

USE OF RESIDUAL ROCK AS RAW MATERIAL FOR PORCELAIN TILE COMPOSITION

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1. ABSTRACT

This study consists of the physical and chemical characterisation of a residual rock from the sieving process of two deposits located in the state of Rio Grande do Sul, Brazil. The tailings were denominated as anorthosite 67 and anorthosite 72, in order to facilitate their identification. The geological study of both deposits has identified the samples as being a sandy raw material from a sedimentation derived from plagioclase, of igneous origin. The rocks found in the deposits are probably derived from the mother rock (matrix), since both are close and show small differences due to the relief that forced different settlements for such deposits.

As the geological studies of the deposits show that the sandy material, which is already commercialised by the company, is a sediment from an anorthosite rock. It was adopted as prerogative that the residual rock of the sieving process is an anorthositic rock. For this, in addition to the physical and chemical characterisation of samples 67 and 72, the study was carried out by the use of the samples in a composition for porcelain tile, also marketed by the company, with the intention of a future use of the samples, because of the higher added value of this ceramic product. The importance of this study lies in the costs of the raw materials in the extraction process, both in relation to the wear and tear of machinery and the hourly productivity of the deposits, since the analysis of these costs has considered the exploitation of these raw materials as being a loss to the company. The current knowledge of the geological origin of the deposits shows that they may have the

potential to be used in ceramic compositions, but to date, the company has not had the opportunity to elaborate a complete study that would enable the use of these raw materials, which is the main purpose of this study. Therefore, the aim of this study was the use of an anorthositic rock, a tailing from two deposits of a sand mining company in Brazil, in a porcelain tile composition..

The anorthosite samples (67 and 72) were submitted to mineralogical (X-ray diffraction, Philips PW 1830, CuK α) and chemical (X-ray fluorescence, Philips PW 2400) characterisation. They are igneous rocks of phaneritic and leucocratic equigranular formation. In addition, a ball clay and a lithium feldspar were used to compose the porcelain paste. The raw materials were received 'in natura', dried in an oven at 110 °C until constant mass and processed in a hammer mill to be used in the compositions. A mixture design (DoE) was used and the main factors were both anorthosites, the ball clay and the Li-feldspar, resulting in 11 compositions of porcelain tile pastes. ANOVA and response surface were used to identify the effect of each raw material in the porcelain tile performance. Each composition was grinded with 30% water and 1% deflocculant (sodium silicate) in a high-speed alumina ball mill for 25 min. The density, viscosity and residue (45 μ m mesh) of the slips were determined. As a control, the density of the slips was kept between 1.63-1.66 kg/L, the viscosity (Ford cup n. 4) between 25-60 s and the residue (45 μ m mesh) between 1-3 %.The slips were totally dried and the powders were mixed with 6.5% water and granulated. The powders were pressed (45 MPa) into 100 mm $\times$ 50 mm compacts, dried (100 °C) and fired at 1200 °C for 50 min in a laboratory roller kiln. The fired samples of each composition were tested for their water absorption and modulus of bending strength (10 mm/min, 3-point method).

Table 1 shows the chemical analysis of the raw materials, given by XRF. Both anorthosites have similar chemical composition, not showing significant differences in the relative percentages of their oxides, which would mean similar behaviour on firing.

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	LoI
Anorthosite 67	53.2	29.4	0.1	0.7	11.4	0.1	0.5	4.1	0.5
Anorthosite 72	53.6	29.3	0.1	0.8	10.5	0.2	0.6	4.5	0.8
Ballclay	50.5	30.9	0.2	1.8	0.6	1.2	1.6	0.2	13.5
Feldspar	77.4	15.6	<0.1	1.1	0.2	<0.1	1.9	2.9	0.2

Table 1. Chemical analysis of the raw materials (mass %, XRF)

Based on the mixture design method and using the four raw materials as main factors, eleven compositions were formulated, with ten vertices and a central point, table 2. Each run is a porcelain tile composition, and the 11 compositions explore the entire sample space of possible combinations between the raw materials.

Run	Ballclay	Feldspar	Anorth.67	Anorth.72	FS (%)	AD (g/cm ³)	WA (%)	LB (kgf)
1	0.3	0.35	0.15	0.2	5.02	2.30	1.35	37.7
2	0.15	0.35	0.3	0.2	4.22	2.18	4.44	38.1
3	0.15	0.55	0.15	0.15	6.76	2.34	0	45.2
4	0.3	0.4	0.15	0.15	5.11	2.30	0.75	35.3
5	0.15	0.4	0.3	0.15	6.22	2.30	0.66	41.9
6	0.3	0.35	0.2	0.15	5.58	2.26	1.98	29.8
7	0.2	0.35	0.3	0.15	5.65	2.27	1.29	42
8	0.2	0.35	0.15	0.3	4.96	2.24	2.21	38
9	0.15	0.35	0.2	0.3	5.52	2.24	2.12	45.2
10	0.15	0.4	0.15	0.3	6.56	2.33	0.19	48.2
11C	0.205	0.385	0.205	0.205	5.46	2.29	0.86	39

Table 2. Mixture design with four-factor constraints, number of initial constraints in the mixture: ten vertices (V) and general centroid (C). The results for firing shrinkage (FS), water absorption (WA), apparent density (AD) and load at break by bending strength (LR) are also shown.

Table 2 shows the results for water absorption. The standard deviation ranged from 0 to 1.9 %. Table 3 shows the ANOVA for the water absorption results. The factor F0 shows that the linear model is the most reliable one ($F = 1.86\%$), and the p-value indicates a reliability of 78%, with a low adjustment to the R2 model = 0.44 or 44%. Figure 1 shows the response surfaces for water absorption. The lower water absorption occurs when feldspar is used due to its low melting point, forming more liquid phase in the composition with its addition (table 2). The anorthosites again have equal behaviours, increasing the water absorption when added, being a material more refractory to the firing temperature used.

waterabsorption	Effect			Error			Reliability		
Model	SS	dF	MS	SS	dF	MS	F ₀	p	R ²
<u>Linear</u>	<u>6.84</u>	<u>3</u>	<u>2.28</u>	<u>8.58</u>	<u>7</u>	<u>1.23</u>	<u>1.86</u>	<u>0.22</u>	<u>0.44</u>
Quadratic	6.08	6	1.01	2.50	1	2.50	0.410	0.83	0.84
Total adjusted	15.4	10	1.54						

Table 3. ANOVA for waterabsorption (%)

The anorthosites are not fluxes due to their high content of Al_2O_3 , about 30%, therefore being refractory. They are also not plastic but show low content of organic matter and low Fe_2O_3 , resulting therefore in a very noble material for use in ceramic compositions. The results show that both anorthosites may decrease the amount of Li-feldspar in some compositions, making it possible for the company to work with anorthosites as raw materials for various ceramic products. Until now, the anorthosite was considered a waste from sand mining by the company, but could become a salable raw material because of its ability to form dense ceramic products.

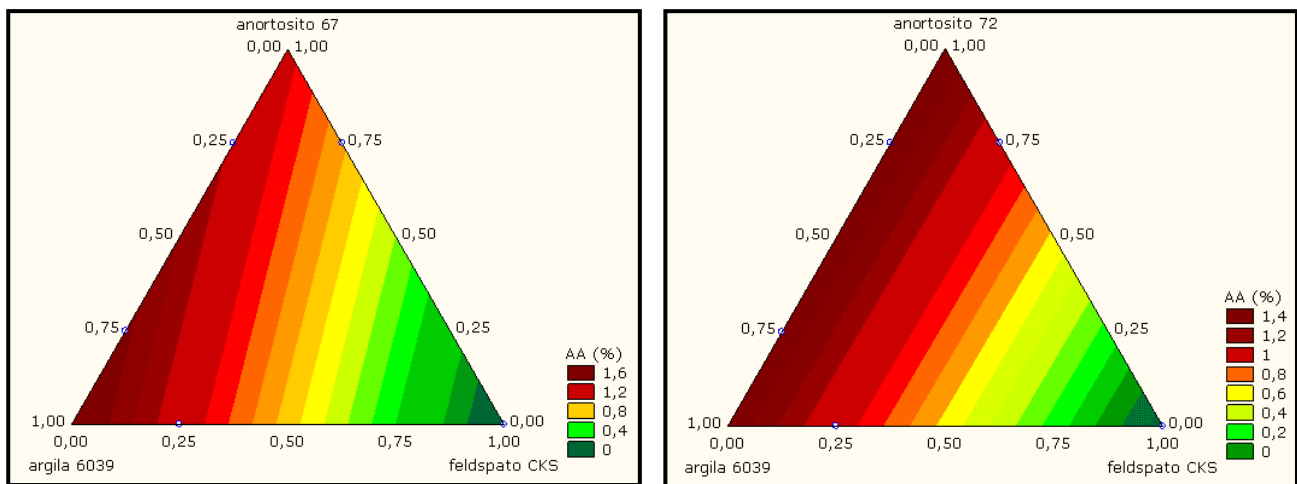


Figure 1. Response surface for waterabsorption (%) ($R^2 = 0.44$, reliability of 78%)