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MECHANICAL AND THERMAL BEHAVIOR OF REFRACTORY CERAMIC COMPOSITES WITH SUBSTITUTION OF RICE HUSK ASH

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Abstract. *Rice husk ashes are agroindustrial residues produced on a large scale after the burning of rice husks for energy generation. The combustion of rice husks in a fluidized bed, with temperature control, is an efficient method to obtain the ashes, rich in silica in the amorphous state, becoming a substitution alternative for the production of refractory ceramic composites. This study aims to obtain refractory ceramic composites with good performance from the use of rice husk ash since this is a low-cost residue and does not yet have adequate disposal. Thus, percentages of 10, 15, 20 and 25% by weight of kaolin clay were substituted for rice husk ash for the production of the composites. For these composites, the thermomechanical properties were evaluated from the compression, three-point flexural and thermal shock tests. The results showed that the composites using substitution showed no improvement in the mechanical compressive behavior and the 10% substitution maintained the levels of tensile strength at three-point flexure. In relation to the thermal shock strength, all composites showed rupture in the first cycle of the test, evidencing a possible formation of internal stresses in the material, besides suggesting the necessity to reduce the aggressiveness of the test.*

Keywords: *rice husk ash, refractory ceramic composites, thermomechanical behavior.*

1. INTRODUCTION

Currently is crescent the worry with a complete production cycle, in which residues from a particular production may have appropriate destinations and has minimal impact on the environment. According to information from the *Instituto Riograndense de Arroz* (IRGA), in 2017 the state of Rio Grande do Sul produced more than 8 million tons of this cereal. In the processing of the rice, the husk is the residue, which have been used as fuel in dryers and in the generation of electric energy, as a source of biomass due to its high calorific content (Della et al., 2005). Thus, as a residue of this application, the rice husk ash (RHA) is obtained from the combustion of the rice husk in a fluidized bed with temperature control. In order to, properly destine the RHA, many researches has been performed for finding applicability for this residue. Della et al. (2001) obtained the characterization of the RHA and observed that it has a high content of amorphous silica and low levels of melting oxides, making this material a natural and renewable source of silica. The high percentage of silica in RHA and the small diameter of its particles contribute to its insertion in several areas of research, such as the production of composite cementitious, ceramic, polymer and electronic materials.

The use of new technologies to improve the incompatible properties of various materials, such as mechanical strength and toughness, has led to the appearance of new materials. Among these, it can be highlighted the composite materials, as they have several applications in industry, being used in order to improve productivity, reducing costs and positively adding to the mechanical properties of materials (Ventura, 2009).

Ceramic materials are a combination of metallic and non-metallic elements that have predominantly ionic atomic bonds and some covalent fraction. Because of this characteristic, there is a mutual attraction between the negative and positive ions, denoting a relatively rigid and resistant mechanical behavior (Callister and Rethwisch, 2012). The main

characteristic points of these materials are their high hardness, good mechanical strength, brittle rupture, high thermochemical stability and thermoelectric insulation potentiality (Isaia, 2010).

Among ceramic materials, refractory ceramics are an important category because they are indispensable for various industrial processes involving high temperatures (Della et al., 2001). Studies by Della et al. (2001) and Andreola, Barbieri and Bondioli (2012) demonstrate the effectiveness of using RHA as a beneficial substitution in obtaining silica to produce ceramics in order to improve its mechanical properties.

Nunes (2017) found increases in compressive strength and three-point flexural tensile strength to replace 20% of kaolin clay with rice husk silica, with an increase of 1.3% and 70.7%, respectively. Sobrosa et al. (2017) obtained an increase of the mechanical strength when evaluating the mechanical and thermomechanical properties of refractory ceramics in percentages of 5, 10 and 20% of substitution of the refractory clay by RHA. Based on the thermal shock tests, the authors concluded that the 20% substitution content caused the samples to fracture in smaller and shorter cycles, characterizing a less resistant ceramic. However, with 10% replacement there was an improvement in mechanical strength, without affecting thermal shock resistance.

In a similar way, Santos et al. (2018) incorporated RHA in percentages of 15 and 20% and steel fibers in volumetric percentages of 1 and 2% in refractory ceramic materials. The authors obtained a slight increment in mechanical strength, possibly due to the reduction of porosity, because the composite exhibited high packing density, or still, owing to the increase of the level of vitrification and higher material toughness.

In this context, the current study aims to develop refractory ceramic composites with good performance, using a low-cost raw material and providing a suitable destination for the RHA, which still is a residue without appropriate disposal. Therefore, were produced refractory ceramic composites in percentages of 0, 10, 15, 20 and 25% substitution of refractory clay by RHA, being evaluated mechanical and thermal behavior of the composites through compression, three-point flexural and thermal shock tests.

2. MATERIALS AND METHODS

2.1 Materials

For the production of the composites, the refractory kaolin clay (KC) by Helager Indústria e Comércio Ltda and the rice husk ash (RHA) supplied by the company Sílica Verde do Arroz (SVA) of the Pilecco Nobre Group were used as raw materials. Both compositions may be viewed in Tab. 1.

Table 1. Chemical composition for refractory kaolin clay (KC) and rice husk ash (RHA).

Element	Concentration (%)	
	KC	RHA
SiO_2	57.83	89.06
MgO	0.36	-
P_2O_5	-	0.84
SO_3	-	0.21
K_2O	1.87	2.99
CaO	0.13	1.18
MnO	< 0.01	0.53
Fe_2O_3	2.25	0.15
CO_2	-	4.30
Al_2O_3	27.52	0.74
Na_2O	<0.001	-
TiO_2	0.38	-

Adapted from Helager Ind. and Com. Ltda and Silva (2019).

Figure 1 shows the KC and RHA employed in this work, has particles of medium size of 11.01 μm and 5.93 μm, respectively.

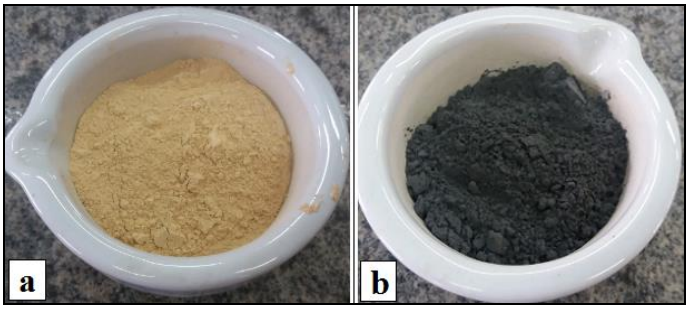

Figure 1. Raw materials used: (a) KC and (b) RHA.

2.2 Molding and conformation of specimens

As the raw materials have a very fine grain size, these were mixed manually until complete homogenization. Optimum moisture content was defined by varying the amount of water previously added to the pressing of the reference mixture. The pressing of the specimens was performed and their behavior was visually analyzed, checking if they had exudation, sharp edges, segregation, as well as by the control of the weight/height ratio. The blend that presented the best compaction in relation to the mass was the one for which the highest weight/height ratio was obtained. Thus, the 7% content was defined as the optimum mass water content to promote uniformity of the blend.

The conformation of the specimens was performed by uniaxial pressing, with the aid of an INSTRON universal testing equipment with a maximum capacity of 1500kN. For rectangular samples, a male-female mold with dimensions 150x30x50 mm was used which produced three samples per procedure. The resulting ceramic composites have prismatic dimensions of 2.5x1.8x15.0 cm and were conformed under a uniaxial compression load of 574 kN, which resulted in a pressure of 42.5 MPa. The process of molding is shown in Fig. 2.

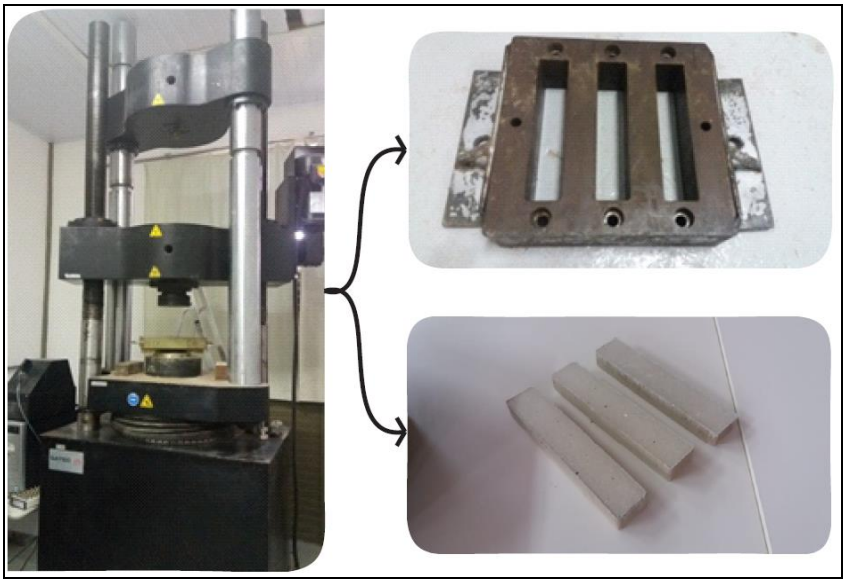

Figure 2. Molding procedure.

The ceramic composites were placed inside a disconnected climatic chamber to avoid the loss of accelerated humidity and the appearance of cracks in the pieces. This initial drying process was carried out for 15 days. Afterward, the specimens were oven dried at temperatures of 30, 60 and 110ºC for a period of 24 hours in each temperature, for the same purpose described above.

Thus, these passed through the sintering process in the oven model FQR 1300/3, with a heating rate of 5°C until reaching 1300°C. This choice is justified based on the studies by Sobrosa (2014) e Stochero (2015), which indicate that, with this temperature, smaller porosity and greater modulus of rupture are obtained. For this process a three stages heating ramp was used, as shown in Fig. 3.

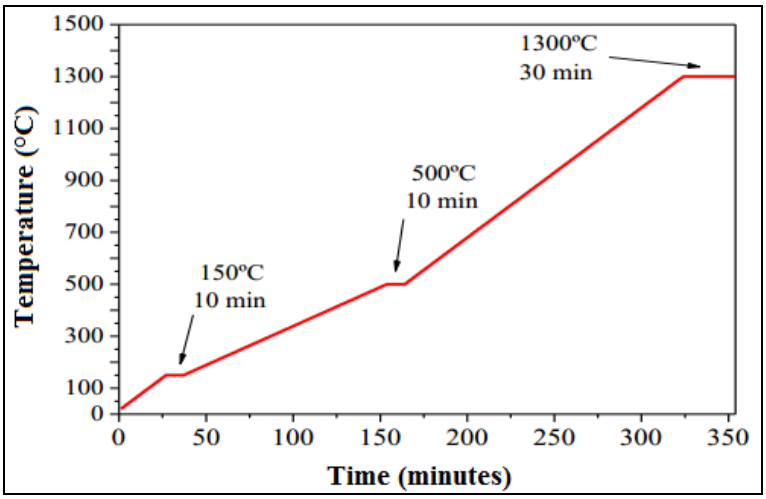

Figure 3. Thermal cycle used. Adapted from Nunes (2017).

In the first one, heating at 5°C/min was used until reaching a temperature of 150°C, remaining for 10 minutes in order to eliminate surface moisture. In the second stage, heating occurred from 3°C/min to 500°C, where it was kept constant for another 10 minutes to eliminate combustion gases and chemical reactions of the material. Finally, at the third level, the heating rate used was 5°C/min to 1300°C, remaining at this temperature for 30 minutes (Pereira at al., 2002). The cooling of the specimens was carried out naturally from the oven shutdown, keeping them inside the oven until it was at room temperature.

Five different proportions were studied, the first being the reference blend, ie, a sample using 100% KC. For the manufacture of blends of composite materials, 10 to 25% replacement of KC by RHA was used. Table 2 presents the nomenclature and composition of the tested specimens. Mix replacement percentages were based on Sobrosa (2014) using a different compaction pressure.

Table 2. Composition and nomenclature of composites.

Nomenclature	KC (%)	RHA (%)
0 RHA	100	0
10 RHA	90	10
15 RHA	85	15
20 RHA	80	20
25 RHA	75	25

2.3. Mechanical and thermal tests

2.3.1 Compressive strength

This test was realized following the specifications of NBR ISO 10059-2 (ABNT, 2014). To assess the compressive strength it was necessary to cut the prismatic specimens in five parts so that they were in the required dimensions for testing, 2.5x1.8x3.0 cm.

The specimens (Fig. 4a) and the test of compressive strength (Fig. 4b) are shown in Fig. 4, being used five test samples for each evaluated blend. Prior to testing, the faces of the samples were regularized to make the contact surface flat, thus ensuring even stress distribution.

The compressive strength (σ_C) of the specimens in room temperature is express in MPa and was calculated by Eq. (1), being: F, the maximum compression load in Newton; A, the initial cross-sectional area of the specimen in mm².

$$\sigma_C = F/A \quad (1)$$

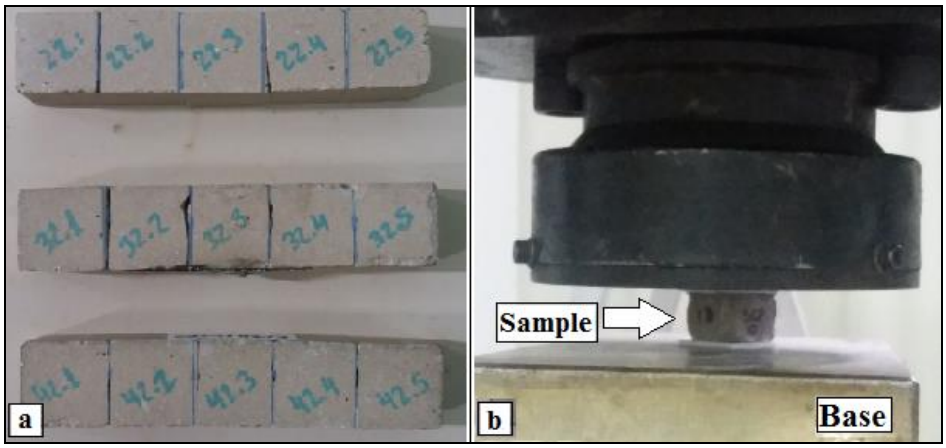

Figure 4. (a) Specimens and (b) compressive strength test.

2.3.2 Tensile strength at three-point flexure

The determination of the tensile strength at three-point flexure obeyed the specifications of standard NBR ISO 5014 (ABNT, 2012). The tests were performed on a Shimadzu universal machine using a 5 kN load cell at a test speed of 0.15 mm/min, with a distance between the 10 cm supports and a central load actuator. The dimensions of the specimens were 2.5x1.8x15.0 cm. The specimens (Fig. 5a) and configuration of the three-point flexure test (Fig. 5b) are shown in Fig. 5, being used three test samples for each evaluated blend.

Based on the load reached at the moment of rupture, it was possible to determine the tensile strength (σ_f) of each specimen through Eq. (2), being: F, the breaking load in Newton; L, the distance between the supports in mm; A and B, width and length of the specimen in mm.

$$\sigma_f = (3FL)/(2AB^2) \quad (2)$$

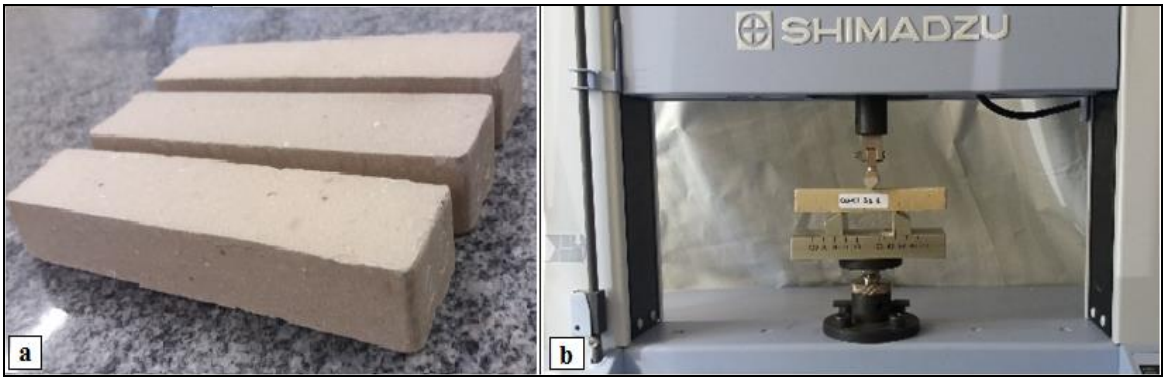

Figure 5. (a) Specimens and (b) three-point flexural test.

2.3.3 Thermal shock

The thermal shock test was performed in accordance with the specifications of NBR 13202 (ABNT, 2015). The composites were preheated at 1200°C for a residence time of 10 minutes (Fig. 6a). Thus, these were cooled in a reservoir with shaken water for 5 minutes (Fig. 6b). After that, the samples were dried outdoors for 5 minutes and these returned to the oven for a new cycle.

According to the standard, the cycle must be repeated until the samples break or until the limit of 20 cycles. The specimens used had dimensions of 2.5x1.8x15.0 cm. For the thermal shock test, the heating and cooling procedure of the samples is similar to shown in Fig. 6.

Importantly, the thermal shock resistance (TSR) is inversely proportional, ie, the lower the value obtained, the better the performance of the composite against thermal shock. The result of this test was obtained by the ratio between the number of cycles in which the first crack occurred *(A)* and the number of cycles required to cause the total rupture of the composite *(B)*, as can be visualized through Eq. (3).

$$TSR=A/B \quad (3)$$

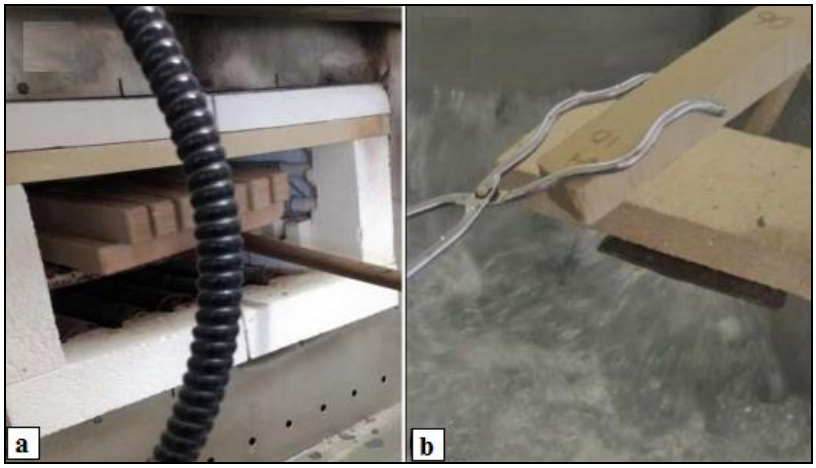

Figure 6. Thermal shock test: (a) heating and (b) cooling. Adapted from Silva (2019).

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The values obtained for the compressive strength of the samples, as well as their standard deviation and coefficient of variation are shown in Tab. 3.

Table 3. Compressive strength results.

	0 RHA	10 RHA	15 RHA	20 RHA	25 RHA
Average compressive strength (MPa)	148.53	98.52	88.96	70.87	103.75
Standard deviation	26.11	19.33	27.94	9.28	14.62
Coefficient of variation (%)	17.58	19.62	31.41	13.09	14.09

Figure 7 presents the results of the average and standard deviation for compressive strength, being the tests performed with five replicates for each composition studied.

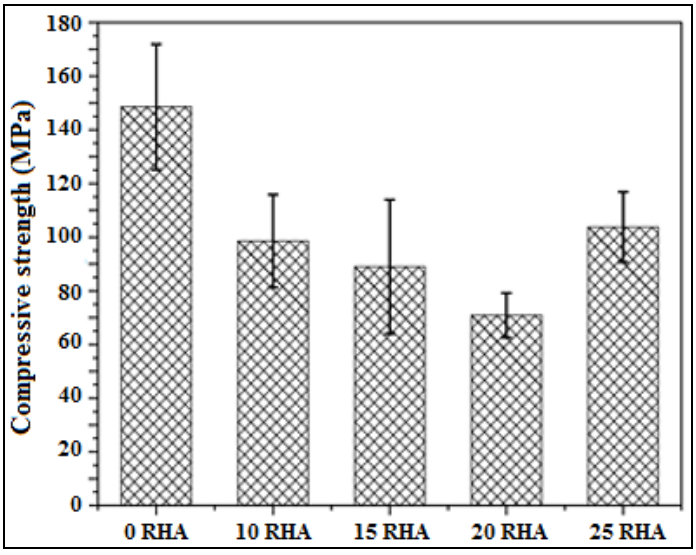

Figure 7. Average compressive strength and standard deviation.

Observing Fig. 7, it is noted that there was a decrease in the compressive strengths obtained using RHA replacement, compared to samples in which only KC was used (0 RHA), being this confirmed numerically by the Fisher's method (Least Significant Difference) for multiple comparisons, using all samples in all compositions analyzed. Also using Fisher's method to compare only the refractory ceramics in which substitutions were made (10 RHA, 15 RHA, 20 RHA and 25 RHA), it was observed that there was no significant difference among resistance levels achieved for most compositions, except for 20 RHA, that presents compressive strength significant difference in relation to blends 10 RHA and 25 RHA.

RHA has a high added value, due to it is a residue that has significant levels of silica in its chemical composition, possibly attractive in various spheres of production, such as electronics, chemical industry, photovoltaic cell manufacturing, construction and ceramic industry. (Foletto et al., 2005). According to Kazmi et al. (2016), there is a potential for the insertion of RHA in the ceramic industry, either in the form of the main or secondary component, aiming to solve the environmental problem of improper ash disposal.

Considering this, although the insertion of RHA has caused a decrease in the compressive strength, it is still interesting to verify the possibility of using ceramics with replacement in distinct applications to their mechanical capacity, due to the use of this residue as an alternative material, as well as, by reduction of production cost of these ceramics.

3.2 Tensile strength at three-point flexure

The mean values found for the tensile strength at three-point flexure, standard deviation and coefficient of variation are shown in Tab. 4, as such as, the load x displacement curves obtained may be visualized in Fig. 8. The average for three specimens in each composition were used to evaluate the results.

Table 4. Results for tensile strength at three-point flexure tests.

	0 RHA	10 RHA	15 RHA	20 RHA	25 RHA
Average tensile strength (MPa)	20.34	21.51	16.64	15.96	15.79
Standard deviation	0.32	4.67	1.94	0.81	0.81
Coefficient of variation (%)	1.58	24.84	11.67	5.13	5.13

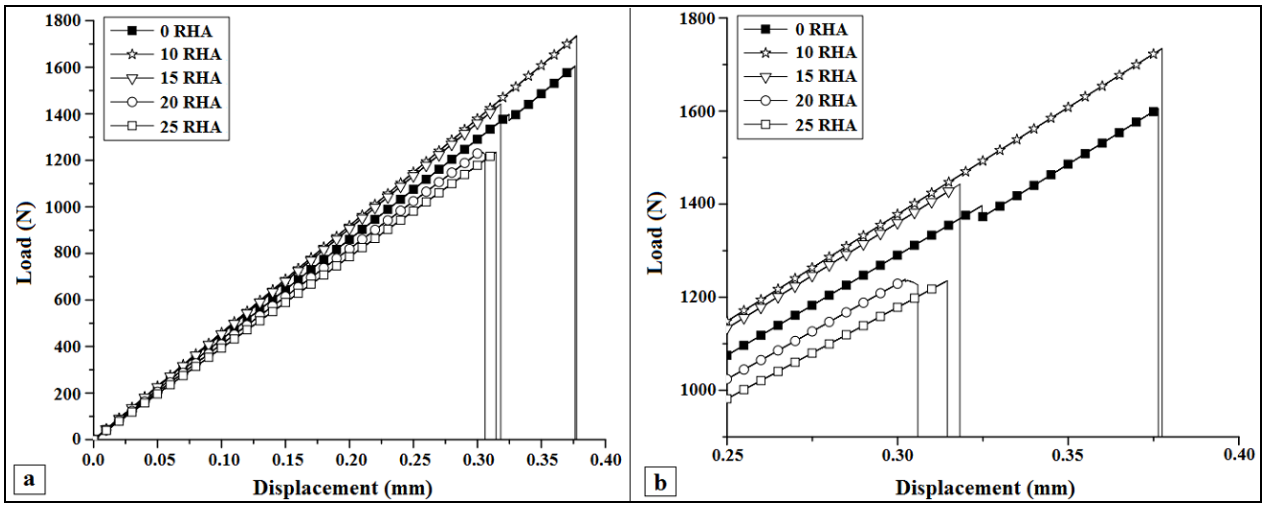

Figure 8. (a) load x displacement curves at three-point flexural tests and (b) enlarged image of the curve.

Based on the analysis of data in Tab. 4, it was noted that the replacement of 10% KC by RHA provided a 5.44% higher tensile strength at three-point bending test. From the load x displacement graph (Fig. 8a), it was observed that in all cases, the rupture occurred in a fragile way and for the 10 RHA blend the displacement was similar to the reference at the maximum rupture load.

In order to verify if the increase of the tensile strength at the three-point bending for the 10 RHA composites in relation to the 0 RHA composites was performed, the analysis by Fisher's test was performed, showing that these resistances are not statistically different, at a 95% reliability level. However, for the other substitutions there was a significant decrease in strength compared to the 0 RHA and 10 RHA blends.

3.3 Thermal shock

All composites tested using different compositions ruptured in the first heat shock cycle, indicating excessive brittleness. In Fig. 9 it is possible to observe the typical failure mode from a specimen after the test, evidencing its degradation by a homogeneous failure mode, that may have occurred due to the possible formation of internal stresses in the material.

In addition, the similarity in the performance of composites with different compositions in relation to thermal shock suggests that the temperature of 1200°C used for heating the specimens may have been very high, promoting an aggressive environment. In order to minimize this effect, it is suggested the tests with milder temperatures, aiming at less aggressive conditions, besides the need to establish parameters not defined by NBR 13202 (ABNT, 2015), since it presents criteria for refractory materials in general and possibly may not suitable for ceramic materials.

These results may be correlated to those found by Nunes (2014), which represents that the addition of RHA to refractory ceramic materials causes a drop in strength to thermal shock. Moreover, the abrupt rupture of the composites in all composition variations may have been caused by the increase in stiffness, due to the fact that the thermal shock strength is inversely proportional to the elasticity of material (Nascimento, 2007).

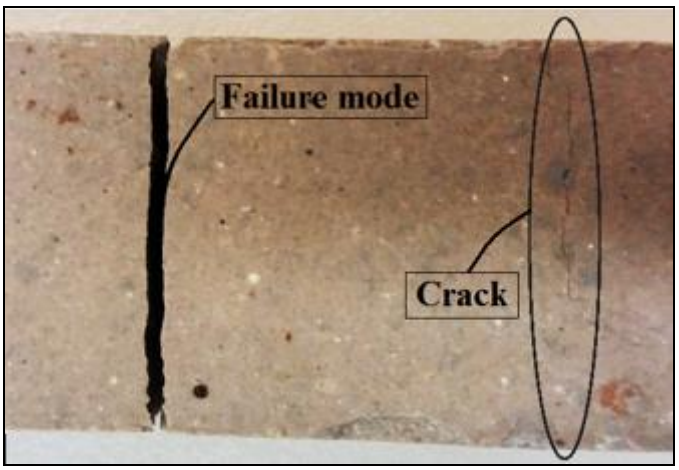

Figure 9. Failure mode of the composites with partial substitution of RHA.

4. FINAL CONSIDERATIONS

The composites with substitution of KC per RHA in all the percentages presented reduction in the resistance to compression. However, for composites 10 RHA, there was an increase at three-point flexural tensile strength, not significantly higher than the reference blend, 0 RHA. In addition, the substitution of KC by RHA did not present any benefits regarding the thermal shock resistance of the composites under the imposed conditions, evidencing the need to re-evaluate the methods used.

In the bending and compressive tests performed by Sobrosa et al. (2017), the resistances found were directly proportional to the replacement levels of 10 and 20% of KC by RHA, behaviors not found in this study. Stochero et al. (2017) and Santos et al. (2018) also obtained better mechanical properties of compressive strength and bending tensile strength by replacing KC with RHA.

In contrast to that obtained in this study, the authors varied the compaction pressure around 20 MPa, thus the 42.5 MPa pressure used may have caused a change in the mechanical behavior of the composites that contained substitution. In view of this, it is necessary to effect out a more in-depth study to prove this theory, confronting composites molded from different pressures by the same operator, under the same climatic conditions and other circumstances that may influence the results.

On the other hand, it is worth noting that, even considering a reduction in the mechanical capacity of composites with partially replacement, the use of RHA may still be beneficial, inducing further studies on the use of RHA as primary or secondary substitution in ceramics. Thus, studies should be conducted with the objective of promoting an environmentally appropriate destination for this waste, since it is produced on a large scale and, consequently, this will lead to reduced production costs in the refractory ceramics industry.

5. ACKNOWLEDGEMENTS

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