Poster 130
Use of n^k Factorial Design in the Optimization of Ceramic Pigment Firing Cycles

Marcelo Dezena Cabrelon (1,2), Rodrigo Togginoti Zauberas (1) and Anselmo Ortega Boschi (1)

[1] Laboratory of Ceramic Tiles, Dept. of Materials Eng. (DEMa), Federal University of São Carlos (UFSCar);
[2] Post-Graduate Program in Materials Science and Engineering (PPGCEM)

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1. Introduction

The manufacture of ceramic pigments by the traditional method of mixing metallic oxides involves several stages in the process that can interfere drastically in the hue of the end product, generating variations that depreciate its value[1]. Because calcination is one of the most important of the various stages of the productive process, since all the thermally activated solid-state chemical reactions occur here, it must be optimized in order to obtain the most satisfactory results possible. Optimization of the firing cycle with three variables (firing temperature, heating rate, and soaking time), using conventional research methodologies, can generate a number of tests which do not always lead to conclusive results. However, the use of statistical tools allows for the selection of process variables and their optimization with far fewer tests, which makes their use feasible on an industrial scale. The n^k factorial design technique is applicable here, for the variables have independent characteristics, unlike a study of formulations by planning with mixtures in which the proportion of raw materials is interdependent. Previous studies have indicated the possibility of using this technique to study the process variables of ceramic pigments[2]. The graphic representation of the experiments (Figure 1) explains the calculations involved in estimating the factors and effects of each variable.

Figure 1 – Schematic diagram of the experiments conducted

2. Objective

The present study aimed to use n^k factorial design to optimize the firing cycle of ceramic pigments of the zirconium silicates class: vanadium turquoise blue and praseodymium yellow, seeking to identify the relations between each process variable and its chromatic coordinates (L*, a* and b*).

3. Materials and Methods

Raw mixtures of industrial formulations were selected from the two principal existing systems: vanadium turquoise blue and praseodymium yellow. These samples were subjected to two successive firing cycles, according to the n^k factorial design method described by MONTGOMERY, D.C.[1], with the variables to be optimized being firing temperature (T), soaking time (S), and heating rate (R), each at two levels (high and low) with a central point inside the predefined space, as indicated in Table I.

Table I – Sampling space of the variables of interest and the corresponding symbols of the n^k factorial design

A statistical program provided the variables and their conditions, indicating the experiments required and the most aleatory order in which to execute them (Table II).

Table II – Experimental order defined for a 2^3 factorial design with a central point

The raw mixtures were calcined in sealed alumina crucibles, under the preestablished conditions given in Table 2. After calcining, the pigments were ground in a mortar down to 0% residue in #170 mesh, washed in three portions of 1 liter of water mixed with 8% NaOH, dried in an electric drier, milled in a zirconium ball mill with water and 50% of solids for exactly 5 min and then dried again. After the samples were completely dry, they were ground with mortar and pestle until they were ready for use, at which time 5% of pigment was incorporated into a standard transparent glaze and applied with a manual glazing device (0.5mm layer) on twice-fired ceramic tiles. The bodies were fired in a laboratory furnace in an industrial cycle of 26 min at a maximum temperature of 1060ºC. They were then subjected to a colorimetric analysis in a MINOLTA CM 2500d spectrophotometer using a D65 illuminant at 10º, using as basis the CIELab colorimetric space. The results were again treated statistically in order to correlate the process variables to the responses of interest.

4. Results and Discussion

The pigments synthesized by the methodology of the n^k factorial design presented the colorimetric results shown in Table III.

Table III – L*, a* and b* colorimetric coordinates for the blue (V-$ZrSiO_4$) and yellow (Pr-$ZrSiO_4$) synthesized pigments

A comparison of the results against an industrial standard revealed the existence of a blue pigment with a stronger hue (sample 3) and other hues with a quality compatible with the standard. The yellow pigment did not show samples with stronger hues than the standard, but it should be noted that the standard pigment undergoes a micronization process which reduces its particle size to a micrometric scale (5-10 μm), thereby increasing its pigmentation ability, which is not the case with pigments prepared in the laboratory. These isolated results are inconclusive and serve merely as a reference for later analysis.
Table 4 shows the results of the effects and the interactions of the two pigments under study, based on a third-degree model.

Table IV – Effects of the interaction factors on the chromatic coordinates (L*, a* and b*) for the blue (V-$ZrSiO_4$) and yellow (Pr-$ZrSiO_4$) synthesized pigments

Figure 2 – Averages of the effects of the three process factors (T, S and R) on the three chromatic coordinates (L*, a* and b*) for the a) V-$ZrSiO_4$ blue, and b) and Pr-$ZrSiO_4$ yellow pigments

The turquoise blue pigment shows the direct influence of temperature on each of the three chromatic coordinates, whose values increase from the low temperature (-1) to the high temperature (+1) stage. Because the important point with this pigment is to reduce the value of coordinate b* to more negative levels, the increase in temperature causes a depreciation of the blue hue, diminishing its quality. The graph in Figure 2a illustrates these observations, showing that it is possible to achieve an optimized result for a firing cycle of 900ºC for 180 min of soaking time at a heating rate of 15ºC/min.
With regard to the yellow pigment, one can see from Table 3 that temperature and time are beneficial factors on the yellow components and that here, the higher the value the greater the contribution of these process variables on the yellow hue required for this product. Figure 2b shows that the optimized firing cycle for this pigment occurs at a temperature of 1060ºC, soaking time of 180 min and heating rate of 15ºC/min. However, because the colorimetric results are very close, sample 7 also presents a satisfactory result but at a lower production cost, which is the point to be exploited during the process.

5. Conclusions

After executing the experimental proposal described above and analyzing the results, we can conclude that:
- The n^k factorial design methodology is completely applicable to the study and optimization of ceramic pigment firing cycles, allowing for the proper adjustment of the production conditions of the pigments under study.
- In the case of the vanadium turquoise blue pigment, the increase in firing temperature to 1060ºC depreciates the three chromatic coordinates to the detriment of the end product, a fact that may be related to the increase in grain size.
- For the praseodymium yellow pigment, the increase in temperature and in soaking time at 1060ºC and 15°C/min led to a gain in the yellow hue (b*), which is fundamental for this product. However, these process variables do not interfere to any significant extent in the chromatic coordinates L* and a*.

6. Acknowledgements

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7. References

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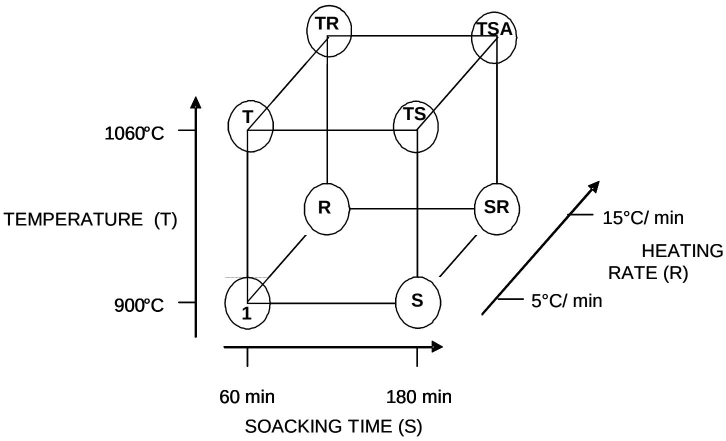

Figure 1 – Schematic diagram of the experiments conducted

Table I – Sampling space of the variables of interest and the corresponding symbols of the n^k factorial design

	Low (-1)	Center Point (0)	Higt (+1)
Temperature (T)	900	980	1060
Soacking time (S)	60	120	180
Heating Rate (R)	5	10	15

Table II – Experimental order defined for a 2^3 factorial design with a central point

Run Order	Temperature (T)	Soacking Time (S)	Heating Rate (R)
1	900	60	5
2	900	60	15
3	900	180	15
4	1060	60	5
5	900	180	5
6	1060	60	15
7	980	120	10
8	1060	180	15
9	1060	180	5

Table III – L*, a* and b* colorimetric coordinates for the blue ($V-ZrSiO_4$) and yellow ($Pr-ZrSiO_4$) synthesized pigments

Samples	**Turquoise blue pigment (V-ZrSiO4)**			**Yellow pigment (Pr-ZrSiO4)**		
	L*	**a***	**b***	**L***	**a***	**b***
Industrial Standard	61,491	-17,388	-13,710	81,220	-0,835	67,206
1	66,606	-17,159	-12,994	82,413	-0,918	43,794
2	68,053	-16,107	-10,449	82,810	-1,430	40,178
3	62,156	-17,434	-19,920	81,788	-1,579	58,443
4	71,581	-14,328	-7,581	81,820	-2,253	57,613
5	66,035	-16,796	-13,238	81,941	-1,334	57,714
6	74,229	-12,959	-5,751	82,213	-2,345	58,873
7	72,389	-13,294	-3,753	82,055	-2,229	59,006
8	74,347	-11,953	-3,244	82,215	-2,904	58,009
9	72,406	-13,198	-4,472	82,390	-2,506	55,204

Table IV – Effects of the interaction factors on the chromatic coordinates (L*, a* and b*) for the blue (V-$ZrSiO_4$) and yellow (Pr-$ZrSiO_4$) synthesized pigments

Factors and Interactions	Turquoise blue pigment (V-ZrSiO4)			Yellow pigment (Pr-ZrSiO4)		
	Colorimetric cordinates			Colorimetric cordinates		
	L*	**a***	**b***	**L***	**a***	**b***
T	7,428	3,760	8,888	-0,078	-1,187	7,392
S	-1,381	0,290	-1,025	-0,231	-0,344	7,228
R	0,539	0,760	-0,270	0,115	-0,312	0,294
T*S	1,853	0,770	3,833	0,516	-0,062	-8,864
T*R	1,755	0,550	1,799	-0,006	0,067	1,738
S*R	-1,508	-0,450	-2,457	-0,280	-0,010	1,472
T*S*R	1,154	0,390	2,156	-0,005	-0,143	-0,700

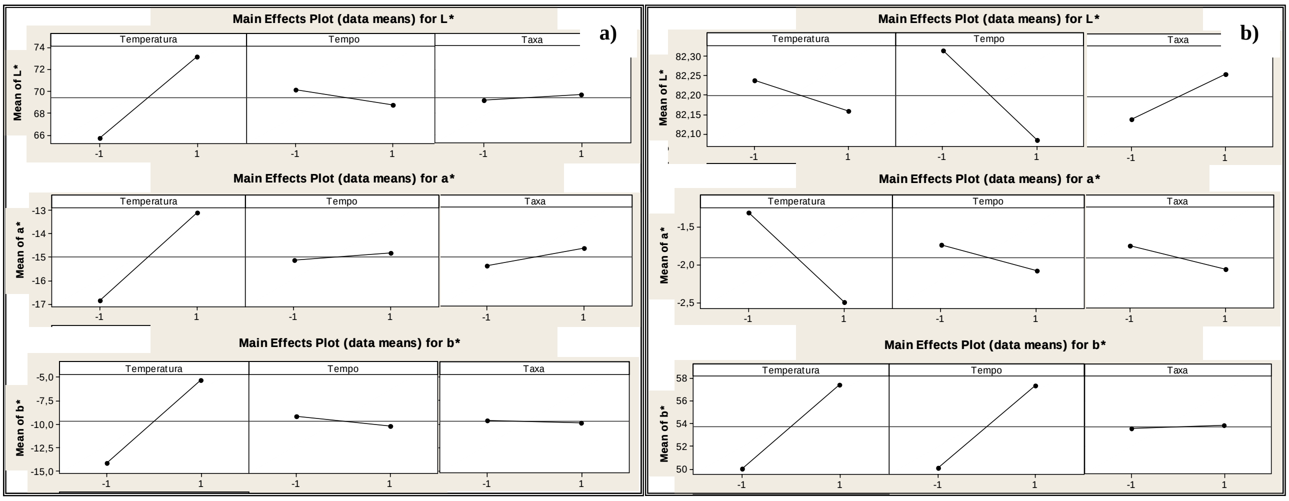

Figure 2 – Averages of the effects of the three process factors (T, S and R) on the three chromatic coordinates (L*, a* and b*) for the a) V-$ZrSiO_4$ blue, and b) and Pr-$ZrSiO_4$ yellow pigments