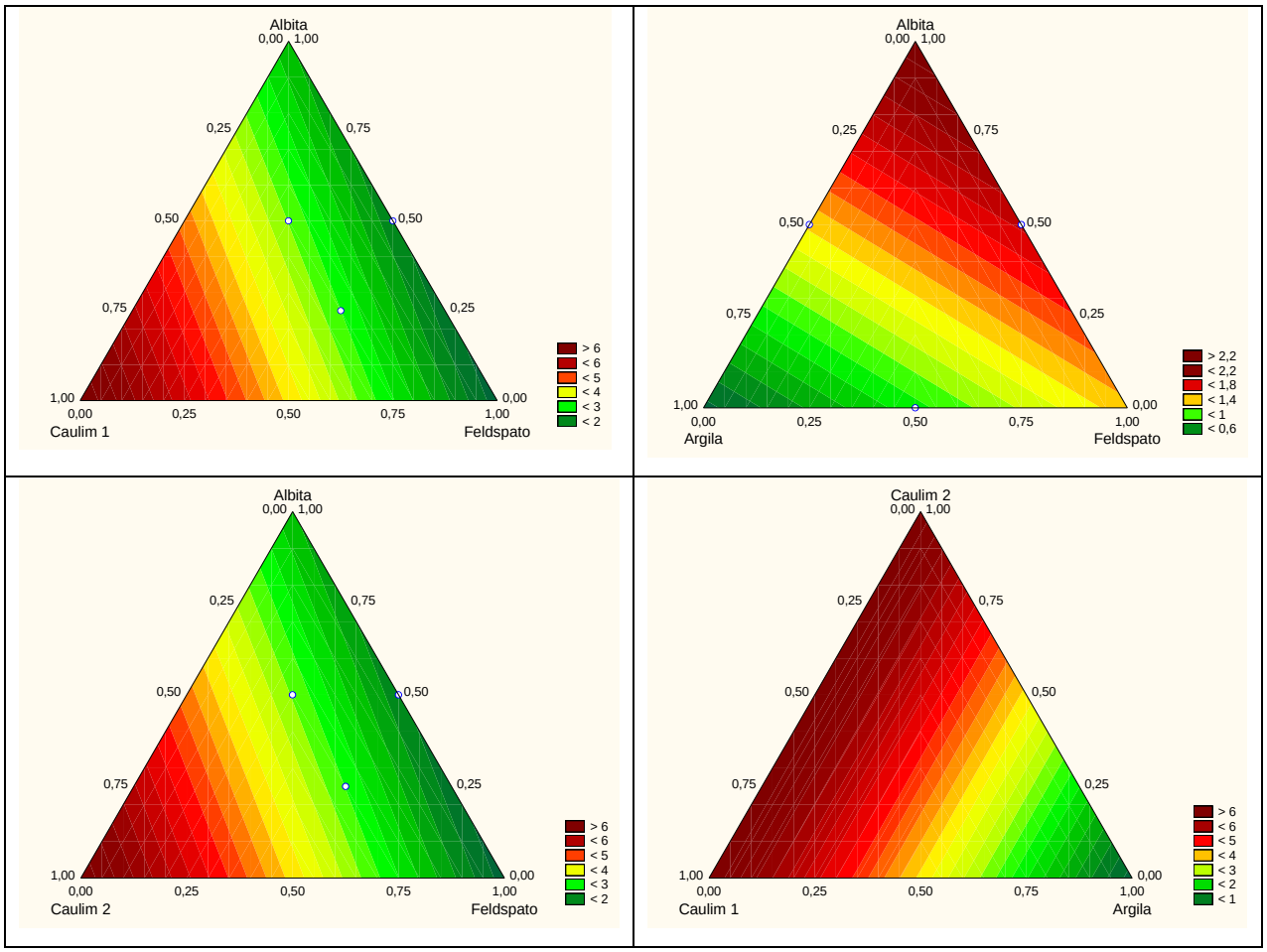


***Figure 3.****Response surfaces for the water absorption after firing*

Five specimens of each of the 19 compositions were tested for the mechanical strength determination. The mechanical strength was determined by measuring the breaking load of the specimens using the bending strength test at three points. By the analysis of the bending strength, the most significant is the linear model, with a p-

value corresponding to 0.22 (reliability of 78%).Thus, the most significant model is the linear model for the bending strength test. The fitting of the observed values to the linear model is small ($R^2$ = 0.32).

The highest values for the modulus of bending strength are obtained with the use of feldspar (> 540 kgf/cm² or ~54 MPa), and to a lesser extent with albite and clay (~500 kgf/cm² or 50 MPa). There is almost 50% more mechanical resistance due to the isolated action of feldspar in relation to kaolin, an effect that has been repeatedly observed in this study.

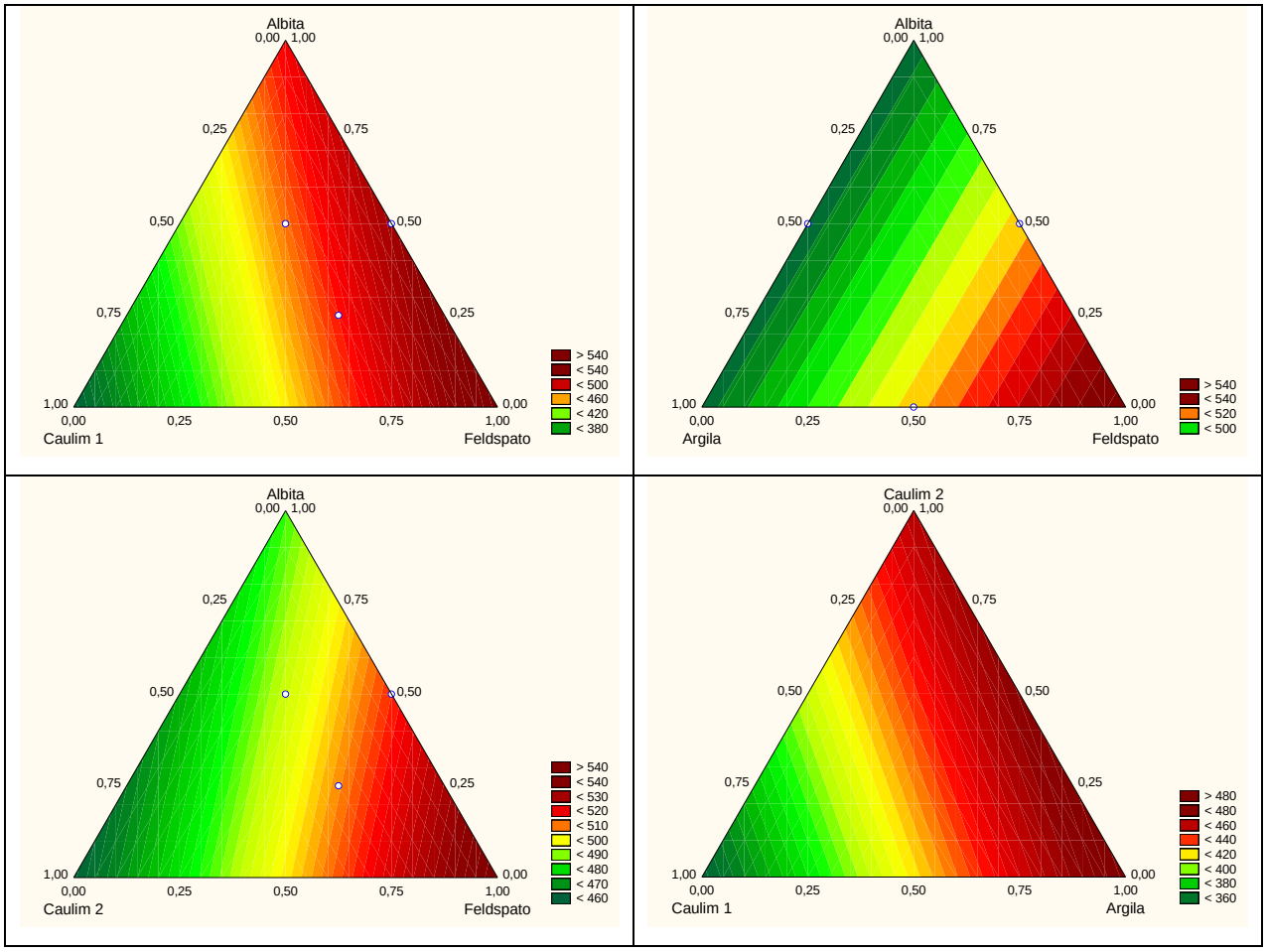


***Figure 4.*** *Response surfaces for the bending strength after firing*

For the tonality variation, five specimens of each of the 19 compositions were tested. In this test the tonality variation was determined between each sample and a standard, the composition M1, that is, where M1 = 80.4 Judds in the CIELAB scale. According to the analysis of variance, the p-value corresponds to 0.0001, indicating in this way a reliability of 99.99% for the results. Thus, the most significant model is the linear one for the tonality variation test, with the highest reliability among the obtained results. The adjustment of the observed values to the linear model is $R^2$ = 0.80, a suitable adjustment to the model. For glossy surfaces, such as ceramic glazes, a value of DE less than 0.5 should be used; for opaque surfaces, as in this study, of

unpolished porcelain, the value to be considered is DE <1 Judd. These are DE values when one does not want to observe a variation of the sample tonality.

Clay is the only raw material that contributes to a value of DE <1.By the response surface curves, figure 5, the action of this mineral is clear in the reduction of the tonality variation, an interesting effect, despite the great content of iron and titanium oxides of this raw material, oxides with strong dyeing action. Both kaolins, in turn, are the raw materials that most affect the tonality variation of the studied system (DE >8), so its use must be careful to avoid great variation in the colour of the product.

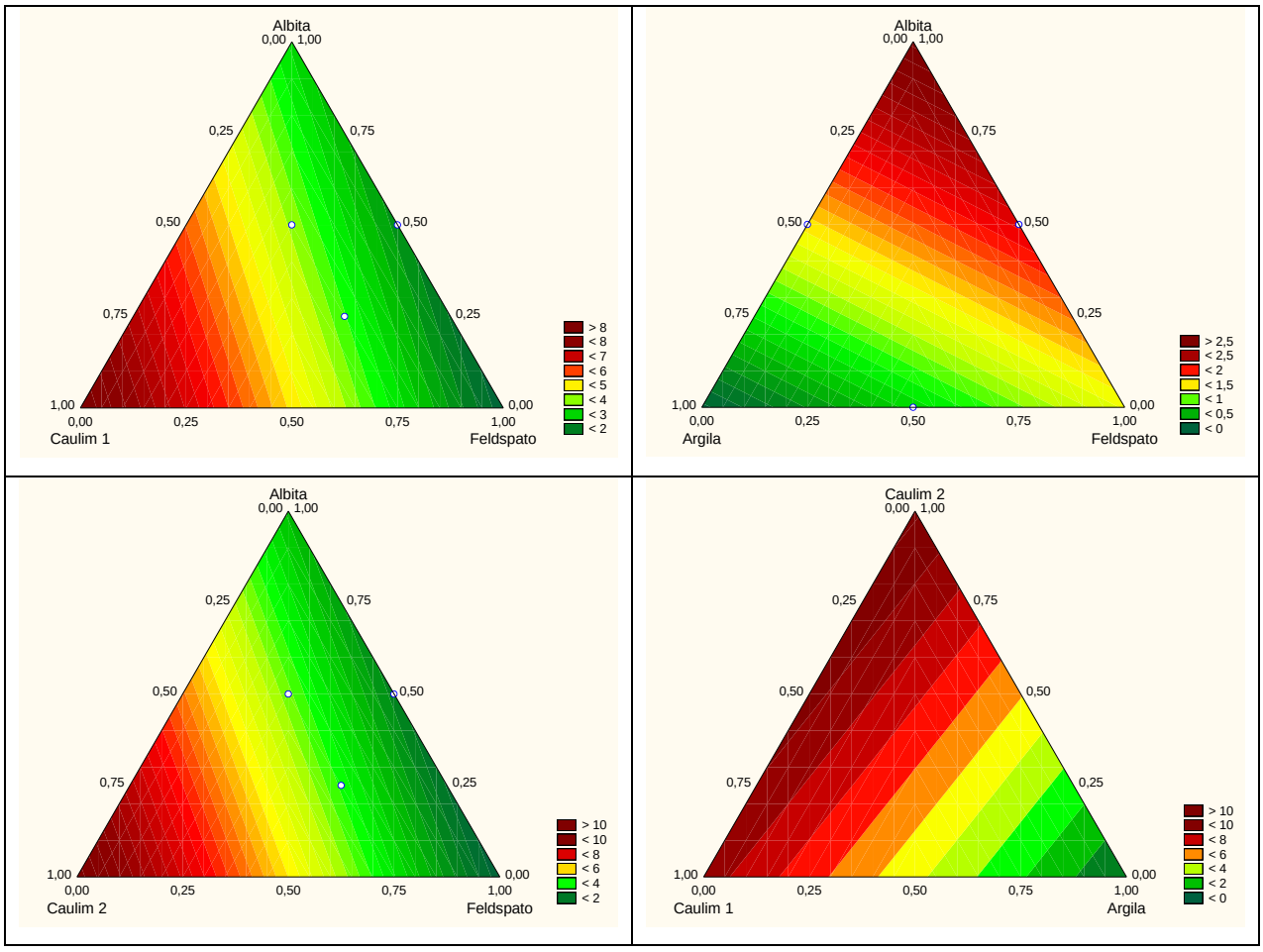


***Figure 5.****Response surfaces for the tonality variation after firing*

Finally, for the pyroplasticity index, five specimens from each of the 19 compositions were tested. The most significant model for the pyroplasticity index is the linear model, with a p-value corresponding to 0.04 (96% reliability).The adjustment of the model to the observed values is also not very large, $R^2$ = 0.48.The response surfaces are shown in figure 6.

The feldspar is the raw material that has the greatest influence on the pyroplasticity index, PI >5.2 $\times 10^{-5}$ $cm^{-4}$.In turn, the clay is the mineral with less tendency to pyroplasticity, followed by the albite (IP <3.8 $\times 10^{-5}$ $cm^{-4}$). Both kaolins had intermediate behaviour.

The response surface curves show that the effect of feldspar as a piroplastic element is clear, due to the presence of lithium oxide-containing minerals, which has been shown to be the main cause of pyroplasticity, a fact evidenced by this study. Apparently, the higher pyroplasticity associated with the presence of lithium oxide in the ceramic compositions is related to the decrease in the viscosity of the liquid phase formed, which would increase the pyroplastic deformation of the materials.

Thus, this study showed the existence of two parallel effects: an excellent densification of the system, caused mainly by the action of lithium oxide, due to the effect of the feldspar in the bending strength modulus; the other effect is that of pyroplasticity, also due to the action of lithium oxide present in feldspar, an expected and proven effect in industrial practice.

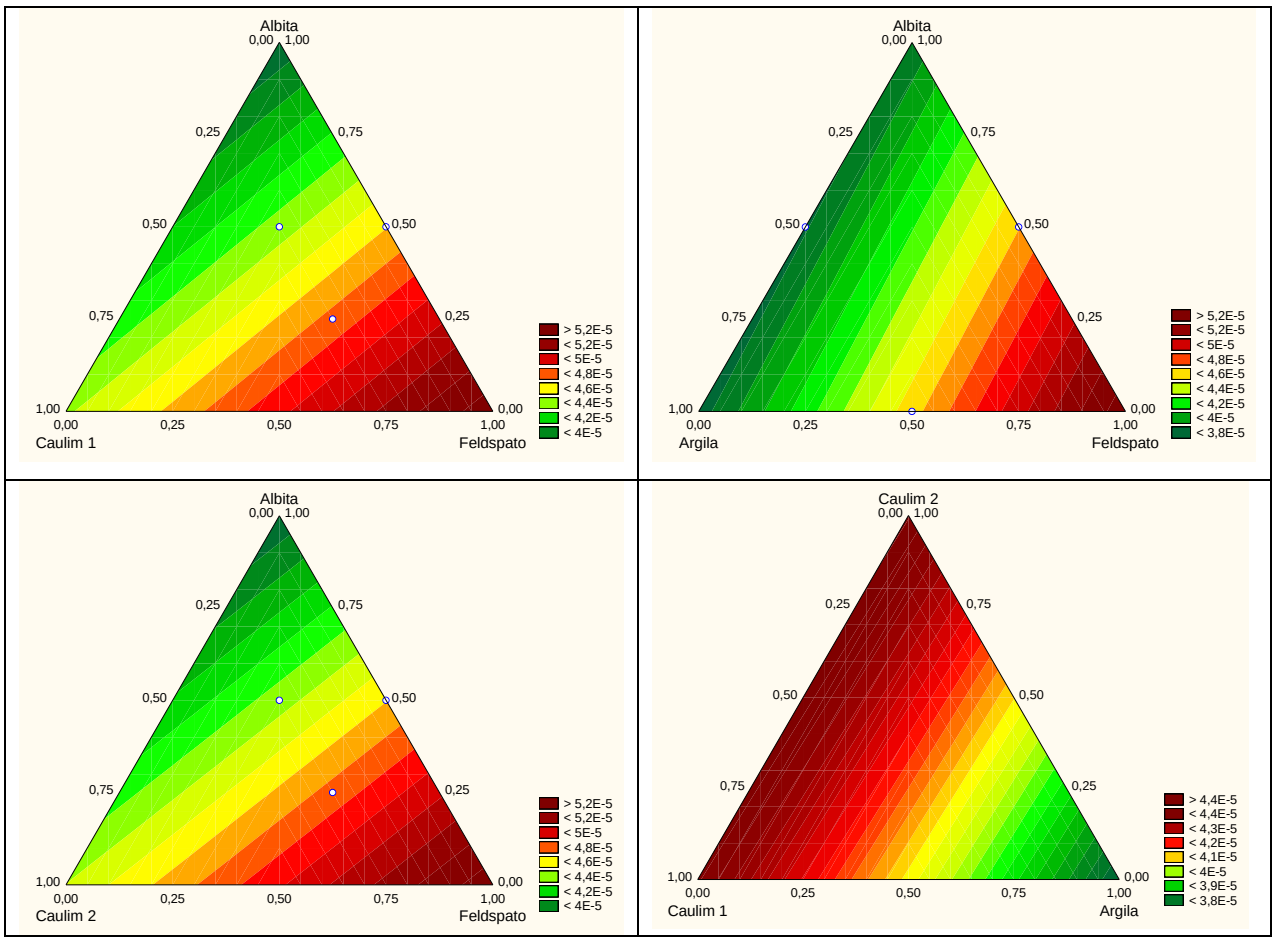


***Figure 6.****Response surfaces for the pyroplastic index*

## 5. CONCLUSIONS

The design of experiments (DoE) using the mixture design technique is a powerful tool for the design and analysis of ceramic compositions in the search for an improved performance for porcelain tile manufacturing. The analysis of variance shows the real effect, based on experimental results, of each raw material on the properties of the final composition. The response surfaces show graphically those effects, being an important tool for the analysis of the results.

Regarding this work, the results showed that the feldspar is the raw material that had the greatest influence on the pyroplasticity index among the minerals due to the presence of lithium oxide in its composition. Both kaolins have shown the smallest effect while the clay alone and the clay combined with feldspar have shown the highest effect.

The highest bending strength was obtained with the use of feldspar and to a lesser extent with albite and clay. There is almost 50% more bending strength using the feldspar in the composition in comparison to the effect of both kaolin.

Besides pyroplasticity and bending strength, other properties like shrinkage, water absorption and tonality variation can be easily linked with the individual effect of each raw material using the design of experiments tools.

## 6. REFERENCES

[1] dos Santos Conserva, L.R., Melchiades, F.G., Nastri, S., Boschi, A.O., Dondi, M., Guarini, G., Raimondo, M., Zanelli, C. Pyroplastic deformation of porcelain stoneware tiles: Wet vs. dry processing (2017) Journal of the European Ceramic Society, 37 (1), pp. 333-342.DOI:10.1016/j.jeurceramsoc.2016.08.015

[2] Pavlovic, A., Fragassa, C. Modelling the viscoelasticity of ceramic tiles by finite element (2016) AIP Conference Proceedings, 1736, art. no. 4949749.DOI:10.1063/1.4949749

[3] Almeida, B.A.D., Almeida, M., Martins, S., Maçarico, V.A., Fonseca, A.T.D. Recycling liquid effluents in a ceramic industry (2016) Boletin de la Sociedad Espanola de Ceramica y Vidrio, 55 (3), pp. 95-104.DOI:10.1016/j.bsecv.2016.04.004

[4] Jeong, S.-I., Kim, N.-I., Lee, S.-J. Synthesis and Sintering Behavior of Cordierite Prepared from Multi-Component Materials Including Alkaline-Earth Minerals (2016) Journal of Korean Institute of Metals and Materials, 54 (10), pp. 752-758.DOI:10.3365/KJMM.2016.54.10.752

[5] Groger, P., Krause, A. ALMAG A1 and TOPMAG A1:Trouble shooters for mechanically-loaded rotary kiln zones seen in historical context (2013) Cement International, 11 (4), pp. 66-75.

[6] Bresciani, A., Spinelli, B. Porcelain tile pyroplastic deformation during firing and post-firing variations of planarity (2012) CFI Ceramic Forum International, 89 (6-7), pp. E41-E45.

[7] Sighinolfi, D. Misura® equipment, solving ceramic problems (2010) Industrial Ceramics, 30 (2), pp. 139-146.

[8] Agrawal, P., Payra, I., Misra, S.N. Pyroplastic behaviour of two plastic kaolins in a triaxial porcelain body (2008) InterCeram: International Ceramic Review, 57 (4), pp. 250-256.

[9] Neckel Jr., L., Prette, A.L.G., Alarcon, O.E., Fredel, M.C. Developing of ceramic roof tiles process by powder Pressing and firing in roller kiln (2008) Materials Science Forum, 591-593, pp. 521-525.

[10] Bernardin, A.M., de Medeiros, D.S., Riella, H.G. Pyroplasticity in porcelain tiles (2006) Materials Science and Engineering A, 427 (1-2), pp. 316-319.DOI:10.1016/j.msea.2006.04.073

[11] Robijn, P. Process of Attack of Highly Aluminous and Clay Bricks in the Regenerator Chambers of Glass Furnaces.[Zerstoerungsvorgaenge in hochtonerdehaltigen steinen und schamottesteinen in regenerativkommern von glasoefen.] (1973) Glastech Ber, 46 (7), pp. 148-152.