Recycling ceramic waste as a raw material in sanitary ware production

(Reciclagem de resíduo cerâmico como matéria-prima na produção de louças sanitárias)

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Abstract

This study characterized discarded sanitary ware waste (SWW) that could not meet quality requirements. To understand the composition of such SWW, samples were collected, processed, and characterized. This SWW was used to substitute granite in ceramic slips, and the final recycled sanitary ware compositions of 5%, 10%, 25%, 50% and 100% were obtained. Then, the mixtures were evaluated based on density, rheology, linear shrinkage, water absorption, and flexural strength. The results for viscosity and pyroplastic deformation in specimens containing the ceramic waste were better than the reference slip used in a production line. Results for density, water absorption and linear shrinkage showed no significant difference from the control samples. Although the replacement of more than 5% of granite reduced the flexural strength, no tested specimen was below the minimum value required by the industry.

Keywords: ceramic, slip casting, sanitary ware, waste, sustainability.

Resumo

Este estudo caracterizou o resíduo de louças sanitárias descartadas que não atendiam aos requisitos de qualidade. Para compreender a composição de tal resíduo, as amostras foram coletadas, processadas e caracterizadas. Este resíduo de cacos de louça cerâmica moídos foi usado para substituir o pó de granito utilizado nas massas cerâmicas em 5%, 10%, 25%, 50% e 100%. As misturas foram avaliadas quanto à densidade, reologia, retração linear, absorção de água e resistência à flexão. Os resultados de viscosidade e deformação piroplástica em barbotinas contendo resíduo foram melhores que a barbotina padrão empregada em um processo de produção. Resultados de densidade, absorção de água e retração linear não mostraram diferenças significativas em relação às amostras de controle. Ainda que a substituição de granito superior a 5% tenha reduzido a resistência à flexão, nenhum corpo de prova testado apresentou resistência abaixo do mínimo exigido pela indústria.

Palavras-chave*: cerâmica, colagem barbotina, louça sanitária, resíduo, sustentabilidade.*

INTRODUCTION

A significant type of industrial waste that requires attention is the ceramic waste, with the majority of this waste coming from the disposal of defective and broken ceramic pieces [1]. Studies of possible applications of the waste from the sanitary ware industry can, in addition to reducing the prevalence and environmental footprint of crushing yards, help reduce the cost of waste disposal. From the ecological point of view, the recycling of industrial wastes is becoming a priority, as a result of an ever-increasing environmental awareness [2]. In producing sanitary ware, despite any improvements made to the process, there is always a percentage deemed inappropriate for sale. The defects in rejected wares include imperfect shapes, cracks, and visual damage to the glaze, defects which do not alter the intrinsic properties of the ceramic material. Therefore, as it is classified as fired clay, this ceramic waste is a material with high strength and resistance to wear [1, 3]. In addition, according to the NBR 10004:04 solid waste classification [4], this ceramic waste is classified as inert, which facilitates its handling for reuse. On the other hand, the rejected ceramic pieces require comminution prior to reuse, and although this recycling process involves initial investment and energy consumption to grind and mill the waste, there are examples of recycling initiatives that are economically viable [5]. Several papers studied applications for sanitary ceramic waste, especially in the field of construction, as an aggregate to concrete [1, 3, 6-8]. However, the recycling of this type of waste as a raw material in the process responsible for generating it has not been thoroughly investigated, as there are no applicable standards yet on its reuse. The recycling of this ceramic waste back into its production process could have some advantages: it does not require high transportation costs; it could also decrease expenses in raw material consumption and waste disposal in landfills.

Independent of the type of ceramic being manufactured,

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the initial slip (or another kind of mix) includes three types of materials, hence the name 'triaxial ceramics', a plastic material (clays) which facilitates casting, a fluxing agent (feldspar) that assists melting and helps to vitrify the structure, and a non-plastic material (quartz) to provide structural strength [2]. Therefore, one of the first steps in recycling wastes into sanitary ceramics is determining which of the three behaviors the waste exhibits. When it comes to sanitary ware production, focusing on materials that are used in the ceramic slip, numerous parameters must be verified. These are typically achieved through characterization that determines the particle-size distribution, composition, crystalline phases and material morphology [3]. Furthermore, the ceramic slips must meet standards regarding density and viscosity, and the final product must be in accordance with standards for linear shrinkage, flexural strength, and water absorption [9-11]. This study evaluated the application of sanitary ware waste as a substitute for one of the standard raw materials used in ceramic slips for sanitary ware production. It is important to note that this study was performed by recycling a sanitary ware waste within an industrial process responsible for its production.

EXPERIMENTAL

Samples of rejected sanitary ware pieces were collected from an industry's landfill; these were crushed, and then pulverized by a planetary ball-mill with jar and beads of zirconia. The particle size distribution and humidity of the waste powder (WP) were determined, the first through laser granulometry (LG), and the second according to the NBR NM 24 standard [10]. The powder was also characterized by X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), and scanning electron microscopy (SEM). The LG analysis was performed under ambient conditions using water as a fluid, without a dispersant, 60 s of ultrasonication treatment and obscuration set to 17%. The XRF was performed under a regular air atmosphere and a collimator of 10 mm. The XRD measurements were performed using a copper X-ray tube with 40 kV accelerating voltage and 30 mA current in the continuous scanning mode with a 2θ range from 10° to 80° at a rate of 2 °/min. The SEM analyses were performed with low vacuum and magnification capacity up to 30000 times and a digital zoom factor of 4x, using an accelerating voltage of 15 kV and a backscattered electron (BSE) detector.

Subsequently, to determine which raw material the WP should replace in testing, the WP and the raw materials used by the industry were separately shaped into cones, which undergone the industrial firing process to compare their after-sintering structure. Once determined which material to be substituted, different formulations of ceramic slips were prepared and labeled according to the degree of substitution of granite by the WP, therefore the labels were WP-5, WP-10, WP-25, WP-50 and WP-100. All formulations applied in the tests, including the control, are described in Table I. Each slip was prepared as a water-based suspension, using 3000 g of dry raw materials, 1000 mL of tap water and 6 mL of dispersant (sodium silicate). The suspensions were pulverized in a ceramic ball-mill operating at 70 rpm for 1.5 h. Test specimens were made from each slip in a casting process using plaster molds. In order to evaluate how the WP substitution degree could influence the ceramic slips, tests of density, residue percentage (44 μm sieve), and rheology were performed, including tactile and detachment evaluations. Furthermore, the physicomechanical properties of ceramic specimens were determined through water absorption, three-point flexural strength for green specimens (before sintering), linear shrinkage and pyroplastic deformation. The density of the ceramic slips was determined by correlating weight and volume for 100 mL of a ceramic slip in a volumetric flask. The residue percentage, which represented the fraction of solids from a suspension that was retained after size exclusion through a 44 μm sieve, evaluated the degree of slip pulverizing.

Table I - Formulation of ceramic slips.
[Tabela I - Formulação das massas cerâmicas.]

Ceramic slip	Substitution degree (%)	Granite (%)	WP (%)
Control	0	22.50	0.00
WP-5	5	21.38	1.12
WP-10	10	20.25	2.25
WP-25	25	16.90	5.60
WP-50	50	11.25	11.25
WP-100	100	0.00	22.50

Note: in each slip, 13.50% of clay and 64.0% phyllite were used.

Rheology is one of the most important variables for ceramic slips, as it influences the flow of the material, which exerts a significant impact on pumping, thus affecting production [12]. The analysis on rheology consisted of tests of viscosity, setting rate and drying time. The first was measured using a dial-reading Brookfield viscometer, RV series, equipped with disc spindle number 2; for measuring the viscosity two speeds were applied, 50 rpm until the reading stabilized, let the slip rest for 5 min, then measuring it at 2.5 rpm. These values were recorded and converted to viscosity using the spindle factors associated with each rotating speed [13]; also, the ratio between the two measured viscosities was calculated to determine the thixotropic index for each slip [14]. The setting rate defines the speed at which a ceramic slip is accumulated on the porous surface of a plaster cast, while the drying time is the time required for excess water to be drained as the mass on the plaster cast loses its pearl shine. For this test, a plaster cast with an internal surface area of 509 cm^2 was filled with the ceramic slips, and after 2 min of setting the cast was drained. At this point, the deposited mass still had a pearl shine, which slowly became matte as the plaster absorbed water; the time taken for the ceramic mass to present a completely matte finish was recorded as the dying time. Simultaneously, the detachment and tactile evaluations were performed to assess the difficulty in removing a layer of accumulated material from the cast and to subjectively appraise consistency of the ceramic slip.

Finally, to analyze the physicomechanical properties of the fabricated materials, three types of test specimens were produced. Cylinders with 200 mm in length and 15 mm in diameter were used for the three-point flexural strength test. Tabular specimens of 290 mm length were measured immediately after slip casting and the values were compared to their lengths after drying and sintering for linear retraction. The third specimen, for testing pyroplastic deformation and water absorption, had a length of 290 mm, with double the thickness at the initial 100 mm (head) and tabular shaped for the remaining length (tail). The pyroplastic deformation test consisted of placing the head of the specimen between two layers of refractory material, while the tail was in suspension; this allowed the tail to deform as liquid-phase was produced during sintering; an increase in deformation represented an increase in the presence of liquid-phase, and thus correlating to flux material content in the mixes [15]. For water absorption tests, an 80 mm section of the specimen's tail was cut, weighted while dried, placed in boiling water for 2 h, rested in that water for 24 h, and then weighted again [11].

RESULTS AND DISCUSSION

After the comminution process, the powder generated from the ceramic shards had white color and a silky touch; also, it was very fine and presented a heterogeneous particle-size distribution. The humidity values obtained were satisfactory, since none exceeded the 5% limit [10]. The results from the LG analysis, presented in Fig. 1, showed that 90% of the sample particles were less than 34.9 μm in diameter, which had an average of 13.57 μm. These dimensions were in accordance with those for standard raw materials used in the ceramic industry [16]. The result of oxide composition obtained by energy dispersive X-ray (EDX) spectroscopy is listed in Table II. As expected, the composition of the WP reflected a mix of the raw materials used by the industry, with the addition of oxides from dyes used for glazing. Fig. 2 shows a well-defined presence of quartz phases (SiO_2, Crystallography Open Database - COD 9013321) [17] in the sample diffractogram. Mullite phase ($Al_6Si_2O_{13}$, COD 9001567) [18] was also detected; this is a stable phase accountable for mechanical strength in sintered clay minerals, and is formed starting at 950 ºC up to 1100 ºC [19], which are compatible with the firing curve in use by the industry that has a peak temperature of 1200 ºC. All phases were identified using the software Match! 3.

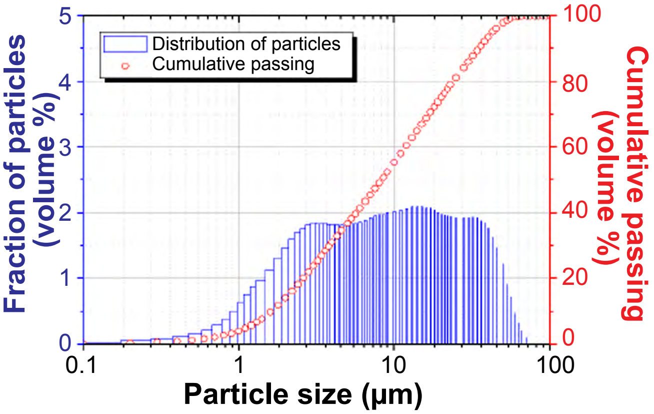

Figure 1: Particle size distribution curves of waste powder.
[Figura 1: Curvas de distribuição granulométrica do pó do resíduo.]

The particle morphology of the sanitary ware waste was observed through SEM analysis. The micrographs shown in Fig. 3 were in accordance with the LG analysis, as the material presented heterogeneous particle size distribution, with a significant fraction of lamellar crystals with sharp edges. Additionally, some particles had brighter shades of grey, which indicated a denser phase as a result of a higher atomic number; this was because the displayed brightness is a function of the material interaction with electron beam, and denser materials tend to have a higher signal in backscattered electron (BSE) analysis [20]. The test using firing cones made from each material demonstrated that the WP acted as a fluxing agent during sintering. In this test, cones made from phyllite and clays resulted in a 'sandy' texture that was easily crumbled apart, which is characteristic of refractory materials. In contrast, cones made from granite and WP presented flux material behavior, with very consistent structure and smooth texture, vitreous shine on the former and matte finish on the latter.

Table III shows that density values for all the ceramic slips; they were in accordance with the range commonly used in manufacturing processes, which is around 1.80 g/cm³ [21]. Additionally, when granite was replaced

Table II - Chemical composition of the sanitary ware waste and raw materials (in wt%).
[Tabela II - Composição química do resíduo de louça cerâmica e matérias-primas (% em massa).]

Material	SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	TiO_2	ZrO_2	ZnO	BaO	Cr_2O_3	Others
Clay A	50.80	31.40	4.56	10.22	-	1.95	0.33	0.05	0.50	-	0.25
Clay B	63.36	30.45	0.96	2.23	0.15	2.35	0.44	-	-	-	0.06
Phyllite	56.73	24.34	8.56	5.46	-	3.22	0.23	-	-	-	1.46
Granite	71.40	13.39	9.32	1.88	1.58	-	0.41	0.01	-	-	2.01
WP	64.53	21.47	5.42	3.51	1.50	1.43	1.08	0.58	0.27	0.06	0.15

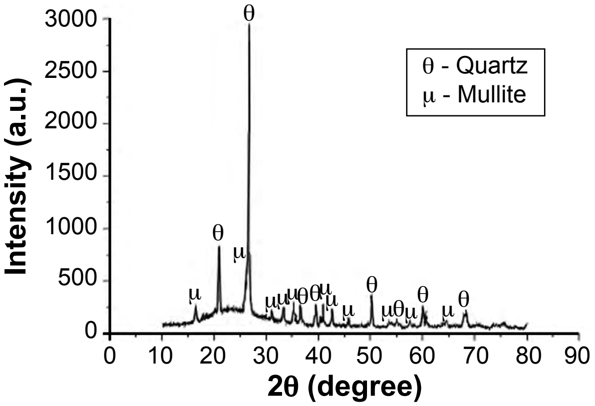

Figure 2: X-ray diffraction pattern of the sanitary ware waste.
[Figura 2: Difratograma de raios X do resíduo de louça cerâmica.]

by the WP in all formulations tested, the amount of residue retained on the 44 μm sieve was less than that observed for the control, possibly due to WP being pulverized prior to its characterization. Measurements of the viscosity and rheological properties showed significant deviation from the standard values exhibited by the control samples, as can be seen in Table III. The results showed that WP incorporation decreased the initial viscosity in most formulations, with the exception of WP-100; similarly, the thixotropy factor decreased with WP increase. In other words, as more WP was added to the mix, it experienced a lower increase in viscosity over time [22]. This is especially important for the production line, where the stabilization of ceramic slips is crucial and usually maintained through constant stirring. In contrast, when comparing setting rates, there was a direct relation to WP incorporation, with the rate increasing as a higher WP fraction was used in the mix. The results for drying times showed an initial decrease for formulations WP-5 and WP-10; this drying time remained constant for WP-25, increased for WP-50 and reached the same value for the control slip in WP-100. Moreover, during the tactile evaluation of these ceramic pastes, all samples were considered good and firm, which indicated that the suspensions did not become soft, pasty, or dry immediately after casting, and some plasticity remained in the mixes. It is worth noting that, for this later evaluation, the ceramic slip that most resembled the control

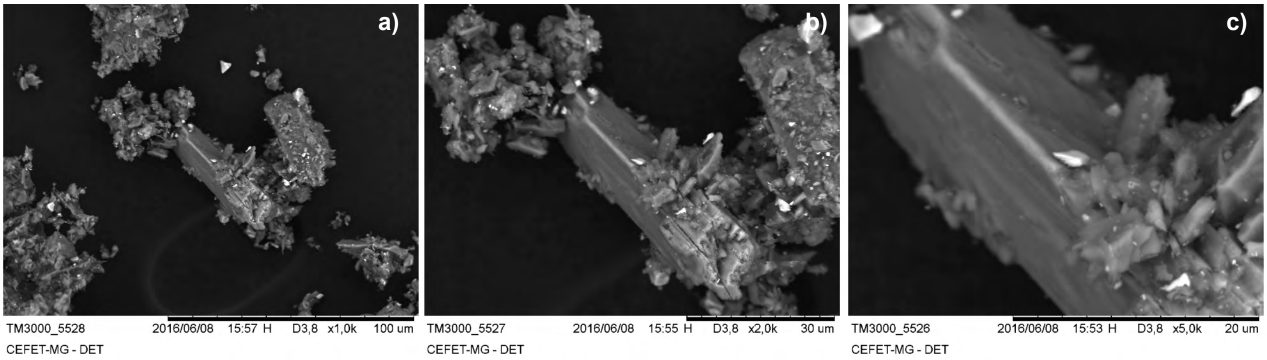

Figure 3: Scanning electron microscopy images of the sanitary ware waste.
[Figura 3: Imagens de microscopia eletrônica de varredura do resíduo de louça cerâmica.]

Table III - Characterization of ceramic slips and sanitary ware pieces.
[Tabela III - Caracterização das massas cerâmicas e peças de louça sanitária.]

Attribute	Control	WP-5	WP-10	WP-25	WP-50	WP-100
Density (g/cm^3)	1.81	1.81	1.81	1.80	1.81	1.80
Residue 44 μm (%)	9.1	6.7	8.5	4.7	5.6	4.9
Viscosity 50 rpm (cP)	640.0	429.6	480.0	496.8	464.8	724.8
Viscosity 2.5 rpm (cP)	4000	2452	2496	2416	2080	3088
Thixotropic index	6.2	5.7	5.2	4.9	4.5	4.3
Setting rate (g/cm^2/min)	0.152	0.153	0.163	0.157	0.158	0.194
Drying time (min:sec)	1:40	1:35	1:25	1:25	1:29	1:39
Tact and detachment	Good and firm (plastic)	Good and firm (plastic)	Good and firm (plastic)	Good and firm (plastic)	Good and firm (little plastic)	Good and firm (little plastic)
Drying shrinkage (%)	2.1	2.1	2.1	2.1	2.1	2.1
Firing shrinkage (%)	9.5	10.2	10.2	10.2	10.6	10.6
Total shrinkage (%)	11.4	12.1	12.1	12.1	12.5	12.5
Pyroplastic deformation (mm)	63	64	66	58	57	55
Water absorption (%)	0.09	0.05	0.10	0.11	0.06	0.11

was the WP-5.

While the drying shrinkage remained the same for all specimens, the total shrinkage increased for the WP formulations as a result of higher firing shrinkages. These results reflected the ones from firing cone tests, restating that the WP acted as a flux material, which formed liquid-phase during sintering and filled open pores, thus increasing the ceramic densification. Although the granite is also used as a fluxing agent by the industry, the smaller particles of the pulverized WP could have been responsible for easing liquid-phase formation [23]. The results for pyroplastic deformation showed no significant deviations from the control for formulations WP-5 and WP-10, while WP contents of 25% and above diminished the pyroplastic deformation. The fact that water absorption results did not show clear correlation to WP levels was due to standardized test of water absorption, which involves keeping samples in boiling water, not being able to ensure complete saturation of test specimens [24]; therefore, the values obtained from this test did not necessarily reflect a difference in surface porosity among the formulations. Nevertheless, all specimens were far below the limit of 0.5% for water absorption established by standard organizations [11].

Regarding three-point flexural strength of raw pieces, the incorporation of WP reflected a decrease in the average values (Fig. 4). Among the tested WP formulations, the one with the lowest WP content (WP-5) presented the highest flexural strength, which was statistically the same as the one obtained by the control (4.5 MPa). In order to avoid breakages during handling, the industry usually adopts 2 MPa as the minimum flexural strength for raw pieces [9]; consequently, regardless of the decreasing in strength, all WP formulations complied with the minimum requirement for flexural strength in an industrial scenario.

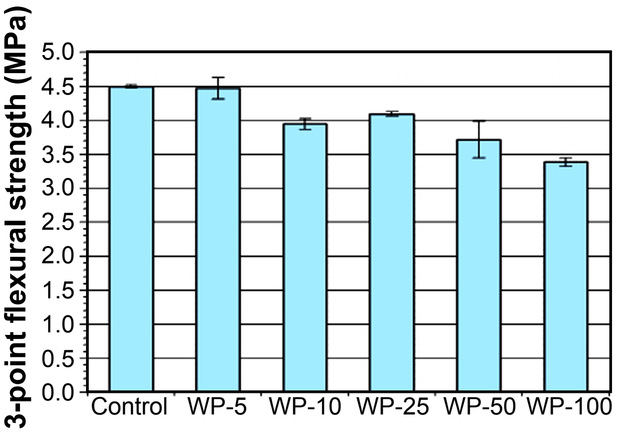

Figure 4: Flexural strength of test specimens.
[Figura 4: Resistência à flexão dos corpos de prova.]

CONCLUSIONS

This study showed that some parameters that define the quality of ceramic slips for use as sanitary ware were dependent on the degree of substitution of granite by waste powder (WP). Although drying time, residue percentage and linear shrinkage were similar to the control, flexural strength showed a decrease as more WP was added to the ceramic slip. On the other hand, the rheology tests showed that adding WP boosted rheological performance as a result of a lower thixotropy index. The flexural strength tests indicated that all formulations had values above the minimum strength required, with an excellent performance by the WP-5, which was statistically equivalent to the control. This is a decisive factor when it comes to applying recycled products for the production of new materials, where the goal is to produce a similar or better product. The results showed that the WP can replace up to 100% of the granite in formulations and still meet the industry's minimum requirements; however, a 5% substitution exhibited the best results and reflected the highest similarity to the mix design employed. Given that the fraction of sanitary ware that is discarded is usually slightly less than 5% of total production, applying the WP-5 formulation as a recycling process could significantly reduce the volume of broken pieces in the crushing yard and landfill; in addition, higher degrees of substitution could be enough to consume all the discarded pieces, thus reducing environmental impacts and costs of disposal.

ACKNOWLEDGMENTS

The authors would like to express their gratitude to Minas Gerais State Research Foundation (FAPEMIG APQ3739-16), the National Council for Scientific and Technological Development (CNPq), to the Brazilian Federal Agency for Support and Evaluation of Graduate Education (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil - CAPES) for their financial support in scientific initiation and master's degree scholarships (Finance Code 001); and to Santa Clara Louças Sanitárias Ltda for providing the materials and some of the equipment used in this study.

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(Rec. 30/10/2017, Rev. 26/11/2018, 26/01/2019, 04/03/2019, Ac. 07/03/2019)