EXPERIMENTAL ANALYSIS OF CERAMIC REFRACTORY MATERIALS BEHAVIOR REINFORCED WITH STEEL FIBER AND SILICA RICE HULL

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Abstract. *The objective of the present work is to develop a new refractory ceramic material, from the use of waste resulting from power generation from rice husk burning, by adjusting the ceramic mass with refractory clay, silica from rice husk and fiber steel. The methodology used in this research is essentially experimental, where were produced test samples with partial replacement of refractory clay by silica from rice husk, in percentages of 10%, 20% and 30%, by volume, and incorporating 1% by volume of steel fibers. The test bodies were molded and uniaxial pressed (20 MPa), dried for 14 days and finally burning at 1300ºC temperature. After burning, were determined physical, mechanical and thermal properties of material. The physical properties evaluated by apparent density, apparent porosity, water absorption and linear shrinkage. The mechanical properties evaluated by compressive test and three-point flexural test. The thermal properties evaluated by thermal shock resistance. The obtained results indicate that mixtures made of 10% and 20% silica have values of thermal shock resistance very similar, however, a mixture with 20% presented the best performance on the mechanical resistance, leading to consider that the ceramic with 20% silica obtained the best performance in general. The addition of this byproduct (silica from rice husk) in the ceramic matrix shows a high potential for application as raw materials for refractory industrial.*

Keywords: *silica from rice husk, fiber steel, ceramic material*

1. INTRODUCTION

The agricultural and industrial processes generate certain quantity of waste, which are not connected to the purposes of the production itself. Rice husk (RH), for example, has a low commercial value in consequence to its hardness, fibrousness and abrasive nature. Normally, this residue is used as an heat alternative source in the generation of energy for drying the grain itself (Gonçalves and Bergmann, 2007).

Rice husk is one of the most abundant agricultural residues, and this creates problems because of its high production volume, associated with the storage location, transportation and handling. The use of this agricultural waste in the industry as by-product or incorporated as a raw material in other industrial areas, appears as a fundamental question for resolving this problem.

Of the rice milling process has as residue the husks, practically no cost and with high calorific power, with values between 15 and 16 kJ / kg, providing high potential as an alternative source of heat (Lim *et al.*, 2012). As a result of high calorific power the rice husk can be used in a sustainable manner for thermal power generation in boilers and generation posterior of electricity due to its high calorific value, and consequently, eliminating massive amounts of bark that are usually deposited in inappropriate places, such as in landfills or riverbeds.

After the burning of organic matter from rice husk, left over ashes, which are composed essentially of silica, ranging from 85% to 95%. The silica rice hull (SRH) has low thermal conductivity, good resistance to chemical attack and high melting point, 1440ºC (Gonçalves and Bergmann, 2007; Onojah, *et al.*, 2013).

The SRH is widely used in civil construction, however its use in other applications have not been consolidated. Due to its good properties, wide availability and low cost, the application of silica should be diversified in other branches of production. According to Foletto *et al.*, 2005 the silica has applicability in fields such as, polymers, electronics, chemical industry, ceramic industry, and others. However, Ugheoke, *et al.*, 2013 reports that for more refined applications, such as electronics, solar panels, and others, the SRH must present high purity (> 98%). Nevertheless, the application that is of direct interest to this study is the use of SRH in the development of refractories.

For presenting high silica content, these "waste" (SRH) can be used as main component in ceramic masses for the production of ceramic refractory. The fabrication of refractory ceramic materials using rice husk ash, rich in silica, whether as a main component or as a secondary component, is an alternative for solve the problem of disposition of ashes on the environment and diversify its application. However, replacement of silica rice hull in ceramics masses, in large quantities, cause the reduction in the mechanical strength and thermal shock resistance (Sobrosa, 2014).

The recent work Pemberton *et al.*, 2011 reports that there have been several attempts to introduce components in the ceramic with the objective of increase its ductility, and the constituent that obtained the best performance was the steel fibers. Because of this, with the intention to increase the ductility and thermal shock resistance, was used the steel fibers in the ceramic mass. Considering that, the fragility of the ceramic is a major limitation for many applications.

This manner, this study has the objective of develop new refractory ceramic materials, and evaluate the use of steel fibers and SRH seeking to improve their mechanical and thermal properties, and also motivate the use of industrial waste.

2. MATERIALS AND METHODS

To evaluate the physical properties of refractory ceramics developed, the samples were submitted the tests of apparent density (AD), apparent porosity (AP), water absorption (WA) and linear shrinkage (LS). To evaluate the mechanical and thermal properties, the samples were subjected to tests the compressive strength (CS), flexural strength at three points (FS) and thermal shock resistance (TSR). The raw materials used to manufacture the samples were: kaolin clay (refractory), silica from rice hull (SRH) and steel fibers.

2.1 Materials

The kaolin clay used in the research is proceeding from Vargem Grande do Sul - SP, supplied by the company Helager Indústria e Comércio Ltda. This clay was chosen due to low presence of iron oxide, which favors the refractivity and can be used in refractory materials.

The chemical composition of clay was obtained by X-ray fluorescence spectrometry. Its composition is 57.83% SiO2, 27.52% Al2O3, 2.25% Fe2O3 and little significant quantities of TiO2, CaO, MgO, Na2O, K2O, MnO.

The silica from rice hulls were obtained from the company SVA (Sílica Verde do Arroz Ltda). Currently, the silica produced by this company is derived from the power generation by burning rice hulls and is commercialized by Pilleco Noble Group (Alegrete - RS) with the commercial name Silica Noble.

The chemical composition of SRH was obtained by X-ray fluorescence spectrometry and shown the composition of 91.48% SiO_2 and little significant quantities of CaO, MgO, Fe_2O_3, K_2O, TiO_2, MnO, SO_3, P_2O_5. This silica is obtained by controlled burning process, with a system of automation and temperature control that allows the extraction of silica from rice husk with amorphous structure.

The Institute Alberto Luiz Coimbra de postgraduate and Engineering Research, COPPE – RJ, donated the steel fibers used in the study. The fibers were imported from KrampeHarex Company based in Germany. These fibers have the following characteristics, length of 6 ± 1 mm, diameter 0.16 mm ± 0:03, form factor 37.5, tensile strength 2200 MPa, elastic modulus 200 GPa and 1500 ° C melting point.

2.2 Methods

The Tab. 1 shows the composition of each mixture and their respective nomenclatures. Opted for 1% of steel fibers because the work Stochero (2015), which was used 3%, 6% and 9% fibers, ductility increased but lost mechanical strength. Thus, the work intends to investigate the performance of ceramics with lower fiber content.

Table 1. Nomenclature of samples with their respective contents the clay, silica and steel fibers.

Nomenclature	Fire clay	Silica	Fibers
RC10	89%	10%	1%
RC20	79%	20%	1%
RC30	69%	30%	1%

2.2.1 Fabrication of ceramic samples

The mixture of ceramic masses were made in a planetary mixer in two stages, one minute to low speed and one minute for high speed. The humidity contents used in the mixture was 12%, because preliminary tests showed difficulty to extract the sample from the mold with lower humidity contents.

For fabrication of test bodies it was used for press molding. The samples of each formulation were molded in the form of parallelepiped, with approximate dimensions: length of 150mm, height of 20mm and 30mm width (Fig.1).

For the molding was used a hydraulic press (EMIC DL-20000) and a male-female steel matrix, which has the capacity to mold two test samples at a time. As were two molded test samples at a time, the pressure of maximum compression achieved by the hydraulic press was 20 MPa for each test body, it acted as a limiting factor for the compaction pressure.

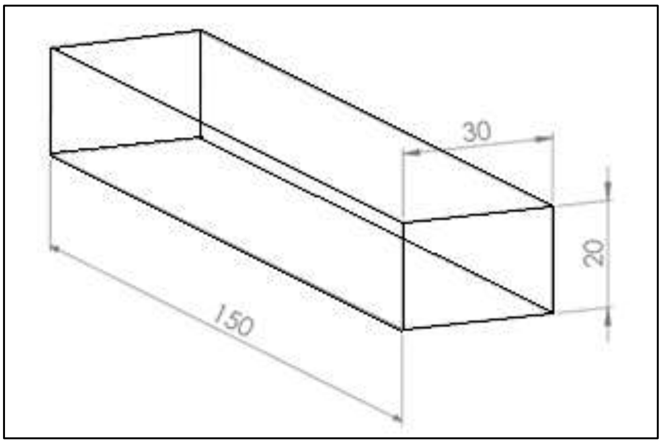

Figure 1. Dimensions of the samples in mm (150x30x20)

The production process of a ceramic material happens with clay still wet and it is necessary the material to be dried before go to the furnace to prevent internal stresses and consequently defects in the piece. After molding the samples were air dried for 14 days and in an oven at 110 ° C for a minimum of 24 hours, with the objective of reduce to zero humidity.

All samples were burned at a temperature of 1300ºC, in a simulator furnace ceramic burning, Inti FL-1400. It was used a heating ramp with three levels: first level with heating 5°C/minute until the temperature of 150°C, where it stayed for 10 minutes. Second level with heating 3°C/minute until the temperature of 500°C, where it stayed for 10 minutes. Third level with a heating rate of 5ºC/minute until the temperature of 1300ºC, where stayed for 30 minute. The cooling was consolidated naturally in the furnace after its shutdown.

2.2.2 Characterization of samples

For testing the AD, AP and WA was used to NBR 6220 (ABNT, 2011) with three samples to each experiment. The LS was found by Eq. (1), using measurements taken before and after burn. For this analysis was done the arithmetic mean the length of ten ceramics samples for each mixture.

$$LS = \frac{c_0 - c_f}{c_0} \ X\ 100 \tag{1}$$

Where:
c_o – initial length (mm);
c_f – final length (mm).

The CS test was governed by NBR 10059-2 (ABNT, 2014), to perform the test was used a hydraulic press (EMIC DL-20000). The velocity adopted for this test was 0.2 mm/minute. The RC was calculated from Eq. (2).Where σ_c is the compressive strength ambient temperature (MPa), “P” is the load reached the breaking point (N) and “A” is the cross-sectional area (mm²)

$$\sigma_c = \frac{P}{A} \tag{2}$$

For FS, was used the NBR 5014 (ABNT, 2012), is determined by Eq. (3). The test was performed in the universal testing machine Shimadzu, with 5 kN load capacity. The velocity adopted for this test was 0.15 mm/minute.

$$\sigma_f = \frac{3FL}{2ab^2} \tag{3}$$

Where σ_f is the flexural strength at three points (MPa), “F” is reached load at the moment of fracture (N), “L” is the distance between supports (mm), “a” is the width of the test body (mm) and “b” is the test body height (mm).

Finally, the test TSR was realized following the specifications of the NBR 13202 (ABNT, 1997). For the heating the samples was using the same furnace the burning the test bodies. For each cycle the samples remained in temperature

1200ºC for 10 minutes and immediately after removed and thrown into a tank with water, where they remained for five minutes. Then, were removed and after 5 minutes at ambient temperature, were taken again the furnace for a new cycle.

The thermal shock resistance was determined by Eq. (4). Where “A” is the cycle number where it appeared the first crack and B is the cycle number where there the total rupture of the test body.

$$TSR = {}^{A}\!/_{B} \tag{4}$$

Three samples of each mixture were used to perform the test CS, FS and TSR.

3. RESULTS AND DISCUSSION

3.1 Apparent density, apparent porosity, water absorption and linear shrinkage

The mean results and their respective standard deviations are shown in Tab. 2. The use of ash and fibers in the ceramic mass of the test bodies had little effect the apparent density (AD), because all the formulations showed similar densities. This is justified because the density of silica (2.03 g/cm³) demonstrates a little less than that of refractory clay (2.73 g/cm³), considering that the apparent density is the relationship between the mass of the sample by its volume.

The Tab. 2 also shows the results of apparent porosity (AP) and water absorption (WA) the compositions studied. With these experiments was observed that the AP and WA decrease with the amount of silica. In general, a refractory material with low porosity has low thermal insulation and low thermal shock resistance.

Table 2. Results apparent density, apparent porosity, water absorption and linear shrinkage.

Mixtures	**AD (g/cm³)**	**AP (%)**	**WA (%)**	**LS (%)**
RC10	2,36 ± 0,008	10,12 ± 0,31	4,50 ± 0,14	10,43 ± 0,21
RC20	2,31 ± 0,006	8,59 ± 0,61	3,78 ± 0,33	10,57 ± 0,26
RC30	2,25 ± 0,006	8,42 ± 0,46	3,71 ± 0,11	11,27 ± 0,20

May also be observed in Tab. 2 the linear shrinkage (LS) has the opposite effect the other observed properties, i.e, value increased along with the increase in silica content. This may be associated with the large amount of liquid phase that develops during firing. The liquid phase causes approximation of the particle and consequently the retraction (Praxedes, 2013). According with Sobrosa (2014), the melting temperature decreases with increasing silica content. Thus, higher concentrations of silica can compromise the use of the material as a refractory.

3.2 Compressive strenght

The Tab.3 shows the compressive strength of the compositions. Through the obtained results, is noted that the substitution of clay by silica and steel fibers, provided better performance for the RC20 ceramic compared the others (RC10 and RC30).

Table 3. Mean results of compressive strength.

Mixtures	**RC (MPa)**	**CV [1] (%)**
RC10	183,35	6,73
RC20	210,05	4,53
RC30	138,21	3,89

[1] Coefficient of variation

The RC10 mixture showed a decrease of 12.71% resistance in relation to RC20, while the RC30 obtained a reduction of 34.20%, also in relation to RC20.

This result supposes that on CR30 mixture the crystalline phases that confers greater mechanical strength not evolved, therefore, this formulation showed the worst performance. This phenomenon can be explained because it is replacing the clay, which has 27.52% of alumina, by the silica that does not have this chemical compound.

This substitution impairs the formation of stoichiometric proportion of the mullite crystalline phase, which corresponds to 71.8% of Al_2O_3 and 28.2% SiO_2 (by weight). To prove the lower mullite formation should be performed the test X-ray diffraction to identify the phases present.

The mullite crystal structure is quite required in refractory materials because of their good properties, such, as high modulus of rupture, high refractoriness, good thermal shock resistance, erosion and chemical attack (Magliano and Pandolfelli, 2010).

The best performance of CR20 samples is possibly associated with a lower formation of the vitreous phase in final product, due to higher production mullite caused by greater proportionality between the forming elements such phase.

Compared with the work of literature Stochero (2015), which utilized larger quantity of steel fibers (3%, 6% and 9%) in the ceramic matrix. It can be observed that the addition of fiber does not present a considerable improvement of this property, due to the bad compaction generated by the increased workability of the mixture generated by steel fibers.

The compression behavior is shown in typical curves stress versus displacement referring to materials tested, as shown in Fig. 2.

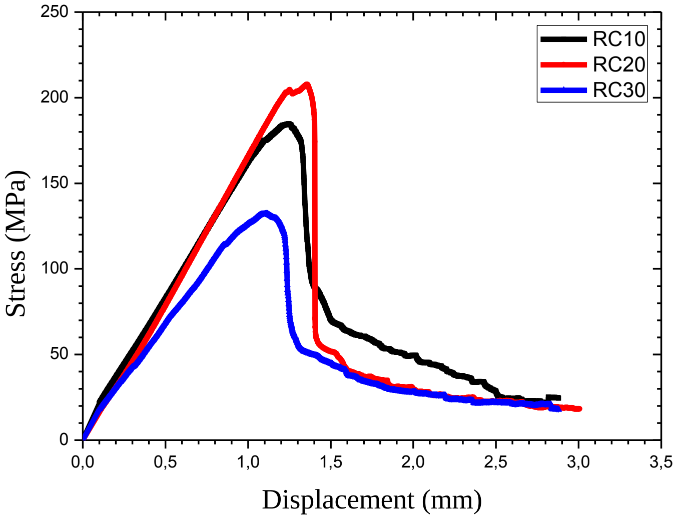

Figure 2. Typical curves obtained from compression tests

The Fig. 2 shows that all of the mixtures exhibited an “almost fragile” behavior, however, more ductile than the typical curves of the ceramic without fibers. Supposes that steel fibers act as a transfer bridge tensions by the fissures, resulting in a smaller fragility of the material.

Comparing the curves found by Sobrosa (2014), that did not use steel fibers, with the curves of this research, there is a greater ductility in materials with steel fibers.

3.3 Flexural Strength

The Tab. 4 shows the mean results and their variation coefficients obtained by the flexural strength at three points. Is observed that the variations in behavior flexural strength if show similar to those observed in the compressive strength results (Tab. 3). This is, the RC20 ceramics continue with better mechanical performance than the others. Such behavior suggests that the mixture of silica 20% and steel fibers 1% confers better distribution of stresses in the refractory ceramic matrix. Is interpreted that for contents above silica 20%, greater fragility of the material.

Table 4. Mean results of flexural strength at three points.

Mixtures	**SF (MPa)**	**CV [1] (%)**
RC10	24,83	3,172
RC20	27,99	3,286
RC30	21,46	2,126

[1] Coefficient of variation

According to Menezes *et al.*, 2007 compositions with excess silica in relation to stoichiometry of the mullite (Al_2SiO_3) form cristobalite crystalline phase, which is developed by the crystallization of free silica, this phase confers greater fragility to the material.

In the recent work by Stochero (2015) was verified higher ductility in the ceramic with a higher content of steel fibers, but, the RF results were lower than those found in this present study. This shows that large amounts of fibers increase ductility, but, reduces the flexural strength.

The typical behavior of load versus displacement for all mixtures is shown in Fig. 3.

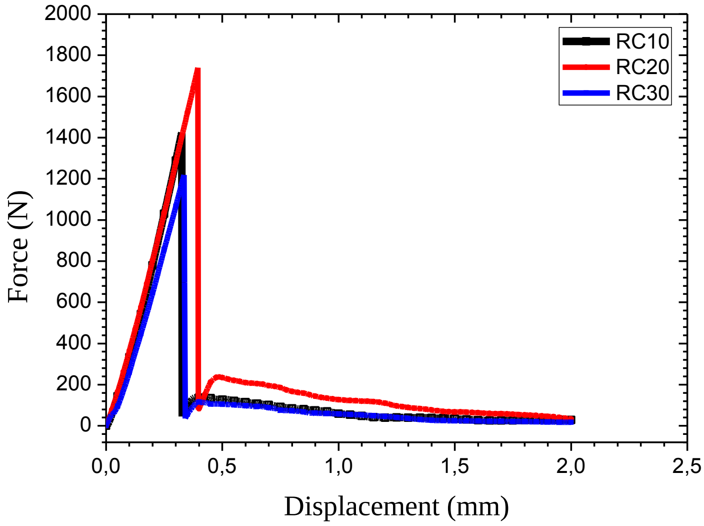

Figure 3. Typical curves obtained from bending test

Is observed that the bending curves for the three cases also occurred the shape "almost fragile", because, after a partial rupture, the samples exhibit a second peak due to the small connecting bridges of steel fibers.

The work without the use of fibers Sobrosa (2014), the curves did not show this second peak. Is understood that the fibers show a tendency of the material to introduce a more ductile behavior.

3.4 Thermal shock resistance

The Tab. 5 shows the resistance to thermal shock results from the different mixtures, obtained by Eq. (2).

Table 5. Results of thermal shock resistance test.

Mixtures	**Cycles number where appeared the 1º crack**	**Mean number of cycles in which occurred the complete rupture of CS**	**TSR**
RC10	1	10,33	0,0968
RC20	1	9,66	0,1034
RC30	1	5	0,2000

There was in the first thermal shock cyclic the appearance of the first cracks in the three mixtures. This result was expected, because Poirier *et al.*, 2009 says that in the refractory ceramic material damage by thermal shock usually occurs in the first cycle.

According to NBR 13202 (ABNT, 1997), the lower the value TSR, more thermal shock resistant is the material.

From Tab. 5 can be compared values of resistance to thermal shock of ceramics RC20 with RC10. Note that the RC10 have a slight advantage, about 6.38% more resistant. However, when comparing the CR30 ceramics with the CR10, note that the CR10 have a substantially higher value, about 51.60% more resistant. Possibly the best performance of CR10 samples were stimulated by higher porosity.

Is concluded that for amounts over 20% silica the material has thermal shock resistance, probably due to decreased formation of mullite crystal phase.

The Fig. 4 shows the typical cases of cracking and breakage of the samples. For uniform comparison, were selected the samples that supported the largest number of cycles for each mixture (CR10 with 12 cycles, with 12 cycles CR20 and CR30 with 6 cycles).

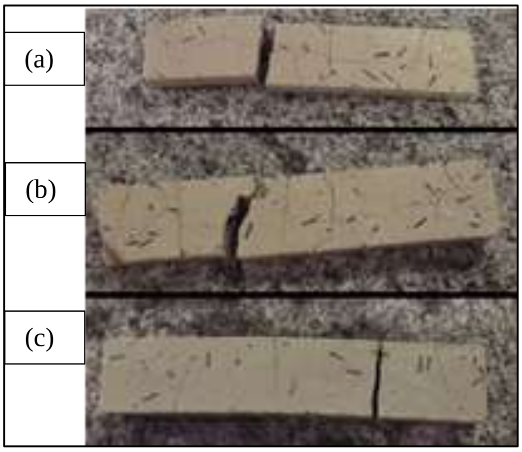

Figure 4. Typical cases of cracking and rupture of the samples, (a) RC10 ceramics, (b) RC20 ceramic and (c) RC30 ceramic

The Fig. 4 emphasizes that the ceramic CR30 break more abruptly and present few cracks. This represents greater fragility and low thermal shock resistance.

Yet the analysis of Fig. 4, it is observed that the amount of cracks present in the mixture CR10 is very similar to the amount displayed on the CR20. In counterpart, the CR20 ceramics have larger openings of cracks, probably due to their smaller thermal shock resistance.

It is believed that CR20 samples did not break due previously the action of steel fibers, provided that the material a greater number of cycles.

4. CONCLUSIONS

This work had the objective develop new refractory ceramic materials with replacement the clay by silica from rice hull and steel fibers, with the intention of improve their mechanical and thermal properties and also motivate the recovery of waste industries. Based on the results obtained it can be concluded that:

1 - In relation the physical properties, samples showed relatively low values of porosity, however, low porosity in refractory materials is undesirable because it causes low thermal insulation and lower thermal shock resistance.

2 - In conclusion, the CR10 and CR20 ceramics showed acceptable mechanical and thermal properties, while CR30 exhibited a pronounced decrease of mechanical and thermal resistance. It is suggested that the lower results of the CR30 samples are caused by decreased formation of mullite crystal phase. To prove this conclusion should be realized the test X-ray diffraction spectra to identify the phases present.

3 - Samples with 20% silica showed better mechanical performance, reaching values on the order of 210 MPa for the compression strength and 28 MPa for bending strength.

4 - The addition of steel fibers at 1% concentration (by volume) attributed greater ductility to the material, taking in account that ceramic materials have typically curves fragile.

5 - The values found in TSR should be maximized, however, is observed the possibility of using the rice hull silica in combination with steel fibers for the production of refractory ceramic for determined applications. The percentages used are at maximum of 20% TSR.

6 - The replacement of refractory clay by SRH which exceed 20% may compromise use of the material as a refractory. This is due to the low thermal shock performance and the highest amount of linear shrinkage of CR30 ceramics.

7 - The processing of RHA with intention to obtain refractory ceramic, was relatively simple and can be conducted with few modifications in the production process.

8 - This study showed an alternative for the recycling of industrial waste, by producing ceramics with high value added, this demonstrates the importance of research developed and the need for continuous quest for solutions that minimizes waste disposal.

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