IMPROVING GLAZE WHITENESS BY STATISTICAL EXPERIMENTAL DESIGN

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ABSTRACT

The high quality demanded of ceramic tile glaze surfaces has, in recent years, entailed obtaining frits (the major component in ceramic glaze formulations for single-fired wall tiles), with improved technical and aesthetic characteristics.

In this study, statistical experimental design was used to improve the whiteness of a frit utilized in obtaining glossy, opaque, white glazes in single-fired wall tiles. Five components of the formulation (Al_2O_3, K_2O, MgO, ZnO and CaO) were selected for this purpose, considering two levels of variation in each oxide (% in wt), which yielded 16 experiments, thus involving a significant drop in the number of tests compared to other empirical procedures.

As a result of the statistical analysis of the experimental findings, a modification is proposed in the opaque glaze formulation whose whiteness and yellowness indices have been significantly improved (respectively increasing and decreasing), while holding the remaining physical properties (gloss, sealing temperature and coefficient of expansion) within preset limits. The methodology adopted also allows the influence to be predicted of the different oxides, whether individually or as the result of interactions, on the properties studied for the kind of frit used.

The predicted results with the modified formulation were subsequently substantiated on an industrial scale.

1. INTRODUCTION

In recent years, one of the strivings in ceramic tile manufacture has been the obtainment of glazed surfaces with better technical and aesthetic characteristics, yielding an optimum quality product.

In single-fired porous wall tile manufacture, this objective can be obtained by changing the frit composition, major raw material in glaze formulation [1]. However, optimizing a formula is often complicated as many components that improve some product characteristics (whiteness, gloss, texture, etc.) harm others (sealing temperature, coefficient of expansion).

Traditionally, modifications in frit formulation have been effected by trial and error, which owing to the complexity of these kinds of compositions entailed performing a great number of experiments that yielded little information.

The experimental design methodology [2-3] is being widely used in ceramic wall and floor tile manufacturing processes (study of firing curves, pressing operation, fabrication defects, etc.), as a result of the many variables concurrently influencing each process stage. Its application to ceramic frit formulation could therefore offer a series of advantages compared to the traditional approach:

- Fewer experiments are required to obtain more information.

- The effect that varying certain compositional components has on frit properties, can be quantified to obtain the componential values that optimize each property.

- Interactions between components can be detected. The inferences drawn are more widely valid.

- Correcting compositions becomes easier, as does their adaptation to each customer's requirements, by means of prediction analysis.

2. OBJECTIVES

To carry out the study, a frit yielding a glossy, opaque, white glaze on single-fired porous ceramic tile was used. The oxide composition of this frit was modified by statistical experimental design in order to:

- Determine the influence that varying some oxide percentages in the frit (in the composition interval studied), has on certain glaze properties (whiteness, yellowness, sealing temperature and coefficient of expansion).

- Establish some valid formulation criteria for frit compositions resembling the studied one from the information obtained.

- Improve the whiteness of the glaze prepared from the starting frit, holding the remaining studied properties within the preset limits for this kind of glaze.

3. EXPERIMENTAL DEVELOPMENT

3.1. DESCRIPTION OF EXPERIMENTAL DESIGN

The starting frit comprised eight oxides, of which the following were taken as factors to be included in the design: K_2O, ZnO, Al_2O_3, CaO and MgO. The other oxides, which remained unmodified in the frit formulation were: SiO_2, B_2O_3 and ZrO_2, the last one acting as opacifier. The levels, (or percentages in weight) to be studied for each factor are listed in Table 1.

Table 1. *Levels chosen for each factor (oxide) considered in the experimental design.*

Factors	Level 1 (% wt)	Level 2 (% wt)
K_2O	3.2	2.2
ZnO	8.8	7.3
Al_2O_3	4.3	5.3
CaO	9.7	10.7
MgO	3.5	4.5

The criterion involved in choosing the factors (oxides) in the design, and their variation interval, was based on foregoing experiments and knowledge of this frit composition's behaviour in fusing, as well as of glaze fabrication.

The properties of the glaze and/or frit in which the effect of modifying the oxide percentages was determined, were:

✓ Properties of the glaze obtained from the frit:
- Whiteness
- Yellowness
- Gloss

✓ Frit properties:
- Surface impermeabilization temperature (sealing temperature)
- Coefficient of expansion

In this kind of system, in which two levels of variation and five factors are considered, the factorial experiment design to be applied is the 2^K kind, where K is the number of factors to be analyzed and 2 the number of levels per factor. The experiments required in applying this design would be 2^5=32. In order to reduce the number of experiments, a partial experimental design was used of the kind 2^{K-1} [2-4]. In this case the number of experiments needed was brought back to 16, relinquishing part of the information, as no interactions could be detected between factors of an order higher than two (three or more oxides). In principle, this is no serious drawback, as interactions are involved which are statistically of less influence, although this should be confirmed for each kind of composition studied, after interpreting the findings.

Applying a partial experimental design to the starting frit composition yields the level (percentage) of the different oxides under study, in each of the 16 experiments (Table 2). The formulae in oxides of 16 frit compositions, one for each experiment, were obtained from these values and the percentages of the oxides not included in the design.

Table 2. Level (percentage) of the different oxides in each of the 16 experiments to be conducted.

Experiments	K_2O	ZnO	Al_2O_3	CaO	MgO
1	2	2	1	1	2
2	2	2	1	2	1
3	1	2	1	2	2
4	1	1	1	2	1
5	2	1	1	1	1
6	1	2	2	1	2
7	1	2	1	1	1
8	1	1	2	2	2
9	1	1	2	1	1
10	1	2	2	2	1
11	2	1	2	2	1
12	2	2	2	1	1
13	2	2	2	2	2
14	2	1	1	2	2
15	2	1	2	1	2
16	1	1	1	1	2

3.2. MATERIALS

The raw materials used in obtaining the frits were: quartz, alumina, calcium carbonate, potassium nitrate, dolomite, colemanite, zinc oxide and zirconium silicate, all commonly used in ceramic frit fabrication.

The batch formula of the targeted frit was calculated from the oxide formula and raw materials composition.

Kaolin was used as a suspending agent, with sodium carboxymethylcellulose as a binder in preparing the glaze compositions from which the ceramic end glazes were obtained.

3.3. EXPERIMENTAL TECHNIQUE

3.3.1. Fritting operation

When fusion took place at the laboratory, the raw materials underwent dry mixing in a fast ball mill; this mix was subsequently fused in a rotary batch kiln, using natural gas as fuel. The raw materials were put in the kiln when the temperature lay at round 1480°C, for a 15 min dwell.

The industrially obtained frits were prepared in a continuous tank furnace operating at a temperature approaching 1480°C, using natural gas as fuel.

In both kinds of fusion, the melt was water-quenched, to obtain the frits.

3.3.2. Preparation of the glaze samples

A mix was prepared with each of the frits obtained, having the following composition: 100 g frit, 5 g kaolin and 0.3 g carboxymethylcellulose. The mix was wet milled in a laboratory ball mill until a reject of 1%, in wt, was obtained on a screen with a 40 μm mesh aperture.

The suspensions resulting from the milling (having the same density: 1.65 g/cm^3) were applied on fired bodies, obtained using a composition like the ones used in manufacturing single-fired wall tile made of white clay. Glazing took place with an adjustable speed automatic applier, obtaining a glaze layer thickness of round 400 μm.

The glazed pieces were fired in an electric laboratory kiln at a maximum temperature of 1180°C, according to the heating cycle shown in Figure 1. Three test pieces were fired for each frit tested in order to average the findings.

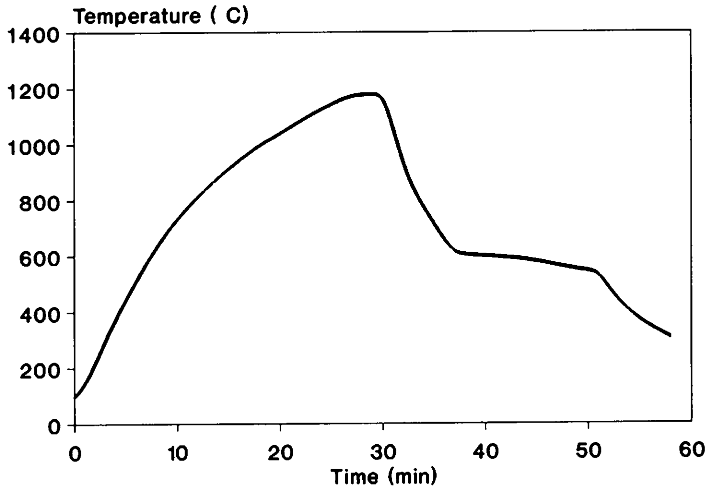

Figure 1. Heating cycle used to fire the glaze samples.

3.3.3. Whiteness and yellowness measurements

A MACBETH COLOR-EYE 7000 spectrophotometer was used to measure the whiteness and yellowness of the glaze surfaces obtained, according to the CIELab system, using a C type light source. Whiteness was assessed by using the HUNTER-60 index, and yellowness with the ASTM D1925 index [5].

3.3.4. Gloss measurement

A DR. LANGE LMG-062 reflectometer was employed, determining the specular gloss value (‰)[5] with an incident light angle of 60°, utilizing a polished black glass plate as a standard, whose specular gloss measured at a 60° angle of incidence is 93.

3.3.5. Determination of sealing temperature

The test pieces coated with each of the prepared glaze compositions (Section 3.3.2) were fired in an electric laboratory kiln at varying maximum temperatures, following a heating cycle like the one depicted in Figure 1, until the temperature was found at which impermeabilization of the glaze surface took place. The firings were carried out at 10°C intervals. To establish whether impermeabilization had been effected, a drop of water was allowed to fall upon the cold piece, which was then examined to verify whether suction occurred. Sealing temperature was taken to be the maximum temperature of the interval in which the glaze lost its suction capability.

3.3.6. Estimating the coefficient of expansion

Each frit's coefficient of linear expansion was estimated from its chemical composition, using the TURNER equation [6] for the 20 to 400°C temperature interval. The calculation was effected by assuming that all the zirconium oxide in the frit crystallizes as zirconium silicate [7].

4. RESULTS AND DISCUSSION

The results obtained after determining the different properties were analyzed according to the "Variance analysis or ANOVA" technique [2]. Processing took place by means of the statistical software package STATGRAPHICS.

4.1. INFLUENCE OF THE DIFFERENT OXIDES ON THE STUDIED PROPERTIES

4.1.1. Whiteness index of the glaze surface

The main effects and first-order interaction effects of greatest influence on the whiteness index of the glaze surface, have been represented in Figure 2 from the data obtained by statistical analysis, in the form of a histogram, quantitatively classifying them in the decreasing order of their absolute values. To see whether an effect was significative, its significance level was determined by a statistical test (F test), performing the computations at a confidence level of 95%. The simple effects, or interactions whose significance level exceeded 0.05 (shown in Figure 2 below the dividing line in the diagram), could not be considered significative, that is, the variation in the oxide percentage cannot be claimed to appreciably affect the measured property.

The main effect of a factor (oxide) is the increment in the value of the property considered (in this case the whiteness index) on taking the oxide percentage from level 1 to level 2. As an example, Figure 3 shows the influence of Al_2O_3 on the whiteness index.

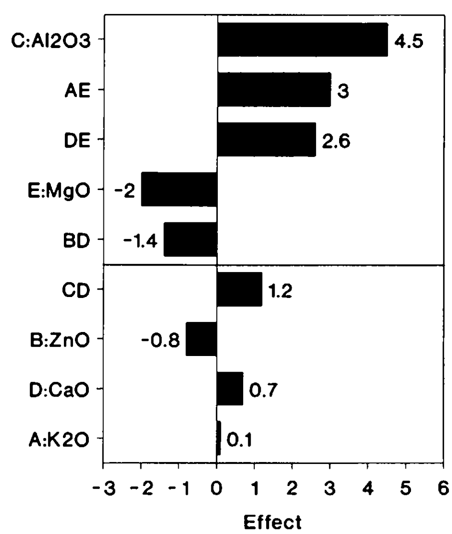

Figure 2. *Main effects and most important first-order interaction effects, corresponding to the whiteness index of the glaze surface.*

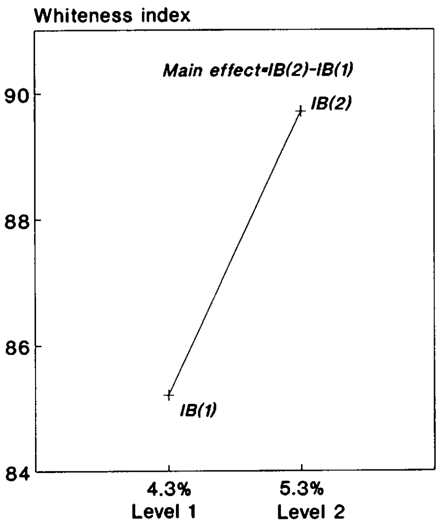

Figure 3. *Main effect of Al_2O_3 on the whiteness index of the glaze.*

There is a firstorder interaction when the joint effect of the variation of two oxides is not additive but depends upon the proportion of each found. Figs. 4 and 5 give an example involving respectively an additive effect and a firstorder interaction.

In order to calculate the effect that the interaction of two oxides has on a certain property, the increments each of these give rise to in this property must be taken into account. Thus, in the case of the interaction (K_2O-MgO) shown in Figure 5, the calculation is as follows:

*Effect of the interaction K_2O-MgO on IB: 1/2 * [(IB(2,2)-IB(2,1))-(IB(1,2)-IB(1,1))]*

where *IB(i,j)* indicates the value of the whiteness index when the K_2O percentage corresponds to level *i* and that of MgO to level *j*.

Bearing in mind the above, it must be highlighted that when the influence of a given oxide on a property is to estimated, and the oxide interacts with other oxides, these effects must be taken into account besides the main effect. This fact underscores one of the major advantages of experimental design compared to other, more empirical methods, as the influence of each oxide in the definitive formulation, in the established composition interval, is considered in relation to the remaining components.

Figure 2 shows that Al_2O_3 is the oxide that most affects the whiteness index, raising the value of this property as its percentage increases. CaO and K_2O do not exhibit important main effects. However, owing to the first-order interactions K_2O-MgO and CaO-MgO, they must be considered oxides that modify the whiteness index. Finally, although MgO gives rise to a main effect of considerable magnitude, its influence on this property cannot be inferred without taking into account its interactions with K_2O and CaO. It can also be observed that the main MgO effect is a drop in the property under study. However, the joint effect of K_2O-MgO and CaO-MgO gives rise to an increase in the glaze whiteness index.

The property optimum (maximum or minimum) value can be obtained from the values corresponding to the main effects, and the interpretation of the existing interactions, from graphs like those depicted in Figure 5.

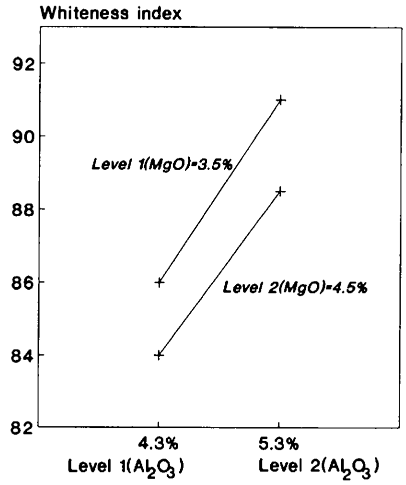

Figure 4. *Effect of the Al_2O_3 and MgO oxides, example of additive effects.*

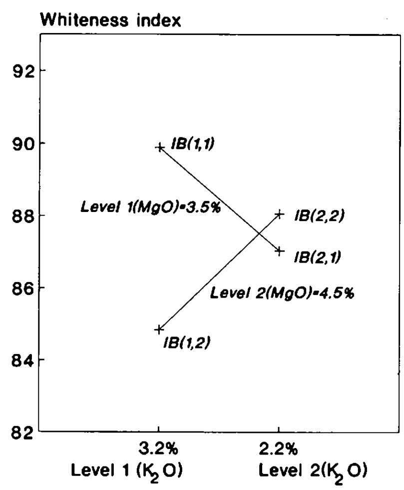

Figure 5. *Effect of the K_2O-MgO interaction, example of non-additive effects.*

As one of the objectives of the study is to improve glaze whiteness, the optimal whiteness index value will be a maximum; Table 3 details the five oxide percentages, obtained after interpreting the results of statistical analysis, which meet this optimal condition.

Table 3. *Five oxide percentages that optimize the glaze whiteness index, for the composition variation interval studied.*

Factors	% wt
K_2O	3.2
ZnO	indifferent
Al_2O_3	5.3
CaO	9.7
MgO	3.5

4.1.2. Yellowness index of the glaze surface

Figure 6 illustrates the main effects and first-order interaction effects found for the yellowness index (ASTM D1925) of the glaze surface.

As was the case of the whiteness index, Al_2O_3 is the sole oxide whose main effect is important and which does not exhibit interactions with other oxides. The effect observed is the opposite one. A drop in the yellowness index takes place as this oxide percentage increases in the frit composition from 4.3% to 5.3%. The same happens with the other oxides and first-order interactions, whose relative importance is virtually the same as for the whiteness index, but with an inverse effect on this property (decrease instead of increase or vice versa).

On interpreting these results, the percentages were found for the five studied oxides, which yield the glaze with the lowest yellowness index (Table 4). These coincide with the ones corresponding to the composition giving rise to the maximum whiteness index (Table 3).

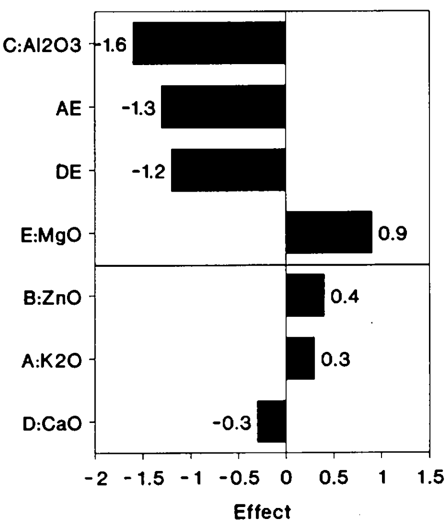

Figure 6. *Main effects and most important first-order interaction effects, corresponding to the yellowness index of the glaze surface.*

Table 4. *Five oxide percentages that optimize the glaze yellowness index, for the composition variation interval studied.*

Factors	% wt
K_2O	3.2
ZnO	indifferent
Al_2O_3	5.3
CaO	9.7
MgO	3.5

4.1.3. Glaze surface gloss

The main effects and first-order interaction effects obtained for the gloss are depicted in Figure 7 in the form of a histogram. It shows that K_2O does not exhibit any interactions, while also being the major main effect. It may therefore be inferred that a drop in the proportion of this oxide in the composition (from 3.2% to 2.2%) entails a 5.9 rise in glaze surface gloss.

To analyze the influence of Al_2O_3 and MgO, the interactions CaO-MgO and Al_2O_3-MgO must be taken into account, besides the main effects.

The interpretation of the data resulting from statistical analysis yield the five oxide percentages that give rise to maximum glaze surface gloss (Table 5).

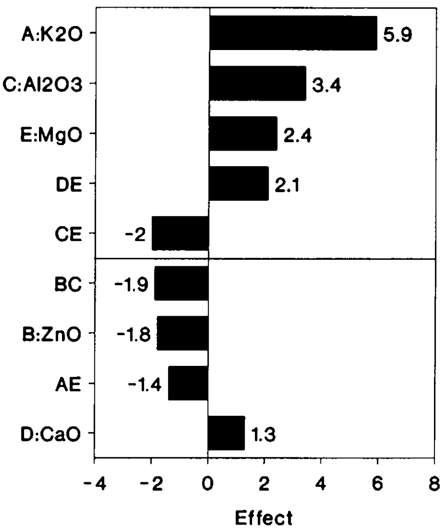

Figure 7. *Main effects and most important first-order interaction effects, corresponding to glaze surface gloss.*

Table 5. *Five oxide percentages that optimize glaze gloss, for the composition variation interval studied.*

Factors	% peso
K_2O	2,2
ZnO	8,8
Al_2O_3	5,3
CaO	10,7
MgO	4,5

4.1.4. Sealing temperature

Figure 8 illustrates the main and interaction effects obtained for sealing temperature. The effects arising as a result of first-order interactions are significantly greater than those corresponding to the oxides separately. However, the variations that occur are of no great magnitude, as this temperature was determined with an assessment interval of 10°C.

Table 6 reports the percentages of each oxide, which raise sealing temperature, obtained after interpreting the interactions.

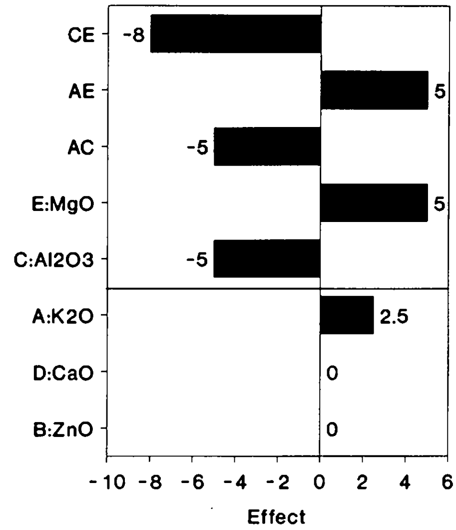

Figure 8. *Main effects and most important first-order interaction effects, corresponding to frit sealing temperature.*

Table 6. *Five oxide percentages that optimize frit sealing temperature, for the composition variation interval studied.*

Factors	% wt
K_2O	2.2
ZnO	indifferent
Al_2O_3	4.3
CaO	indifferent
MgO	4.5

4.1.5. Coefficient of expansion

Figure 9 shows that all the oxides exhibit an appreciable effect on the frit coefficient of expansion, without there being any significant first-order interactions. However, the most striking variation corresponds to K_2O, in lowering the value of this coefficient by 2.9×10^{-7}°C^{-1} on dropping from 3.2% to 2.2%.

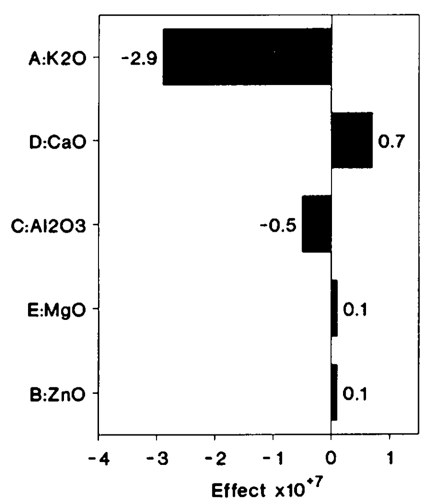

Figure 9. *Main effects corresponding to the frit coefficient of expansion.*

Table 7 lists the percentage of each oxide that yields the optimal (maximum) coefficient of expansion.

Table 7. *Five oxide percentages that optimize the frit coefficient of expansion, for the composition variation interval studied.*

Factors	% wt
K_2O	3.2
ZnO	7.3
Al_2O_3	4.3
CaO	10.7
MgO	4.5

4.2. RESULTS OBTAINED WITH THE FRIT ON FUSING IT ON AN INDUSTRIAL SCALE

Using the results obtained above, in order to improve the whiteness of the starting glaze, it was decided to fuse industrially the frit composition containing the percentages of the five studied oxides listed in Table 8.

Table 8. *Five oxide percentages chosen for fusion on an industrial scale.*

Factors	% wt
K_2O	3.2
ZnO	8.8
Al_2O_3	5.3
CaO	9.7
MgO	3.5

These percentages were chosen as the percentages corresponding to K_2O, Al_2O_3, CaO and MgO are the ones yielding a higher whiteness and a lower yellowness index in the resulting glaze. As the amount of ZnO does not affect these two properties, the value 8.8% was chosen as it yields a higher gloss value, together with an Al_2O_3 percentage of 5.3% (as a result of the interaction Al_2O_3-ZnO). The reason for this choice lies in the very characteristics of the glaze under study: glossy, opaque, and white.

The oxide formula of the frit (modified frit) was obtained from these percentages and those corresponding to the oxides that were not used as design factors, and the composition was fused in an industrial kiln.

The properties described above (Section 4.1) were compared in the modified frit and the industrially produced starting frit. Table 9 lists the results obtained.

Table 9. Values of the properties studied in the starting frit and the frit modified on the basis of the experimental design results.

Properties	Starting frit	Modified frit
Whiteness index (HUNTER [60])	83.7	92.5
Yellowness index (ASTM D1925)	2.6	-0.2
Gloss (‰)	88.1	89.5
Sealing temperature (°C)	1030	1030
Coefficient of expansion ($°C^{-1}$)	53.2×10^{-7}	54.7×10^{-7}

On comparing both results, a frit is observed to have been obtained yielding a whiter glaze (higher whiteness index and lower yellowness index), with slightly increased gloss and coefficient of expansion, while holding the same sealing temperature. However, this increment in gloss and coefficient of expansion can be considered quite favourable, bearing in mind the characteristics usually required of opaque glazes for single-fired porous wall tiles.

5. CONCLUSIONS

The results obtained in the present study allow inferring that factorial experiment design can be a useful tool in formulating ceramic frits, as a result of the following:

1. Whiteness was improved in a glossy, opaque, white glaze, commonly used in manufacturing single-fired porous wall tile, by performing some changes in the frit composition (major glaze component), virtually without modifying the other studied properties (gloss, sealing temperature, and coefficient of expansion), by conducting only a few experiments.

2. It was, at the same time, possible to determine the influence that the oxides K_2O, ZnO, Al_2O_3, CaO and MgO, have on some physical properties of the starting glaze, in the composition interval considered for each oxide. This information has allowed certain formulation criteria to be derived, which are valid for the kind of frit composition studied and the variation interval of each component tested.

The validity of the results obtained also enables this methodology to be applied in formulating other kinds of ceramic compositions, such as bodies, glazes, pigments, screen-printing suspensions, etc.

6. REFERENCES

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