EFFECTS OF RAW MATERIALS TYPE AND CONTENT ON TECHNOLOGICAL PROPERTIES OF DRIED CERAMIC BODIES: RESULTS OF A STATISTICAL DESIGN OF MIXTURE EXPERIMENTS

S.L. Correia [(1), (2)], D. Hotzab, A. M. Segadães [(3)]

[(1)] State University of Santa Catarina, UDESC/CCT, Joinville-SC, Brazil
[(2)] Federal University of Santa Catarina, EQA/EMC, Florianópolis-SC, Brazil
[(3)] University of Aveiro, Dept. Ceramics & Glass Engineering/CICECO, Aveiro, Portugal (segadaes@cv.ua.pt)

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. In the particular case of industrial ceramics, if the processing conditions are kept constant, a number of properties of dried and fired bodies are basically determined by the combination (or mixture) of raw materials. This is the basic assumption in the design of mixture experiments to obtain a response surface using mathematical and statistical techniques [1] and this methodology has already been applied to ceramic products [2], [3], [4].

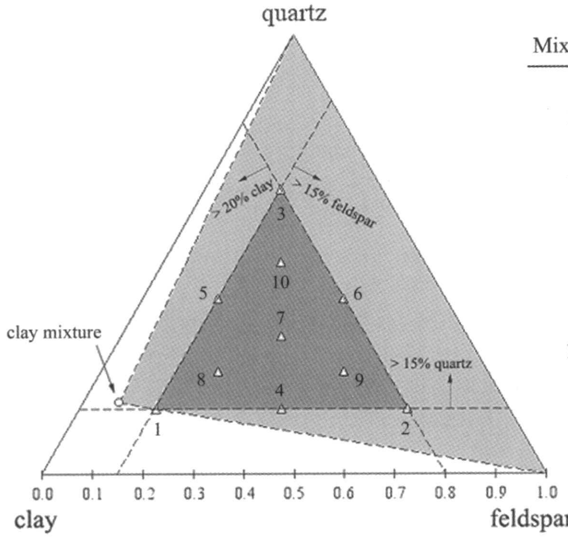
In the case of ceramic floor and wall tiles, dry mechanical strength and bulk density are often used as quality and process control parameters. Both are simple to evaluate in the laboratory (resistance to rupture in bending and immersion in mercury) and, under constant processing, basically depend on the raw materials contents. Therefore, the optimisation methodology specific to the design of mixture experiments can be used to obtain an equation (model) that relates each property with raw materials contents in the starting mixture.

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. There are three major components or ingredients to be considered in ceramic mixtures, given the distinctive roles they play during ceramic processing [4]: a plastic component (clays), a fluxing component (feldspar) and an inert component (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 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.

The response function can be expressed in its canonical form [1] as a low degree polynomial (typically, second degree). This 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. When some or all the component fractions are not allowed to vary from 0 to 1.0, the calculations must be carried out within a restricted composition triangle (i.e. a sub-region of the original triangle), using the concept of pseudo-components [1], [3], [3], [4]. Then, the values of the property are experimentally determined on those selected N lattice points and a regression equation is fitted to the experimental values. 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 and a common variance.

2. RESULTS

In the present study, the raw materials used were a mixture of clays, potash feldspar (99.5 wt% microcline) and quartz sand (99.5 wt% α-quartz), all supplied by Colorminas, Brazil. The potash feldspar and quartz sand were assumed to be pure, whereas the clay mixture was divided into its clay, feldspar and quartz fractions. The lower bound limits of 20% clay, 15% feldspar and 15% quartz were used to define a restricted composition triangle of pseudo-components on which a {3,2} centroid simplex-lattice, augmented with interior points, was set to define the ten mixtures of those raw materials that should be investigated. Those mixtures were wet processed under constant conditions, as in conventional wall and floor tile industrial practice (wet grinding, drying, granulation and uniaxial pressing) and characterized. Regression models were then calculated (STATISTICA—StatSoft Inc., 2000), relating dry bending modulus of rupture (DMoR) and bulk density (DBD) with the mixture composition. Figure 1 shows the location, in the ternary system clay-quartz-feldspar, of the raw materials, the designed ten mixtures (in the pseudo-components triangle) and the corresponding measured values of DMoR and DBD.



Mixture	DMoR (MPa)	DBD (g.cm-3)
1	1.97±0.30	1.83±0.02
2	1.08±0.11	1.71±0.01
3	1.14±0.15	1.75±0.01
4	2.79±0.44	1.90±0.02
5	2.92±0.52	1.94±0.03
6	1.28±0.22	1.77±0.02
7	2.54±0.23	1.86±0.01
8	3.04±0.38	1.91±0.02
9	1.43±0.33	1.83±0.02
10	2.10±0.18	1.82±0.02

Figure 1. The ternary system clay-quartz-feldspar, showing: the raw materials triangle, the restricted pseudo-components triangle and the simplex points, and the measured values of DMoR and DBD.

Using the measured values for the properties, only the second-degree model, in both cases, was found to be statistically significant at a 2% level and present small variability. The resulting surface equations can be rearranged in order to relate the property with the weight fractions of the original raw materials (X_1 = clay mixture, X_2 = feldspar and X_3 = quartz). Equations (1) and (2) are the final result:

$$DMoR = -2.86X_1-1.99X_2-1.88X_3+24.53X_1X_2+28.36X_1X_3-5.15X_2X_3-1.78X_2^2-4.61X_3^2 \quad (1)$$

$$DBD=1.87X_1+1.22X_2+1.08X_3+2.42X_1X_2+2.73X_1X_3-0.22X_2X_3-0.18X_2^2-0.44X_3^2 \quad (2)$$

The analysis of the properties raw residuals (*i.e.* difference between the experimentally determined value and the calculated estimate) shows that the errors are uncorrelated and their distributions are normal, meaning that the models obtained are valid: a good estimate of the DMoR and DBD can be obtained, using Eqs. (1) and (2) and the fractions of the raw materials. The two properties are related and behave similarly as the mixture composition changes, as is well known in the industrial practice that both properties are similarly affected by the same processing parameters. This 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: for the particular raw materials used, the clay content has a critical effect, whereas the quartz sand content can be changed with a rather mild effect. Still, even within the optimum DMoR and DBD region, the values do not reach the level usually recommended by the floor and wall tile industries. These results throw a strong light onto the role of the hidden variables (*i.e.* those that were kept constant throughout the work), namely, particle packing and size distribution on one hand, and processing conditions on the other.

3. ACKNOWLEDGEMENTS

Authors appreciate the financial support received from the Brazilian Research Agency CAPES (S.L. Correia, Ph.D. grant) and are thankful to Colorminas for providing the raw materials used.

REFERENCES

[1] Cornell, J.A., Experiments with mixtures: designs, models and the analysis of mixture data, John Wiley & Sons, 3rd edition, New York, 2002.

[2] Piepel, G. and Redgate, T., Mixture experiment techniques for reducing the number of components applied for modelling waste glass sodium release. J. Am. Ceram. Soc., 80 (1997) 3038-3044.

[3] Schabbach, L.M., Oliveira, A.P.N., Fredel, M.C. and Hotza, D., Seven-component lead-free frit formulation. Am. Ceram. Soc. Bull., 82 (2003) 47-50.

[4] S.L Correia, K.A.S. Curto, D. Hotza and A.M. Segadães, Using statistical techniques to model the flexural strength of dried triaxial ceramic bodies. J. Eur. Ceram. Soc. (in press), 2003.