

## MINERAL CIRCULARITY OF KAOLIN FOR INDUSTRIAL APPLICATION IN BRAZILIAN PORCELAIN TILES

A.B. Comin<sup>1,2</sup>, A. Zaccaron<sup>2</sup>, E. Saviatto<sup>2</sup>, F. Raupp-Pereira<sup>2</sup>, M.J. Ribeiro<sup>3</sup>, G.S. de Souza<sup>1</sup>

<sup>1</sup> Mining Engineering Department, SATC University, Rua Pascoal Meler, 73, Universitário, 88805-380, Criciúma - SC, Brazil

<sup>2</sup> Post-Graduate Program on Materials Science and Engineering (PPGCEM), University of the Extreme South of Santa Catarina - UNESC, Avenida Universitária 1105, 88806-000, Criciúma, SC, Brazil.  
[fraupp@unesc.net](mailto:fraupp@unesc.net)

<sup>3</sup> Materials Research and Development Center (UIDM), Polytechnic Institute of Viana do Castelo, Rua Escola Industrial e Comercial de Nun'Álvares, 4900-347, Viana do Castelo, Portugal.

**Abstract:** Kaolin is one of the main compositional raw materials of porcelain tiles, which has an important role in regulating the ceramic body refractoriness, avoiding dimensional problems caused in the firing process. For this, a high level of purity is required, reducing the presence of oxides that could affect the final product quality. The ceramic center in the south of Santa Catarina (Brazil) is supplied by kaolin from other regions, resulting in a cost increase in the process, motivated by the logistics of this material. In order to reduce operating costs, it is necessary to create alternatives for the use of mineral deposits close to the industrial production centers. In this way, a source of regional kaolin geologically contained in a sedimentary deposit of the southern ceramic center of Santa Catarina was sought from the adequacy of the kaolinite concentration, through unit operations of beneficiation by classification. The results indicate that the sieving method reduces the amount of quartz, resulting in aluminum oxide contents in the order of 28.20%, compared to the 19.05% contained in its natural state. In the mining activity, large volumes and tonnages of materials are extracted and moved, and the total use fits within the circularity concepts.

**Keywords:** Processing, kaolin, ceramic industry, porcelain tiles.

### 1. INTRODUCTION.

Brazil is one of the main players in the world market for ceramic tiles, occupying the third position in production and the second in consumption in the world, in addition to being the seventh in the ranking of exports [1]. In response to this great demand, a considerable volume of natural raw materials is needed, which grows according to production [2].

Among the materials developed and commercialized, porcelain tiles stand out for their technical characteristics, being considered a noble finished ceramic product for floor covering, whose production grows annually [3, 4]. The normative complexity and procedural specifications for porcelain tiles would consequently be associated with the nature of its raw materials, which require greater purity and quality [5]. Another aspect of great relevance, in the case of the ceramic tile producing complex located in the south of Brazil, is the scarcity of reserves of ores with the necessary technical characteristics and the strong influence on the costs of the final products, related to the distance from their origin and use place [6].

The raw materials for the production of porcelain tiles have been of great interest in the development of scientific studies since the end of the 90s [7–9]. However, with the growth in demand for ceramic industrial materials, as well as their high level of demand and quality, it is up to the extractive industry to develop products with a good cost-benefit ratio, through

satisfactory mining and processing techniques in their deposits use [10, 11].

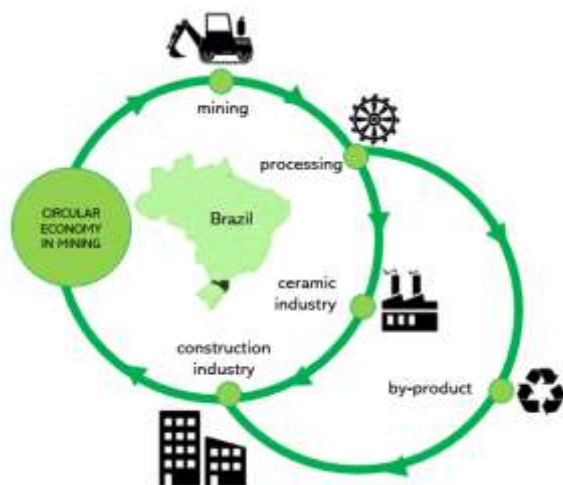
Porcelain tiles are vitreous ceramic products commonly composed of a triaxial clay-feldspar-quartz raw material [12]. Each incorporated raw materials, in the formulation of porcelain tile, has decisive functions in obtaining a high-performance product [13]. Kaolin or china clay ( $\text{Al}_2\text{O}_3\text{Si}_2\text{O}_5(\text{OH})_4$ ) is the main source of the mineral kaolinite which is chemically expressed as  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . When fired at temperatures above  $1100^\circ\text{C}$ , it crystallizes into mullite fibers ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). As a result, flexural strength and dimensional control are increased as this new crystalline phase appears [14].

For a better product performance there is a need to minimize impurities in the raw materials [15, 16]. However, by nature, it is very common for there to find variations within a deposit, resulting in a lack of mineralogical consistency between batches [17].

It should be noted that in order to develop any mineral product, the whole process begins with a satisfactory geological study, qualifying and quantifying deposits with technical and economic viability. For this, it is necessary to invest in the parameterization of engineering studies, aimed at technological characterization, and processing tests.

In parallel to the technological issues that refer to the mining-ceramic sector, the beneficiation process generates a by-product that fits the premises of mineral

circularity (Figure 1). CNI data [18] reveal that in Brazil, 76% of companies already develop some circular economy initiative.



**Figure 1** - Schematic image of mineral circularity.

Thus, this study adds alternatives to the raw materials demand, based on the availability of processed kaolin from places much closer to producing regions, in this case, in the State of Santa Catarina, in the south of Brazil.

## 2. MATERIALS AND METHODS.

### 2.1 Raw material collection

The raw kaolin sample (Kr) was collected directly from the mining front in 3 different locations, with a volume of approximately 10 kg, which was subsequently quartered and packaged.

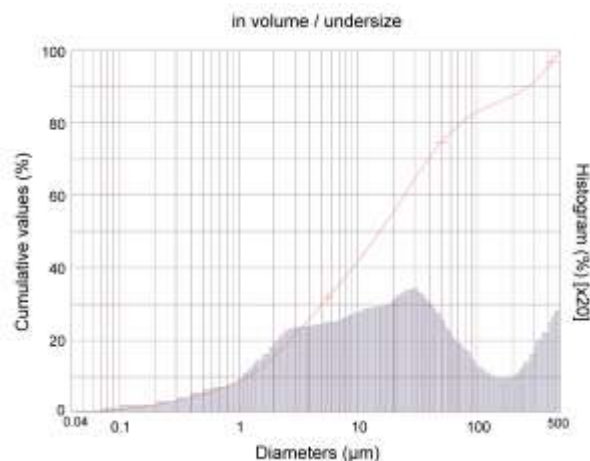
### 2.2 Processing and characterization

The collected sample (Kr) had the particle size distribution determined by laser diffraction (CILAS 1064 equipment) in the range of 0.04  $\mu\text{m}$  to 500  $\mu\text{m}$  during a period of 60s, and using sodium polyacrylate (Disperlan LP/G, Lamberti, Brazil) as a dispersant, in order to evaluate the distributed coarser and finer concentrations of the sample. Thus, a percentage of retained material (coarse kaolin - Kc) and another percentage of material passing through (passing kaolin - Kp) of the classified material were obtained.

All samples (Kr, Kc and Kp) were wet sieved (#4, #8, #16, #30, #50, #100, #200 and #325 ASTM mesh sieves) to evaluate the granulometric distribution, and were chemically characterized by X-ray fluorescence spectrometry in an X-ray spectrometer (Philips, model: PW2400) by wavelength dispersion (WDXRF). The loss on ignition (LoI) of the samples was performed after calcination at 1000°C for 3 h. Their mineralogical characterization was performed by X-ray diffractometry (XRD) in a Shimadzu diffractometer (XRD-6100), with 2 $\theta$  scanning from 4 to 70°, reading at 15 rpm, acceleration of 40 kV and 30 mA, with an incident radiation  $\text{CuK}\alpha_1$  of  $\lambda = 1.5406 \text{ \AA}$ .

## 3. RESULTS AND DISCUSSION.

In order to understand the granulometric distribution of Kr (Figure 2 and Table 1), in the condition of its homogeneity or heterogeneity, the indicators where the particle sizes are represented are shown. The results demonstrate that the passed over material has a heterogeneous distribution, although it presents 50% of the particles below 15.2  $\mu\text{m}$ , which shows a satisfactory presence of clay mineral fractions. The granulometric average is presented with a value of 66  $\mu\text{m}$ .



**Figure 2** - Cumulative granulometric distribution and frequency curve of raw kaolin.

**Table 1** - Size distribution and average particle diameter of raw kaolin.

Raw material	Diameter ( $\mu\text{m}$ )				
	D <sub>10</sub>	D <sub>50</sub>	D <sub>90</sub>	D <sub>100</sub>	D <sub>average</sub>
Kr	1.21	15.25	265	500	66

The samples underwent the wet granulometry test (Table 2). For Kr, the 300  $\mu\text{m}$  (#50 ASTM mesh) cutting range shows 37.59% retained and 62.41% passing through. The retained material has a coarser granulometry, represented by quartz and feldspar minerals. The passing fraction consists of clay minerals and finer quartz. Kc was basically uniformly concentrated in three ranges of particle size distribution, approximately 30% per cut range. It is therefore a medium quartz sand. This material materializes as a by-product of this unitary operation. It is observed that the fine fraction of the Kp sample was concentrated below 45  $\mu\text{m}$  (#325 ASTM mesh), that is, it represents a good concentration of clay minerals. In a future test, it is possible to evaluate the cut for Kr in a 150  $\mu\text{m}$  (#100 ASTM mesh), since there is a percentage of 19.08% of Kp in this granulometry, tending to be a material with a greater presence of quartz.

The chemical analysis (Table 3) shows that Kr is a clay mineral, with the presence of oxides such as silica ( $\text{SiO}_2$ ) in the order of 69.89%, alumina ( $\text{Al}_2\text{O}_3$ ) with 19.05%, alkaline oxides such as potassium oxide ( $\text{K}_2\text{O}$ ) with 4.75%, and presence of chromophore oxides such as iron ( $\text{Fe}_2\text{O}_3$ ) and titanium ( $\text{TiO}_2$ ) together in the order of 1.27%. The loss on ignition (LoI) of 4.64%, although low, is indicative of the water loss in the constitution of

kaolinite, in the form of clay mineral. For Kc it shows a considerable concentration of SiO<sub>2</sub> content (83.93%), also a small increase in the alkali content, with 5.19% of K<sub>2</sub>O, and on the other hand, great reduction for the Al<sub>2</sub>O<sub>3</sub> contents (9.86%) and Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> chromophores (0.25%). The Kp sample shows an important concentration of Al<sub>2</sub>O<sub>3</sub> content (28.20%). Therefore, there is also an increase in the percentage of LoI (8.64%). A reduction in SiO<sub>2</sub> content (56.41%) and a reduction in K<sub>2</sub>O (3.87%) can also be observed. On the other hand, an increase in the content of chromophore oxides (Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>) is observed with a sum of 2.38%.

**Table 2 -** Wet granulometry test of the studied samples.

Sieve (ASTM mesh)	Passing (%)		
	Kr	Kc	Kp
#4	-	-	-
#8	0.62	1.65	-
#16	12.08	32.13	-
#30	12.21	33.74	-
#50	12.68	31.17	-
#100	11.88	1.01	19.08
#200	5.68	-	9.13
#325	5.72	-	9.18
base	39.12	0.30	62.59

**Table 3 -** Chemical compositions (% w) of the samples, obtained by X-ray fluorescence.

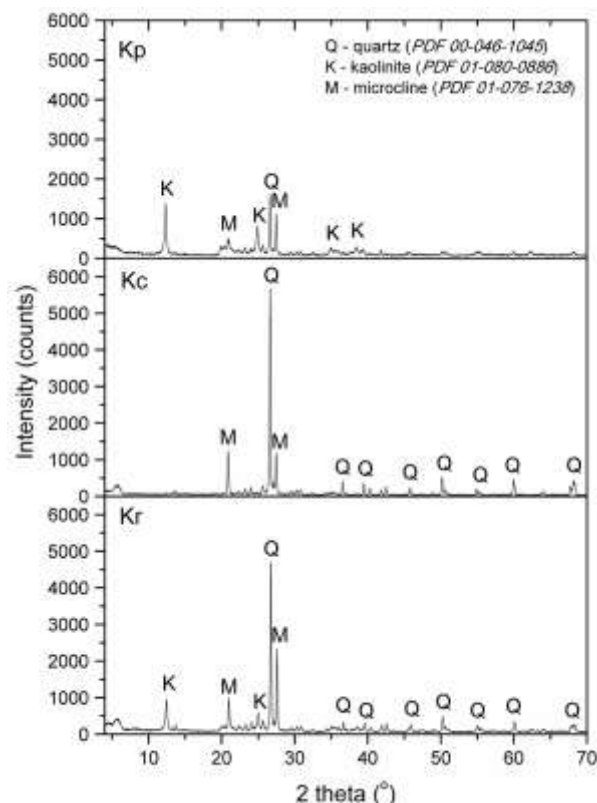
Oxides	Kr	Kc	Kp
Al <sub>2</sub> O <sub>3</sub>	19.05	9.87	28.21
CaO	0.07	0.05	0.08
Fe <sub>2</sub> O <sub>3</sub>	1.01	0.14	1.88
K <sub>2</sub> O	4.75	5.20	3.87
MgO	0.05	<0.05	0.12
MnO	<0.05	-	<0.05
Na <sub>2</sub> O	0.23	0.20	0.22
P <sub>2</sub> O <sub>5</sub>	<0.05	<0.05	<0.05
SiO <sub>2</sub>	69.90	83.93	56.42
TiO <sub>2</sub>	0.28	0.11	0.51
LoI	4.65	0.51	8.64

For the mineralogical analysis (Table 4 and Figure 3), it is understood that Kr is a clay with the presence of quartz and feldspar. For Kc, there is a higher percentage of quartz and a lower percentage of feldspar. The contained microcline fraction justifies the presence of alkaline oxides (potassium), which denotes that the deposit did not undergo a complete physical and chemical change from feldspar to clay minerals, such as kaolinite. For Kp, there is a higher concentration of kaolinite, as it is the typical fine fraction of the clay mineral, as well as the presence of feldspar and quartz in a finer form.

**Table 4 -** Quantification of mineralogical phases

phase	Quantification (%)		
	Kr	Kc	Kp
quartz	36.46	67.10	17.18
kaolinite	32.51	-	57.93
microcline	31.03	32.90	24.89

Thus, the increase in the alumina (kaolinite) content and reduction of silica (quartz) was positive by the granulometric separation in the analyzed fraction. An increase in the iron presence, and titanium oxides is also observed according to the chemical analysis of the passing powders, but absent in the mineralogical characterization.



**Figure 3 -** Mineralogical analysis of Kr, Kc, and Kp obtained through X-ray diffraction

**4. CONCLUSIONS.**

The results showed the viability of the applied technique, as there was a substantial gain in aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), in the order of 9.15%, resulting in a cumulative percentage of 28.20% of alumina above the 25% passed over. Other factors achieved were fundamental, with the reduction of silica (SiO<sub>2</sub>), represented by a decrease in content in the order of 13.77%, and with a final cumulative silicon oxide around 56.41%. In ceramic paste formulations for porcelain tiles, this major source of alumina in clay minerals becomes an important property, especially in terms of thermal stability, formation of crystalline phases such as mullite, and its influence on the pyroplastic deformation reducing in the ceramic substrate. This raw material option integrates a possibility of cost reduction in ceramic compositions, mainly the logistical cost, because even with associated processing, it presents a simple production technique.

It is also necessary to continue the research and development work to add value to this mineral deposit. For this, an important line of study is the iron oxide contained reduction in the passing fraction, as a way to obtain a material rich in kaolinite and with a lower iron oxide content. However, considering the residual

material retained from the beneficiation process, as this materializes in a by-product rich in quartz, greater alignment will be achieved by mineral circularity aimed at product design, sharing, and reuse of this material. This approach represents a systemic change that proposes economic and new business opportunities, in addition to providing environmental and social benefits, in a logic of a local mineral deposits profitability.

#### ACKNOWLEDGMENTS.

The authors are very grateful to Coordination for Higher Education Improvement (CAPES), National Council for Scientific and Technological Development (CNPq), for the financial support to this work.

#### DECLARATION OF INTERESTS.

The authors declare that they have no conflict of interest.

#### 5. REFERENCES.

- [1] ANFACER. Números do Setor Cerâmico <https://www.anfacer.org.br/setor-ceramico/numeros-do-setor> (accessed Apr 14, 2022).
- [2] Dondi, M.; García-Ten, J.; Rambaldi, E.; Zanelli, C.; Vicent-Cabedo, M. Resource Efficiency versus Market Trends in the Ceramic Tile Industry: Effect on the Supply Chain in Italy and Spain. *Resour. Conserv. Recycl.*, **2021**, *168*, 105271. <https://doi.org/10.1016/j.resconrec.2020.105271>
- [3] Pinter Junior, J.; Zaccaron, A.; Arcaro, S.; Rodrigues Neto, J. B.; de Noni Junior, A.; Raupp Pereira, F. Novel Approach to Ensure the Dimensional Stability of Large-Format Enamelled Porcelain Stoneware Tiles through Water Absorption Control. *Open Ceram.*, **2022**, *9*, 100203. <https://doi.org/10.1016/j.oceram.2021.100203>.
- [4] Ke, S.; Wang, Y.; Pan, Z.; Ning, C.; Zheng, S. Recycling of Polished Tile Waste as a Main Raw Material in Porcelain Tiles. *J. Clean. Prod.*, **2016**, *115*, 238–244. <https://doi.org/10.1016/j.jclepro.2015.12.064>.
- [5] Güngör, F. Investigation of Pyroplastic Deformation of Whitewares: Effect of Crystal Phases in the "CaO" Based Glassy Matrix. *Ceram. Int.*, **2018**, *44* (11), 13360–13366. <https://doi.org/10.1016/j.ceramint.2018.04.169>.
- [6] Luz, A. P.; Ribeiro, S. Use of Glass Waste as a Raw Material in Porcelain Stoneware Tile Mixtures. *Ceram. Int.*, **2007**, *33* (5), 761–765. <https://doi.org/10.1016/j.ceramint.2006.01.001>.
- [7] Dondi, M. Clay Materials for Ceramic Tiles from the Sassuolo District (Northern Apennines, Italy). Geology, Composition and Technological Properties. *Appl. Clay Sci.*, **1999**, *15* (3–4), 337–366. [https://doi.org/10.1016/S0169-1317\(99\)00027-7](https://doi.org/10.1016/S0169-1317(99)00027-7).
- [8] Carty, W. M.; Senapati, U. Porcelain? Raw Materials, Processing, Phase Evolution, and Mechanical Behavior. *J. Am. Ceram. Soc.*, **1998**, *81* (1), 3–20. <https://doi.org/10.1111/j.1151-2916.1998.tb02290.x>.
- [9] Bedoni, G.; Carbonchi, C.; Danasino, P. Feldspars and Feldspathic Sands for Porcelain Stoneware Tile. *Ceram. Acta*, **1999**, *11* (5), 33–43.
- [10] Comin, A. B.; Zaccaron, A.; Nandi, V. de S.; Inocente, J. M.; Muller, T. G.; Peterson, M. Characterization and Use of Clays from the Rio Bonito Formation/Paraná Basin for Ceramic Industry Application. *Int. J. Appl. Ceram. Technol.*, **2021**, *18* (5), 1814–1824. <https://doi.org/10.1111/ijac.13749>.
- [11] Agus, M.; Angius, R.; Ghiani, M.; Peretti, R.; Serici, A.; Zucca, A. Beneficiation of Low Grade Feldspar Ores for the Ceramics Industry. In *Proceedings of the XXI International Mineral Processing Congress*; Elsevier: Rome, Italy, 2000; pp C11-17-C11-25. [https://doi.org/10.1016/S0167-4528\(00\)80087-3](https://doi.org/10.1016/S0167-4528(00)80087-3).
- [12] Ochen, W.; D'ujanga, F. M.; Oruru, B.; Olupot, P. W. Physical and Mechanical Properties of Porcelain Tiles Made from Raw Materials in Uganda. *Results Mater.*, **2021**, *11*, 100195. <https://doi.org/10.1016/j.rinma.2021.100195>.
- [13] Njindam, O. R.; Njoya, D.; Mache, J. R.; Mouafon, M.; Messan, A.; Njopwouo, D. Effect of Glass Powder on the Technological Properties and Microstructure of Clay Mixture for Porcelain Stoneware Tiles Manufacture. *Constr. Build. Mater.*, **2018**, *170*, 512–519. <https://doi.org/10.1016/j.conbuildmat.2018.03.069>.
- [14] Stathis, G.; Ekonomakou, A.; Stournaras, C. J.; Ftikos, C. Effect of Firing Conditions, Filler Grain Size and Quartz Content on Bending Strength and Physical Properties of Sanitaryware Porcelain. *J. Eur. Ceram. Soc.*, **2004**, *24* (8), 2357–2366. <https://doi.org/10.1016/j.jeurceramsoc.2003.07.003>.
- [15] De Noni, A.; Hotza, D.; Soler, V. C.; Vilches, E. S. Influence of Composition on Mechanical Behaviour of Porcelain Tile. Part I: Microstructural Characterization and Developed Phases after Firing. *Mater. Sci. Eng. A*, **2010**, *527* (7–8), 1730–1735. <https://doi.org/10.1016/j.msea.2009.10.057>.
- [16] Nastri, S.; Quiorato, G. A.; Melchiades, F. G.; Biscaro, E.; Ferrari, A.; Boschi, A. O. Avaliação de Caulim Sedimentar Do Estado Do Pará Como Matéria-Prima Para o Setor Cerâmico. Parte II. Avaliação de Desempenho Em Aplicações Cerâmicas (Engobe, Esmalte e Massa de Porcelanato). *Cerâmica Ind.*, **2011**, *16* (1), 15–20.
- [17] Motta, J. F. M.; Cabral Junior, M.; Tanno, L. C. Panorama Das Matérias-Primas Utilizada Na Indústria de Revestimentos Cerâmicos: Desafios Ao Setor Produtivo. *Cerâmica Ind.*, **1998**, *3* (4–6), 30–38.
- [18] CNI. *Economia Circular: Caminho Estratégico Para a Indústria Brasileira*; Confederação Nacional da Indústria: Brasília, DF, 2019.