CHAPTER 1

EXPLORING THE POTENTIAL REUSE OF SLATE WASTE IN THE CERAMIC INDUSTRY: A CONTRIBUTION TO CIRCULAR ECONOMY AND ENVIRONMENTAL CONSERVATION

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ABSTRACT: Throughout the years, mining activity has had great importance for economic progress, despite its repercussions of generating significant amounts of waste, impacting sustainability and environmental conservation. The present study aimed to investigate the feasibility of using slate waste in ceramic processing, specifically through slip-casting techniques. By conducting detailed experimental procedures and characterization tests, the study seeks to provide insights into the suitability of slate waste as a substitute for conventional raw materials. Additionally, the study aimed to evaluate the technical properties and performance of ceramic pieces produced using slate waste, thereby addressing concerns about the quality and applicability of such materials in practical applications. Slate rejects collected from quarries were characterized and ceramic pieces were produced by slip casting. The cast green and sintered samples were characterized by density, pore size distribution by mercury porosity, surface area evaluation, X-ray diffraction techniques, and scanning electron microscopy. The X-ray results, when confronted with thermal analyses, have shown major structural transitions at approximately 550ºC and 850ºC. The studies of porosity and density of pieces, before and after heat treatment, provided a better understanding of the slate sintering process. The results indicate that the density decreases after heat treatment and the pieces show a volume reduction due to slate reactions. Compacts formed by slip-casting different suspensions showed an average pore size of approximately 0.72 mm, suggesting that the structural changes that occurred in the slate greatly influenced the porosities and densities of the resulting materials. The results allow us to infer that slate powder from rejects has a great potential for being recovered, recycled, and applied in ceramic processing, producing various ceramic products. These products encompass a wide range of applications, including but not limited to sanitary ware, decorative pieces, and architectural elements.

KEYWORDS: Slate waste, Material reuse, Recycling, Ceramic processing, Sustainability.

INTRODUCTION

Different society segments have been devoting attention to slate waste treatment techniques and recycling, especially universities, tech institutes, and industries, focusing on the massive amount of waste produced in its extraction sites. These rejects are almost always incorrectly disposed of by the respective companies, contributing to environmental degradation.

Brazil is accounted for its varied geodiversity, supporting its worldwide importance as an exporter of ornamental rocks. Truly, the country is the third largest slate producer and exporter, with the state of Minas Gerais accounting for about 90% of this production (approximately 0.4 million tons/year) and almost all Brazilian exports. Slate derivates from Minas Gerais unfold into approximately 18 million square meters of slabs, tiles, pool countertops, roofs, and other products, according to Abirochas (2018). The natural slate extraction, cutting, and polishing process is extremely wasteful and its reject stream from quarrying is not properly managed in the present day. According to Oti, Kinuthia and Bai (2010) finished pieces derived from slate have shape and size requirements that make it unfeasible to use all extracted raw material, so only around 10% end up entering the production process, and even less reach the final phases. Frias *et al*. (2014) report that slate used in civil construction generates between 75% and 90% in weight of waste, and one possible way of reusing it is through thermal activation and manufacturing new cementitious materials. The large amounts of engendered slate waste happen because of many variables: poor extractive and processing activity technological profile; research deficiency on qualifying new mining fronts; lack of boulder-type slate exploitation; resistance to directing sales to the foreign market as long as the domestic one, which would be more profitable allied to public-private partnerships to promote less bureaucratical processes, to name a few. All of those result in an excessive quantity of rejects – small pieces of irregularly shaped or liquid-effluent rocks, and also mud from cutting and polishing processes (Palhares, Santos and Hunter, 2016).

The waste produced annually by Brazilian slate industries is nearly 0.3 million tons (Oti, Kinuthia and Bai, 2010). It is composed mainly of water, lubricants, crushed rock, and slate fragments. The production of alternative materials with the slate waste brought as a constituent to the rock manufacturing industries may reduce or even eliminate pollution in the extraction areas, aside from promoting new job opportunities and income – essential to the country's progress and development. Many studies have reported the production of new materials with slate waste through traditional ceramic processes, such as pressing, extrusion, slip casting, and others. In Palhares *et al*, (1997) work, there were several slate bricks produced by pressing and heat-treating the samples up to 1000°C. Their compressive strength tests showed that bricks have great potential for use in civil construction. Catarino *et al*. (2003) used residue powders from cutting and machining operations in slate quarries to produce flooring and roofing tiles by a press (at 40 MPa) and sintering route (up to 1150 °C). The authors showed that the properties of the products obtained were suitable for flooring tiles. Cambronero, Ruiz-Roman and Ruiz-Pietro (2005) obtained foams (porous ceramic) without any foaming agent addition and, according to them, the resulting material reaches adequate strength after the transformations suffered by the slate components during heating. Silva and Peres (2006) investigated the pozzolanicity of slate wastes and confirmed such activity with calcinated slate samples but not with natural ones. They proposed the use of slate wastes in the cement industry as mineral addition in partial substitution to Portland cement clinker. Snelson *et al.* (2010) reviewed the potential of using slate waste and suggested the great potential for using slate waste in many situations, including engineering applications despite reported transportation difficulties. Generally, the use of slate wastes is feasible and could minimize the environmental impact of their disposal but in countries with a large territorial area such as Brazil, without an adequate railway network, this transport can increase costs and make their use impracticable for ceramic industries. Zhen, *et al,* (2018) processed the slate wastes to form ceramsite slate, a kind of artificial foam, similar to that obtained by Cambronero, Ruiz-Roma and Ruiz-Pietro (2005). The ultra-light ceramsite could be directly used as building aggregate since its properties were shown to be superior to other ceramsites. At present, mercury intrusion porosimetry (MIP) is still today the reference experimental method to obtain the pore size distribution of dry samples of porous media (Cieszko, Kempinski and Czerwinski, 2019), despite its environmental health and safety concerns. Some substantial benefits of this extensively used technique include the relatively fast measurements, the possibility of covering a large range of pore sizes, i.e., from 10^{-9} up to 10^{-3} m (Zhang, *et al,* (2016), and the richness of accessible databases.

In the present work, the utilization of slate waste in ceramic processing was examined, emphasizing its feasibility as an alternative resource and its potential contributions to sustainability and resource conservation. This initiative aimed to enhance economic efficiency while concurrently addressing the issue of overexploitation of clay quarries. The pore structure of ceramic pieces manufactured via slip casting was evaluated. Characterization tests, utilizing Mercury Intrusion Porosimetry (MIP) techniques, were conducted before and after burning to investigate morphology modifications and pore structure changes during thermal treatment.

EXPERIMENTAL PROCEDURE

The slate powder used in this work was kindly donated by the Company Micapel Slate, located in the city of Pompeu, state of Minas Gerais, and was produced via block extraction for the production of slabs, floors, and roofs.

It was pre-treated before characterization to remove impurities such as organic waste and lubrification contamination. The steps of this treatment were: preparing for powder suspension in distilled water, wet sieving with the #400 sieve; 24-hour decanting; siphonation (water removal), and oven drying at 120°C for 24 hours.

Powder composition and crystallinity were determined with a diffractometer XRD Philips - X-Ray Generator, No. DY 1308, type PW 1730/10 with Cu-K_a rad radiation, 35kV, goniometer speed of 0,02°/min in 2θ per step, with a 5 seconds per step time count and collection from 5° to 80° in 2θ. For the refinement, the General Structure Analysis System Program (Larson and Von Dreele, 2001) was employed with the EXPGUI interface, using the Thompson-Cox-Hastings pseudo-Voigt profile function, with background radiation adjusted by the Chebyshev polynomial**.** The mineralogical analysis of the slate powder was obtained through refinement by the Rietveld method. The adjustment parameters c2, $R_{p,}$ and R_{wp} for the analyzed samples were 5.5%, 5.6%, and 6.6%, respectively. The semi-quantitative analyses were carried out on a Shimadzu 7000, model EDX-720 equipment.

SEM images were obtained with a Scanning Electron Microscope LEO/Zeiss 1530 (LEO Elektronmikroskope GmbH, Germany) joined with energy dispersive spectroscopy (EDS). The slate particles were suspended in water and a few drops of these suspensions were added to the stub and dried at 60°C. After that, the samples were uniformly coated with gold.

Thermogravimetric analyses were performed on a Shimadzu TA 50-WSI heat analyzer. The analysis was carried out in the temperature range of 20 °C–1150 °C with a heating rate of 10 K min^{-1} under air atmosphere. The slate powder suspensions in distilled water were prepared with solids percentages varying from 48%w/v to 78%w/v (suspensions 1 to 3) and homogenized with a magnetic stirrer for 24 hours. Ammonium polyacrylate (pureness degree – 98%) was used as a dispersant (varying from 1%v/v to 2.5%v/v – suspensions 4-6) and poly (vinyl alcohol) as a binder (pureness degree – 99.8%, varying from 1%v/v to 2.5%v/v – suspensions 7-9); both chemicals were purchased from Aldrich and used as received.

For the manufacture of plaster molds, preforms were used and cut into sizes of about 2 inches in length. The molds were obtained with plaster to water ratio of 70 (100 g gypsum to 70 mL of water), and the mixture was stirred for 1 minute and poured into the pre-mold to form the wish piece structure. After curing the mold, it was dried at room temperature for 15 days before use.

After casting, the pieces were dried at room temperature for 24 hours, followed by oven heating at 100˚C and finally heat-treated in an electric furnace at the temperatures 500ºC, 700ºC, 1000ºC, 1050ºC and 1100ºC with a 10ºC/min heating rate in air. The green sample is generally referred to as *"cast"* since it is measured before heat treatment. The *as-cast* and after-sintering densities were determined by a helium pycnometer (Multipycnometer – Quantachrome). The Auto Pore III 9420 (Micromeritics) was used to measure the mercury penetration porosimetry, for determining pore size distributions. Both low-pressure (0 to 345 kPa) and high-pressure (345 MPa to 414 MPa) penetration volumes were measured and collected automatically. A computer program was used to combine the low-pressure and high-pressure data and to convert the volume-pressure data to volume-diameter data. The BET method (Autosorb-1, Quantachrome), based on the N_2 adsorption model (at 77 K), was used to evaluate the average surface area.

RESULTS AND DISCUSSION

Powder Characterization

SEM images of the slate powder (Figure 1) show agglomerated particles having sizes ranging from 10 to 30 mm. There were different shapes identified among the particles, isotropic and laminar, with the appearance of leaves or small plates due to the large variety of minerals present in the slate.

The density values found via helium pycnometer and surface area analysis via nitrogen adsorption were, respectively, 2.76 $g.cm^{-3}$ and 12.3 $m^2. g^{-1}$.

EDX analysis of the powder indicated abundant contents of SiO_2 (61.6%), Al_2O_3 (16.6%), K_2O (10.8%) and Fe_2O_3 (5.9%). These four oxides are the major constituents of slate. Catarino *et al*. (2003) found comparable values using the chemical analysis by FRX and reported the presence of 54.68% SiO_2, 9.95% Fe_2O_3, and 23.52% Al_2O_3. According to Cambronero, Ruiz-Roman and Ruiz-Pietro (2005) the chemical composition of the slate powder consists mainly of SiO_2 (50–60%) and Al_2O_3 (20–25%) and the XRD analysis of the powder showed peaks corresponding to the following constituents: quartz, hematite, chlorite, and muscovite.

The XRD analysis of slate powder identified the components: (Q) Quartz - SiO_2 (29,6%), (C) Chlinoclore (19,2%), (M) muscovite (29,0%), (A) Albite (14,5%), (Ca) Calcite (1.8%), and (O) Orthoclase (5,9%) with errors 0,5; 0,4;0,4;0,7;0,7;0,4 respectively.

Comparing the chemical and mineralogical analyses, it is generally observed that silica (SiO_2) is the dominant mineral present in quartz, phyllosilicates (micas and chlorites), and feldspars. Alumina (Al_2O_3) is mainly contained in phyllosilicates and, to a lesser extent, in feldspars, the same way as sodium and potassium oxides. Part of the potassium is present in muscovite, and the magnesium oxides originate from the clinochlore and the magnesium calcite.

Brazilian slate samples reported elsewhere displayed values similar to those found in this work. The values were 26-30% quartz, 32-34% mica, 18-20% chlorite, 12-15% feldspar, and 0.5-1% carbonates. Campos, Velasco e Martinez (2004), Chiodi Filho, Rodrigues e Arthur (2003) and Frias *et al*. (2014) also mention the presence of chamosite, quartz, muscovite, and feldspar.

The values obtained for the parameters c2, $R_{p,}$ and R_{wp} refinements all fall within the range observed for natural multi-mineral systems, as demonstrated by Hill, Tsambourakis and Madesen (1993), Mumme *et al.* (1996) and Weidler *et al.* (1998).

The thermal analysis showed the main transitions of slate powder. At transition at 578ºC, it may be assigned to the allotropic transformation of quartz and clinochlore and muscovite dihydroxylation. Around 740˚C, the muscovite and clinochlore elements lose their lattice structure, and around 889ºC, the calcite is decomposed. The mass losses associated with the described events were, respectively, 1.5%, 3.2%, 1.6%, and 0.87%.

Characterization of pieces

Table 1 shows the bulk density and volume reduction for the pieces obtained. Suspensions 1 to 3 confirm that when the solids percentage increase, the green density increases, due to the larger number of particulates in suspension, leading to less water release during the casting process. Conversely, when the dispersant percentage increased (suspensions 4 to 6), the green density decreased. This is explained by the particles being further apart, due to the increasing amount of dispersant used. When comparing the suspensions 1 to 3 with 4 to 6, the density found is higher in the latter set. In these cases, the dispersion is more effective inducing a slower deposition of the particle, which renders filling the empty spaces more effective, resulting in higher densities. This suggests that the binder could be competing with the dispersant in the surface particle, resulting in a less effective dispersion and an attraction between the slate particles, leading to lower densities. The use of the binder to obtain “as cast” pieces with adequate handling strength was adverse to the bonding process. For suspensions 7 to 9, the density is always higher than other suspensions due to the binder, which promotes particle bonding. By increasing the binder fraction, the green density decreases. It was also observed density reduction for all suspensions subsequently to the heat treatment.

When assessed, the density values were distant from the natural slate stone theoretical estimates, and these deviations could be caused by the thermal expansion of clinochlore and muscovite constituents. Along with it, there was an 8-10% weight loss caused by outgassing and volatile decomposition.

The pore distribution curves for the slate samples obtained through mercury porosimetry after casting, across all suspensions, reveal a tendency towards the macroporous range with a higher average size, corroborating with the density values.

The pore size distribution curves before and after heating of the suspensions prepared with different solids percentages and with constant dispersant and binder showed similar behavior. Before the heat treatment, the curves are not monomodal and the pore size range is relatively wide. The highest porosity range for green pieces is around 0.1 to 1mm. As the percentage of solids increased, the average pore diameter decreased from approximately 0.72 to 0.45mm, suggesting that the particle cluster was different and more efficient when the percentage of solids was increased. These values are consistent with the density growth, which in turn occurs along with the increase of solids percentage.

After the heat treatment, the distribution becomes relatively narrower and shifts to an average pore size of approximately 0.72 mm. This may be explained by crystal transitions and slate dihydroxylation. This process is not homogeneous, and it occurs in two steps. The first stage occurs at about 500ºC and involves transitions related to interlayer water loss, whereas the second phase is caused by dihydroxylation and takes place at approximately 700ºC (Guggenheim, Chang and Van-Gross, 1987). Furthermore, at high temperatures, changes in lattice structure could be taking place so that the tetrahedral sheets become hexagonal and fully extended onto their sides, resulting in structure expansion (Hazen, 1997).

For all samples, the porosity observed varied between 1 and 0.1 mm after the heat treatment. This suggests that changes in additive and solids percentages did not have an accentuated effect on the pore size distribution of the pieces and the structural transformations on the slate are primarily responsible for the bulk residual porosity. The thermal treatment reduces the total porosity but not quite the pores' size. These results are consistent with some clays that burn up to 1000ºC and show a porosity increase as a result of the loss upon ignition, related to the decomposition of clay minerals and organic materials (Shu, *et al.,* 2012).

Usually, higher densities are related to smaller volume reductions; however, in this case, the green density is not the only factor influencing the volume shrinkage after the heat treatment. The structural changes that occurred in the slate at higher temperatures have a significant effect on the final properties of the ceramic pieces obtained through slip casting.

The structural changes describe the complex thermal transformations of the phase minerals of which the slate is formed. Many authors have studied the slate and reported its mineral reactions. Sanchez-Soto *et al.*, (2010) reported that chlorite and muscovite disappear at around 800ºC and quartz is undragged, making this process exothermic. An increase in expansion up to 1020ºC was interpreted by a bloating effect, caused by trapped gases in the pores and the release of oxygen gas, being the latter characteristic of raw materials containing iron oxides. All reactions promote a piece expansion, reducing the final density and increasing porosity.

According to Moura and Grade (1977) slate residual pores are due to the thermal expansion resulting from gases formation - CO_2, SO_3, and H_2O - accumulated in gas pockets, gases which are derived from the decomposition of organic matter, hydrous fine-grained phyllosilicates, such as illite, chlorite, muscovite, calcite, and hematite. Some of the evolved gases could become sealed inside the inorganic mass constituting the fired slate piece. The reactions that promote slate expansion take place within the temperature range of 400ºC-820ºC, and essentially consist of the aforementioned evolved gases; from 820ºC onwards the vitrification phase is initiated and progressively developed, resulting in the formation of an essentially alkaline alumino-silicate glass that provides gas retention in the most internal parts of black slate pieces. The slate expansion increases up to 1050ºC-1150 ºC, being the highest when the temperature reaches the maximum temperature value. As far as temperature increases and provides gas dilatation, this gas phase presses the glassy material that acquires and develops plasticity and elasticity. Gases can migrate up to the external surfaces of the slate pieces and escape to the kiln atmosphere (Costa, Almeida e Gomes, 2013).

The density and pore size of green compacts produced through slip casting are also influenced by the dispersion state of powder particles in suspension. The development of agglomerates may be controlled by adjusting the pH. Meanwhile, the dismantling of agglomerated particles may help obtain pieces with higher density and lower porosity. In addition, the thermal treatment at higher temperatures may form a liquid phase and fill the existing voids in the slate pieces, reducing the initially present porosity in the green fraction.

Table 1 shows the porosity of the samples before (green samples) and after heat treatment. As expected, all samples showed a porosity reduction after heat treatment. The remaining porosity is due to the structural modifications suffered by the slate, as discussed above.

The ceramic slate pieces' porosities presented a substantial value to all suspensions. Suspension 7 offered the best values, which can be associated with a more dispersed suspension and lower binder and dispersant concentrations, hence reducing agglomerates. In the case of suspensions formed by different minerals, their stability depends on each component's physicochemical surface characteristics. Their contribution depends on their relative quantity as well as their surface reactivity towards the other elements of the system. The minerals present in the slate have very different surface characteristics regarding their acidity/basicity concerning water. Therefore, it is inferred that suspension 7 was the most stable among those investigated in this work.

The series of SEM images in Figure 2 exhibits the microscopic evolution of the pieces obtained after heat treatment of suspension 7 at temperatures from 500ºC to 1100ºC. Figure 3 illustrates the corresponding evolution of the diffractograms.

From the SEM analysis, it was noticed that after burning, the samples acquired a smoother surface, making them less porous and stronger than the respective green pieces.

At elevated sintering temperatures, the presence of a liquid phase was perceived, but it was not enough to fill the pores (Costa, Almeida, and Gomes, 2013).

From X-ray diffraction results, it was possible to identify important reactions that occurred in slate pieces. New phases were identified, such as gehlenite, hercynite, and spinels. According to Binda *et al.* (2020), the presence of these minerals was anticipated, due to the presence of calcite in the raw material. The gehlenite is formed by reacting calcium oxide with Si and Al from the clay decomposition. At temperatures up to 500ºC, the slate powder does not change. Starting at 700ºC, the peaks referring to muscovite and clinochlore begin to disappear due to the release of structural water present in these minerals and the modifications in their crystalline structures. This observation is confirmed using differential thermal analysis with peaks between 700ºC and 800ºC. At temperatures above 1000ºC, the presence of the amorphous phase is evidenced by the area under the peaks, due to a low-melting liquid phase formation (Palhares *et al.,* 2006).

The rise in temperature during the thermal process provides a reduction in surface area and the number of pores and voids (Table 2).

CONCLUSIONS

An experimental study was conducted to investigate the use of slate waste powder to produce ceramic pieces via the slip-casting process. It evaluated the influence of residue on the density and porosity of the pieces in temperatures until 1100oC.

Employing the slip-casting technique with slate waste as a raw material opens up avenues for the production of various ceramic products. These products encompass a wide range of applications, including but not limited to sanitary ware, decorative pieces, and architectural elements. The utilization of slate waste not only offers economic benefits but also contributes to sustainability by reducing the exploitation of clay quarries and facilitating the recovery of slate waste. By harnessing this alternative resource, the ceramic industry can diversify its product portfolio while minimizing its environmental footprint. The investigation underscores the potential of slate waste as a viable raw material in ceramic processing, highlighting its significance in promoting resource conservation and advancing sustainable practices within the industry.

The major constituents of slate powder were identified by X-ray diffraction as quartz, muscovite, and clinochlore not presenting different components of slate stone.

The studies of porosity and density of slate ceramic pieces, before and after heat treatment, provided a better understanding of the slate sintering process. The results indicate that the bulk density decreases after heat treatment and the pieces show a volume reduction due to slate reactions. Compacts formed by slip-casting different suspensions showed an average pore size of approximately 0.72 mm, suggesting that the structural changes that occurred in the slate greatly influenced the porosities and densities of the resulting materials.

Based on XRD results and thermal analysis of the slate samples and burned ceramic pieces, it was possible to identify several important alterations during the burn, which may have contributed to the porosity surge. Evaporation of free water, both physically and chemically adsorbed (at 250ºC and 320ºC, respectively), dihydroxylation of clays with the elimination of structural water (muscovite and clinochlore, 570ºC–580ºC), and calcite decomposition with CO_2 release (800ºC–950ºC) are all events which increase porosity.

The use of slate as a raw material has great potential due to its physical and chemical properties, them being similar to natural clays. Its powder may be used: in extrusion processes to produce tiles and bricks; as a filler in various ceramic processing; as a concrete aggregate; and, if heat treated, may be employed as a light aggregate, in the production of artificial stone materials for many applications.

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REFERENCES

[1] ABIROCHAS - Associação Brasileira da Indústria de Rochas Ornamentais. Brasília, DF. Disponível em: https://abirochas.com.br/wp-content/uploads/2022/01/Informe_05_2018_Setor_de_Rochas_Ornamentais_c.pdf. Accessed: 07 Jan. 2022.

[2] OTI, J. E.; KINUTHIA, J. M.; BAI, J. Unfired clay masonry bricks incorporating slate waste. W. Res. Management, Leeds, v. 163, p. 17-27, Fev. 2010. DOI10.1680/warm.2010.163.1.17. Available in https://doi.org/10.1680/warm.2010.163.1.17

[3] FRIAS, M. VIGIL-DE-LA-VILLA, R. GARCIA, R. SOTO, I. MEDINA, C. SANCHEZ-DE-ROJAS, M.I. Scientific and technical aspects of blended cement matrices containing activated slate wastes. Cem Concr Compos. v. 48, p. 19-25. Apr. 2014. DOI10.1016/j.cemconcomp.2014.01.002. Available in: https://doi.org/10.1016/j.cemconcomp.2014.01.002.

[4] PALHARES, L. B., DOS SANTOS, C.G. AND HUNTER, T.N. Study of citric acid dispersant in the settling behavior of slate powder suspensions. Int J Miner Process, Amsterdam, v. 150, p. 39-46, May 2016. DOI. doi.org/10.1016/j.minpro.2016.03.005. Available in: https://doi.org/10.1016/j.minpro.2016.03.005

[5] PALHARES, L.B., CARDOSO, A. V. Experiments with slip casting of fine ceramics and v-SiO2. In: Gazzinelli, R. Moreira, R. L., Rodrigues, W. N. (org.). Proceedings of Second International Conference on Physics and Industrial Development – Bridging the Gap. Singapore: World Scientific, 1996. v. 1. p. 332-337.

[6] CATARINO, L., SOUSA, J., MARTINS, I. M., VIEIRA, M. T., OLIVEIRA, M. M. Ceramic Products Obtained from Rock Wastes. J. Mat. Proc. Tech. Amsterdam, v. 143-144, p. 843-845, c1990, 2003. DOI10.1016/S0924-0136(03)00341-8. Available in: https://doi.org/10.1016/S0924-0136(03)00341-8.

[7] CAMBRONERO, L.E.F. RUIZ-ROMAN, J.M. RUIZ-PIETRO, J.M. Obtentión de espumas a partir de resíduos de pizarra. Bol. de La Soc. Esp. Cer. y Vid. Madrid, v. 44 (6), p. 368-372. DOI10.3989/cyv.2005y44.i6.330. Available in: https://doi.org/10.3989/cyv.2005y44.i6.330.

[8] SILVA, M. E. M. C. PERES, A. E. C. Thermal expansion of slate wastes. Miner Eng. New York, v.19, p. 518-520, 2006. DOI10.1016/j.mineng.2005.10.008. Available in: https://doi.org/10.1016/j.mineng.2005.10.008.

[9] SNELSON, D. G. OTI, J. E. KINUTHIA, J. M. BAI, J. Applications of slate waste material in the UK. W. Rec. Management. Leeds, v. 163, p. 19-15, 2010. DOI10.1680/warm.2010.163.1.9. Available in: https://doi/10.1680/warm.2010.163.1.9

[10] ZHEN, L. et.al. Manufacturing of Ultra-light Ceramsite from Slate Wastes in Shangri-la, China. J. K. Cer. Society. Seul, v. 55, n.1, pp. 36-43, 2018. DOI10.4191/kcers.2018.55.1.02. Available in: https://doi.org/10.4191/kcers.2018.55.1.02.

[11] CIESZKO , M., KEMPINSKI, M., CZERWINSKI, T. Limit models of pore space structure of porous materials for the determination of limit pore size distributions based on mercury intrusion data. Transp. Porous Media, Springer, v. 127, p. 433-458, 2019.

DOI:10.1016/j.juogr.2016.02.002. Available in: https://link.springer.com/article/10.1007/s11242-018-1200-5.

[12] ZHANG, L. et al. Effect of shearing actions on the rheological properties and mesostructures of CMC, PVP and CMC + PVP aqueous solutions as simple water-based drilling fluids for gas hydrate drilling. J. Unconv. Oil Gas Resour, Elsevier, v. 14, p. 86–98, 2016. DOI10.1016/j.juogr.2016.02.002. Available in: https://doi.org/10.1016/j.juogr.2016.02.002.

[13] LARSON, A. C.; VON DREELE, R. B. General structure analysis system (GSAS). Los Alamos National Laboratory, Los Alamos, EUA, Copyright, 1985-2000, The Regents of the University of California, 2001.

[14] CAMPOS, M. VELASCO, F. MARTINEZ, M. A. TORRALBA, J. M. Recovered slate waste as raw material for manufacturing sintered structural tiles. J. Eur. Cer. Soc. Oxford-UK, v. 24, p. 811-819, 2004. DOI10.1016/S0955-2219(03)00325-X. Available in: https://doi.org/10.1016/S0955-2219(03)00325-X.

[15] CHIODI FILHO, C. RODRIGUES, E. P. ARTUR, A.C. Ardósias de Minas Gerais, Brasil: Características Geológicas, Petrográficas e Químicas. Geociências. São Paulo, v. 22, n.2, p. 119-127., 2004. Available in: https://www.researchgate.net/publication/237351262_Ardosias_de_Minas_Gerais_Brasil_caracteristicas_geologicas_petrograficas_e_quimicas. Accessed on 25 Jan. 2018.

[16] HILL, R.J., TSAMBOURAKIS, G., MADESEN, I.C. Improved petrological modal analysis from X-ray powder diffraction data by use of the Rietveld method. I. Selected igneous, volcanic, and metamorphic rocks. J. of Petrology. Oxford-UK, v.35, p. 867–900, 1993. DOI10.1093/petrology/34.5.867. Available in: https://doi.org/10.1093/petrology/34.5.867

[17] MUMME, W.G., TSAMBOURAKIS, G., MADSEN, I.C., HILL, R.J. Improved petrological modal analysis from X-ray powder diffraction data by the use of the Rietveld method. II. Selected sedimentary rocks. J. Sediment. Research. Tulsa, v. 66, p.132–138, 1996. DOI10.1306/D42682D4-2B26-11D7-8648000102C1865D. Available in: https://doi.org/10.1306/D42682D4-2B26-11D7-8648000102C1865D

[18] WEIDLER, P.G., LUSTER, J., SCHNEIDER, J., STICHER, H., GEHRING, A.U. The Rietveld method was applied to the quantitative mineralogical and chemical analysis of a ferritic soil. Eur J Soil Sci. Oxford-UK, v. 49, p. 95–105, 1998. DOI10.1046/j.1365-2389.1998.00138.x. Available in: https://doi.org/10.1046/j.1365-2389.1998.00138.x

[19] GUGGENHEIM, S.; CHANG, Y., VAN-GROOS, A.F.K. Muscovite dehydroxylation: High-temperature studies. American Mineralogist. Chantilly, v. 72, p. 537- 550, 1987. Available in: https://rruff.geo.arizona.edu/doclib/am/vol72/AM72_537.pdf

[20] HAZEN, R.M. Temperature, pressure, and composition: structurally analogous variables. Phys Chem Miner. Berlin, v. 1, p. 83-94, 1997. DOI10.1007/BF00307981. Available in: https://doi.org/10.1007/BF00307981.

[21] SHU, Z. GARCIA-TEN, J. MORNFORT, E. AMOROS, J. L. ZHOU, J. WANG. Y. X. Cleaner production of porcelain tile powders - Fired compact properties. Ceram Int. Oxford-UK, v. 38, p. 1479-1487, 2012. DOI10.1016/j.ceramint.2011.09.031. Available in: https://doi.org/10.1016/j.ceramint.2011.09.031

[22] SÁNCHEZ-SOTO, P. J. RUIZ-CONDE, A. BONO, R. RAIGÓN, M. GARZÓN, E. Thermal Evolution of a Slate. J. Ther. Anal. Cal. Springer, v. 90, p. 133–141, 2007. DOI10.1007/s10973-007-7751-2. Available in: https://doi.org/10.1007/s10973-007-7751-2.

[23] MOURA, A. C., GRADE, J. As argilas do jazigo de Aguada de Cima: síntese dos resultados do seu estudo tecnológico aplicada à exploração. Boletim de Minas, 1977. Available in: https://repositorio.lneg.pt/bitstream/10400.9/2427/1/34246.pdf

[24] COSTA, J. C.; ALMEIDA, T.; GOMES, C. S. F. Ardósia piro-expandida em arte escultórica. Cerâmica. São Paulo, v. 59, n. 349, p. 134-140, mar. 2013. DOI: 10.1590/S0366-69132013000100015. Available in: https://doi.org/10.1590/S0366-69132013000100015

[25] PALHARES, L. B., DOS SANTOS, C. G., OLIVEIRA, V. A., FORTULAN, C. A., BINDA, F. F. Friction elements based on phenolic resin and slate powder. J Mater Res Technol. Elsevier, v. 9, n. 3, p. 3378-3383, 2020. DOI 10.1016/j.jmrt.2020.01.032. Available in: https://doi.org/10.1016/j.jmrt.2020.01.032

[26] PALHARES, L.B., MANSUR, H.S. Production and characterization of ceramic pieces obtained by slip casting using powder wastes. J Mater Process Techno. Amsterdam, v.145, p.14-20, 2004. DOI10.1016/S0924-0136(03)00857-4. Available in: https://doi.org/10.1016/S0924-0136(03)00857-4

Sample number suspension	Green bulk density (g/cm^3) ± 0,1	Density after heat treatment (g/cm^3) ± 0,1	Volume reduction (%) (±1)	Green porosity (%) ± 0,1	Porosity after heat treatment (%) ± 0,1
1	2,1	1,9	17	56,9	46,9
2	2,4	2,2	19	56,5	45,7
3	2,5	2,4	19	55,4	43,5
4	2,7	2,6	23	59,6	44,6
5	2,5	2,4	23	63,4	45,4
6	2,4	2,2	22	64,7	41,1
7	3,5	2,7	24	50,5	39,8
8	3,4	2,6	25	50,9	43,4
9	3,1	2,4	26	52,9	46,5

Table 1: Green porosity/density of pieces and porosity/density after heat treatment,

Temp. (ºC)	Specific surface BET (m^2/g)	Total Vol. of Pores (cm^3/g)
100	12,26	0,0378
500	12,78	0,0365
700	9,99	0,0353
1000	4,76	0,0059
1100	4,22	0,0054

Table 2: Porosity and surface area of pieces after burning.