STUDIES ON FORMULATIONS FOR PORCELAIN STONEWARE TILES

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1. INTRODUCTION

Formulations for the production of ceramic tiles are based on strongly empirical information, since the diversity of the physical, chemical and mineralogical characteristics of the raw materials used in these formulations makes it difficult to concoct "recipes". This study aimed to establish correlations among some of the aforementioned characteristics of the mixtures in order to obtain products having a water absorption lower than 0.4% and mechanical strength exceeding 40MPa.

2. METHODOLOGY

The methodology can be divided into five stages:

1) Identification of the processing conditions, the raw materials, and their content in industrial formulations;

2) Selection and physical, chemical and mineralogical characterization of the raw materials;

3) Definition of the formulations;

4) Processing under standardized conditions on a laboratory scale;

5) Characterization of fired samples and analysis of the results, correlating mixtures' $\%Al_2O_3$ / $\%SiO_2$ ratio (excluding the content of quartz and free alumina), and the percentages of alkaline oxides, alkaline earth oxides, plastic phases and particles smaller than 9.2μm, with water absorption and modulus of rupture.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The first stage of the experiment allowed for the identification of the process control parameters: grinding residue of less than 0.5% in a 63μm mesh; compaction pressure greater than 400MPa; bulk density of pressed pieces greater than 1.95g/cm^3; and firing cycles at temperatures above 1180°C, with 60-70 min duration. The conventional raw materials and their content in the formulations are clays containing kaolinite and illite (30 to 50%), fluxing agents, especially those containing sodium and potassium (30 to 50%), quartz (up to 10%), and up to 5% each of other raw materials such as talc, limestone, opacifiers and dyes. The second stage of the experiment consisted of characterizing twenty raw materials, as to their water absorption and firing colour when fired at 1220°C. Three clays, three kaolins, three fluxing agents and a talc were selected. These materials were characterized as to their chemical and mineralogical composition and particle size distribution. The third stage of the experiment consisted of formulating twenty mixtures containing 20% to 45% clay, 10% to 25% kaolin, 30% to 50% fluxing agent, and 0% to 6% talc. Table 1 lists the values of the characteristics evaluated in the formulated mixtures. In the fourth stage, ten samples of each mixture (five for each firing temperature) were pressed to bulk densities of approximately 1.95g/cm^3, and fired for about 70 min cycles at 1200°C and

1225°C with a 5 min soaking time. The fifth stage consisted of characterizing the fired samples (Table 2) and evaluating the results based on Pearson's correlation analysis (Table 3) to identify correlations between the characteristics of the mixtures and their water absorption (WA) and modulus of rupture (MOR).

Mixture	% Al_2O_3 / % SiO_2 corrected	% of alkaline oxides	% of alkaline earth oxides	% of plastic phases	% of particles smaller than 9.2μm
1	0.59	5.1	0.2	68.0	66.0
2	0.53	3.5	2.1	63.9	66.2
3	0.31	4.7	0.6	38.3	47.1
4	0.61	5.0	0.2	68.9	66.2
5	0.43	5.7	0.6	44.6	47.1
6	0.38	2.5	2.1	56.7	66.0
7	0.56	4.9	1.8	64.7	65.2
8	0.58	3.3	1.6	68.7	65.1
9	0.28	5.0	0.6	32.8	52.4
10	0.71	7.1	0.5	79.9	63.0
11	0.49	3.8	2.4	59.9	66.1
12	0.38	4.8	0.3	36.2	48.1
13	0.61	6.1	0.4	79.1	58.2
14	0.56	3.4	1.7	67.4	64.8
15	0.49	5.4	0.6	70.9	71.5
16	0.51	4.8	0.5	56.1	52.2
17	0.28	4.7	0.6	34.6	50.3
18	0.37	4.9	0.4	34.9	47.8
19	0.38	2.5	2.1	56.7	65.8
20	0.50	3.3	3.6	60.8	65.4

Table 1. Characterization of the formulated mixtures.

Mixture	$WA_{1200°C}$ (%)	$WA_{1225°C}$ (%)	$MOR_{1200°C}$ (MPa)	$MOR_{1225°C}$ (MPa)
1	6.12	4.30	58.2	59.5
2	1.65	0.13	78.2	95.2
3	3.58	1.84	54.1	59.0
4	6.42	4.87	63.8	62.8
5	1.43	0.17	60.6	74.9
6	3.51	1.33	66.9	75.0
7	5.46	2.78	53.4	61.4
8	2.96	1.39	49.4	66.3
9	4.19	1.87	49.4	66.3
10	2.03	0.14	49.1	54.3
11	1.13	0.23	70.4	80.2
12	7.61	5.03	36.5	40.1
13	4.80	2.81	45.5	54.6
14	2.92	1.38	64.9	74.0
15	2.10	0.79	58.9	67.8
16	3.63	2.03	48.9	62.9
17	5.39	3.32	31.7	43.7
18	7.60	4.61	25.8	33.9
19	3.33	2.55	52.6	59.9
20	0.29	0.27	62.5	78.6

Table 2. Characterization of the test specimens made of the formulated mixtures

	$WA_{1200°C}$ (%)	$WA_{1225°C}$ (%)	$MOR_{1200°C}$ (MPa)	$MOR_{1225°C}$ (MPa)
% de Al_2O_3 / % SiO_2 corrected	-0.108	-0.049	0.440	0.257
% of alkaline oxides	0.227	0.141	-0.369	-0.429
% of alkaline earth oxides	-0.613	-0.542	0.527	0.629
% of plastic phases	-0.331	-0.286	0.471	0.363
% of particles smaller than 9.2 μm	0.636	0.536	-0.374	-0.299

Table 3. Pearson's correlation analysis; the numbers in bold showed values of $p < 0.1$

The results indicated that the reduction in the water absorption of the mixtures was associated with the increased content of alkaline earth oxides and with the reduction in the percentage of particles smaller than 9.2μm. The modulus of rupture of the pieces fired at 1200°C showed a positive correlation with the corrected %Al_2O_3 / %SiO_2 ratio and with the alkaline earth oxide and plastic phase content, and a negative correlation with the percentage of particles smaller than 9.2μm. At 1225°C, the modulus of rupture showed a negative correlation with the alkaline oxide content and a positive correlation with the alkaline earth oxide content.

4. CONCLUSIONS

The analysis of the results from the pieces fired at 1225°C indicated that the production of tiles with a water absorption of less that 0.4% was favoured by increasing the contents of CaO and MgO, which act as eutectic formers, and of particles larger than 9.2μm, associated with harder minerals such as feldspars and quartz. Products with greater mechanical strength are obtained by reducing the alkaline oxide content (vitreous phase formers) and increasing the CaO and MgO content. The results also indicated the complexity involved in the development of formulations for porcelain stoneware tiles. Although several of the mixtures produced from the newly developed formulations showed WA and MOR congruent with standardized values, it was impossible to pinpoint any correlation, for example, between alkaline oxide content and water absorption in the fired pieces.

5. ACKNOWLEDGMENTS

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