Journal of Building Pathology and Rehabilitation (2018) 3:1
https://doi.org/10.1007/s41024-017-0030-0

RESEARCH ARTICLE

# Effects of the addition of red ceramic, limestone filler and rice husk ash in alkali silica reaction

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Received: 10 October 2017 / Accepted: 24 November 2017 / Published online: 18 December 2017


**Abstract**

Studies about the reactive potentiality of the Red Ceramic Waste (RCW) and of the rice husk ash (RHA) and their use in the composition of Portland cement, avoiding inadequate disposal, is a theme of strong relevance for the environmental sustainability of the productive chain of a country. Analysis of the feasibility of incorporating RCW and RHA to Portland cement demands studies involving the effects on compressive strength and, overall, about the performance of the hydrated matrix when susceptible to the action of deleterious physical–chemical interactions. This work has the objective of evaluating the influence of incorporating milled RCW and RHA in the composition of Portland cement over the resistance to the occurrence of the alkali silica reaction (ASR), based on Brazilian Standards. In order to that, mortar of CPV-ARI cement (reference) and compositions with substitution of 10% of cement in weight, by limestone filler, RHA or RCW, with three different finenesses, were evaluated regarding ASR, according to the Brazilian Standards. Results evidence that RCW and RHA caused increase in ASR expansion. On the other hand, the greater fineness of RCW impacts, positively, the behavior of the material in face of degradation. Limestone filler did not influence the result of expansion by RCW. Regarding RAS, it is important to increment the comminution of the grounded RCW by 1.5 h in order to approximate its particle size distribution to the distribution of cement, which as a tendency of potentiating the mitigating capacity of this mineral addition.

**Keywords** Alkali silica reactivity · Rice husk ash · Portland cement · Red ceramic waste

## 1 Introduction

Activities of industries such as the metallurgical, chemical, petrochemical, paper, food, among other, generate important residues regarding the sustainability of the environment. Those residues are several, being by plastic, paper, ashes, scoria, glass, mud, oils, alkaline residues or acids, wood, fibers, rubber, metals, ceramic and many others represented. As the volume of those industrial residues is large, their proper disposal became primordial for the preservation of the environment, being necessary the development of solutions for implementing technologies able to minimize the impacts from the disposal of those residues in the environment and to reduce the costs involved in this activity.

In this context, construction is an industry that generates large amounts of residues and, according to Lucas e Benatti [1], it may be considered as an industry widely indicated to absorb solid residues. In the construction industry, the reuse of solid residues may help to reduce costs and environmental losses regarding the treatment and/or final disposal of those residues, and also for decreasing the environmental impacts from the extraction of raw materials from the environment. Thus, this industrial sector may have a relevant role as a receptor of solid residues regarding their final disposal. The incorporation of those residues in ceramic and cementitious pastes, aiming the production of artifacts for construction, if made judiciously, allows to give an environmentally correct destination for residues that, otherwise, would be sources of pollution [1].

Thus, any study focusing in the possibility of reusing residues generated during their own production process is

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relevant, because in case of viability, it may be transformed in an important tool for preserving natural resources, decreasing the production cost of edifications and improving some characteristic of the commonly used materials.

Within this panorama, this work aims to disclose information about an alternative of using Red Ceramic Waste, from bricks and ceramic blocks in composites of Portland cement. This theme has been studied in some works [2–12], where were compared properties such as: compressive strength, diametric compression traction, flexural strength, modulus of elasticity, water absorption, retraction, apparent porosity and dimensional variations due to oscillation of humidity. The comparisons are always between concretes with aggregates from residues of ceramic and concretes molded with commonly used aggregates.

This work also aims to produce advancement in the knowledge about the possibility of using rice husk ash, another industrial residue whose discharge in environment is an environmental liability to be resolved, for producing concrete. This residue has been much studied, as is possible to exemplify with works from Geraldo [12], Cordeiro [13], Rodrigues and Beraldo [14], Isaia [15], Zerbino [16] and Zerbino [17] however, its effect in the occurrence of the alkali silica reaction is not approached, frequently, in studies published so far.

It was opted by focusing the effect of incorporating those residues in the capacity of mitigating the alkali silica reaction due to the fact that most of the studies about incorporating those two residues in composites of Portland cement being focused in changes of mechanical resistance and, eventually, in the water absorption and chlorides penetrations. However, the technical consecration of a residue to be incorporated in the concrete or mortar needs a broad investigation study involving not only mechanical resistance, but also the different mechanisms of degradation that may admittedly act in concrete structures.

## 2 Experimental procedure

During the study of incorporating Red Ceramic Waste in composite of Portland cement, a ceramic material from rejects of ceramic blocks (red ceramic bricks) was used. The blocks went through a pre-processing in crusher, that will be described next. The rice husk ash used comes from the controlled combustion in Boiler with fluidized bed from the "Geradora de Energia Elétrica Alegrete (GEEA)".

The test for evaluating the mitigation of the alkali-silica reactivity was performed according to NBR 15,577-5/2008 [19]. Comparisons were made using two reference mortars, one without addition and the other with addition of limestone filler. For all cases, the percentage of partial replacement of the cement was fixed in 10% of the mass. The amount of 10% of ceramic residue was used by representing the average of the range of permissible amounts (6–14%) for pozzolanic material to be incorporated into the composition of Portland cement type CP II-Z, according to standard NBR 11,579/1991 [19]. In the case of rice husk ash, the value of 10% of partial replacement of Portland cement was adopted because it is a usual value for this type of pozzolanic material of high reactivity.

### 2.1 Materials

#### 2.1.1 Aggregates

The fine aggregate selected to the experiment, from the metropolitan region of Curitiba, was characterized by Tiecher [20] and used by Valduga [21], being classified as granite from potentially reactive rock, with expansion between 0.1 and 0.2% at 16 days according to specifications of ASTM C 1260/2007 [22]. The same aggregate has history of pathologic manifestations diagnosed as alkali-silica reaction in national hydraulic works.

The aggregate used was processed with the less possible crushing, using an abrasion apparatus Los Angeles. With the sifting of the crushed material, the granulometric ranges required in NBR 15,577-4/2008 [23] were obtained. Those are the ones retained in sieves: 2.36, 1.18, 0.60, 0.30 and 0.15 mm.

#### 2.1.2 Cement

The used Portland cement was of type CP-V ARI (similar to cement type III – High Early Strength, according to ASTM C150), since this is the one most used in tests aiming to measure the resistivity of aggregates regarding the alkali silica reaction, besides being the cement with less amount of additions in fabric.

The chemical and physical characteristics of the cement used are displayed in Table 1, obtained using testing methods standard in the country. Data of $SiO_2$, CaO, MgO, $Fe_2O_3$, $Al_2O_3$ and $SO_3$ were obtained by means of X-ray fluorescence. The specific mass of cement is 3.12 g/cm$^3$, determined according to NBR NM 23/2001 [24].

#### 2.1.3 Additions: ceramic waste, rice husk ash and limestone filler

The ceramic material used comes from blocks of red ceramic from potteries in the region of Prudentópolis, PR. Blocks were crushed in Jaw crusher brand Furlan for getting 100% of passing material by the sieve of 4.8 mm opening. After crushing, the passing material in the 4.8 mm sieve was milled in ball mill brand Gardelini, during the times

**Table 1** Results of cement CP V—ARI characteristics

Chemical analysis (%)

| Parameters | $SiO_2$ | CaO | MgO | $Fe_2O_3$ | $Al_2O_3$ | $SO_3$ | Loss to fire | CaO free | Residue insoluble | Total alkali with $Na_2Oe$[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Results | 18.34 | 59.72 | 5.35 | 2.52 | 4.12 | 3.05 | 3.2 | 1.49 | 0.63 | 0.62 |

Physical tests

| Parameters | Hot exp. (mm) | Handle start (h:min) | To handle (h:min) | Normal cons. (%) | Blaine fineness ($m^2$/kg) | Retained in | | Compressive strength | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | # 200 | # 325 | 1 day | 3 days | 7 days | 28 days |
| | | | | | | % | % | MPa | MPa | MPa | MPa |
| Results | 0.5 | 02:15 | 03:00 | 27.6 | 437 | 0.10 | 2.80 | 23.40 | 37.60 | 42.70 | 51.10 |

[a]Equivalent of sodium oxide ($Na_2O_e$) = $Na_2O + 0.658\ K_2O$

determinate: 0.5; 1.0 and 1.5 h. The specific mass of the ground ceramic used in this study is 2.60 g/cm$^3$.

Rice husk ash is a material obtained by controlled combustion in boiler with fluidized bed and has a specific mass of 2.12 g/cm$^3$.

The limestone filler used comes from factory "Itaú de Minas da Votorantim Cimentos", being normally used for producing cements and mortars. The specific mass of this material is 2.70 g/cm$^3$.

The chemical composition of the ceramic material, rice husk ash and limestone filler are displayed in Table 2.

## 2.2 Detailing of tests

The physical characterization of the additions and of the cement of this work was made determining the granulometric curves by laser diffraction and by the surface area specified by the technique of BET. The pozzolanic activity of the additions was investigated determining the index of pozzolanic activity (IPA) with lime [25] and the index of pozzolanic activity [IPA] with cement [26], in order to quantify the reactive potential. Beside, X-ray diffractometry (XRD) was used for identifying the crystalline phases, as well as, the amorphous halo that signalizes the reactive potential of additions.

IPA method with lime prescribes the molding of three cylindrical test specimens of ϕ50 × 100 mm and posterior rupture at compression, at 7 days. The test was executed in molded mortar with addition of mineral in test, normal sand of ABNT (234 g of each fraction 1.2; 0.6; 0.3 and 0.15 mm) 104 g of calcium hydroxide p.a. and the water necessary to obtain the consistency of the mortar in 225 ± 5 mm. The quantity of addition is calculated according to Eq. 1.

$$m_{add} = 2 \cdot \frac{ME_{add}}{ME_{lime}} \cdot 104 \text{ (in grams)} \quad (1)$$

where $m_{ad}$ is the mass of the mineral addition in test, $ME_{add}$ is the specific mass of the addition, $ME_{lime}$ is the specific mass of lime.

Index of pozzolanic activity (IPA) with lime indicates that the addition is pozzolanic when the result reaches, at least, 6.0 MPa.

In the case of IPA with Portland cement a reference mortar is prepared, containing just Portland cement and another one for each mineral addition being tested, in order to have 35% of the absolute volume of cement replaced by pozzolanic material. Three cylindrical test specimens were molded with ϕ50 × 100 mm for each mortar. The reference mortar is composed by 312 g of Portland cement and 936 g of normal sand, divided into equal portions of the four fractions that constitute it, and the mortar with the possibly pozzolanic material is composed by 202.8 g of cement, the mass of the

**Table 2** Chemical composition of the ceramic material, rice husk ash and limestone filler

| Material | Chemical composition (%) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | CaO | MgO | $Fe_2O_3$ | $Al_2O_3$ | $K_2O$ | $SO_3$ | $TiO_2$ | ZnO | MnO | Total alkali with $Na_2Oe^a$ |
| Limestone filler | 2.97 | 78.03 | 15.06 | 0.44 | 1.73 | 0.31 | 1.21 | – | – | 0.11 | 0.20 |
| Rice husk ash | 88.94 | 1.10 | – | 0.11 | 2.42 | 4.18 | 2.08 | – | 0.01 | 0.88 | 2.75 |
| Ceramic material | 55.32 | 0.19 | – | 5.27 | 35.50 | 1.28 | 1.23 | 1.09 | 0.01 | 0.04 | 0.84 |

[a]$Na_2Oe = Na_2O + 0.658\ K_2O$ Observation: Was not found $Na_2O$ in samples

addition being tested, determined by means of Eq. 2, and 936 g of normal sand. The water used in each case is the necessary in order to obtain the consistency of the mortar of 225 ± 5 mm. Calculation of the quantity of mineral water to be used in the composition of the mortar for IPA with cement follows Eq. 2.

$$m_{add} = 109,2 \cdot \frac{ME_{add}}{ME_c} \tag{2}$$

where $m_{ad}$ is the mass of the mineral addition being tested, $ME_{add}$ is the specific mass of the addition; $ME_c$ is the specific mass of cement.

Preparation of the sample for Diffratogram collection was executed by means of manually pressing the powder in the sample holder, followed by exposition to X-rays in diffractometer RIGAKU model Ultima IV. Measurement was made between 5° and 75° 2θ, with angular step of 0.02° 2θ and time per step of 1 s. In collection was used tube with copper anode, 40 kV/30 mA, and divergence slit of 1°.

### 2.2.1 Alkali silica reaction (NBR 15,577-5/2008)

The experiment was performed according to NBR 15,577-5/2008—Determining the mitigation of expansion in mortar bars by the Accelerated method [18].

The procedure of mixing the mortars followed recommendations from the mentioned technical standard regarding the order of mixing the materials, time of mixing, molding of bars, procedures of initial cure and getting the bars of mortar out of the molds.

According to 15,577-5/2008, the quantity of cement for the test must be 440 g and the quantity of aggregate must be 990 g, represented by the sum of the several granulometric bands, for relation w/c = 0.47. For this study the proportions of materials recommended in the standard were kept, however, in an greater total amount in order to allow the molding of six bars of mortar for each series of test in order to proportionate a greater statistical representation of results, because NBR 15,577-5/2008 [18] prescribes the use of just 3 bars. A substitution content of 10% regarding the mass of Portland cement was adopted, both for limestone filler as well as for rice husk ash and red ceramic waste, with different times of milling. The amounts of aggregate fractions, cement and additions are in Table 3.

Bars remained immerse during the whole period of testing in solution of NaOH p.a., concentration of 40 g for each litter of distilled water, using a thermoregulator bath with controlled temperature and kept at (80 ± 2) °C. For each age of reading, bars were removed from solutions and placed again inside the thermoregulator bath during a maximum period of 10 min.

NBR 15,577-5/2008 [18] recommends initial readings, including ages of 16 and 30 days. Aiming a more complete evaluation of the expansion of bars, readings were made in the first 66 days, twice per week, including the 16th and 30th day of testing. The apparatus used for measures was a metallic gantry with a length comparator, with precision of 0.001 mm.

## 3 Results and discussion

Results are divided in: characterization of materials and results of the alkali silica reaction, as follows.

**Table 3** Fractions of materials used in the test alkali silica reaction

| Material | Amount (g) | Percentage |
|---|---|---|
| Cement CP V ARI | 792.0 | 90% |
| Mineral addition (limestone filler, rice husk ash or red clay) | 88.0 | 10% |
| Binder material (cement + mineral addition) | 880.0 | 100% |
| w/c ratio = 0.47 | 413.6 | – |
| Fine aggregate | 1,980.0 | 100% |
| Aggregate retained # 2.36 mm | 198.0 | 10% |
| Aggregate retained # 1.18 mm | 495.0 | 25% |
| Aggregate retained # 0.60 mm | 495.0 | 25% |
| Aggregate retained # 0.30 mm | 495.0 | 25% |
| Aggregate retained # 0.15 mm | 297.0 | 15% |

The reference mortar, without mineral addition, it contains 880 g of cement CP V—ARI

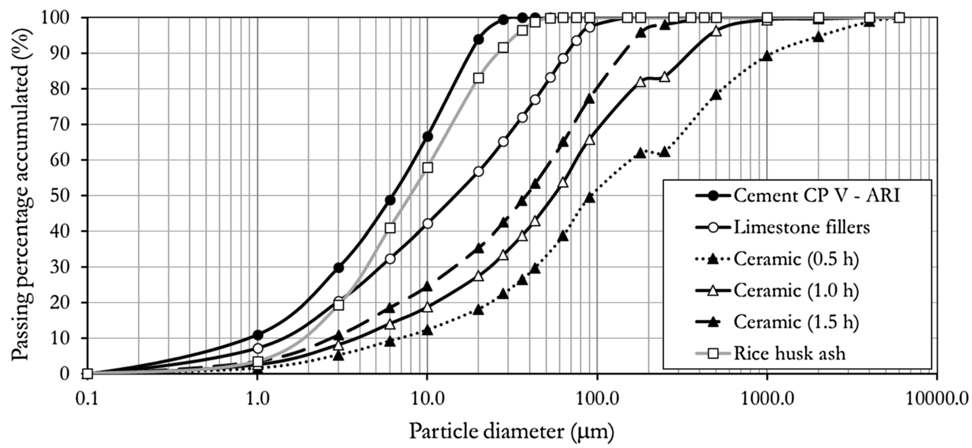


**Fig. 1** Particle size distribution of additions compared with the cement used

**Table 4** BET specific surface area and average particle of the agglomerates

| Material | Bet specific surface area ($m^2/g$) | Average particle of the agglomerates (m) |
|---|---|---|
| Cement CPV-ARI | 1.1 | 6.3 |
| Limestone filler | 1.4 | 15.4 |
| Rice husk ash | 14.7 | 8.1 |
| Ceramic material 0.5 h | 12.9 | 93.3 |
| Ceramic material 1.0 h | 13.0 | 56.1 |
| Ceramic material 1.5 h | 13.0 | 38.1 |

## 3.1 Fineness of the binders and limestone filler

Tests regarding the fineness of binders were executed because they have a relevant role regarding the behavior and reactivity of the composite of Portland cement. The cement, limestone filler, ash from rice husk and ceramic ground for the three milling periods (0.5; 1.0 and 1.5 h), were characterized regarding the granulometric distribution and the BET specific surface area.

Figure 1 shows the granulometric distribution of materials and, in Table 4, are results of the determination of specific surface area by the BET method and the average size diameter of particles. Rice husk ash was the addition with closer granulometric curve to Portland cement. On the other hand, the specific surface area BET of ground ceramic is nearly 12 times greater than the area of cement, independently of milling time. The specific surface area BET of limestone filler is 9 times smaller than red ceramic. It is worth to highlight that a greater milling time and, consequently, a greater fineness, did not alter significantly the specific surface area BET of RCW. On the other hand, the technique of laser granulometry indicated that the milling time influences the granulometric distribution of grains, with increase of material fineness according to increase of milling time.

## 3.2 Pozzolanic activity of mineral additions

The techniques used for investigating the pozzolanic potential of residues from red ceramic and rice husk ash were: test Chapelle modified [27], IAP with lime [25] and IPA with cement [26].

### 3.2.1 Modified Chapelle test

Table 5 has the values of modified Chapelle test for the samples of ceramic with different finenesses and for rice husk ash. In the case of limestone filler, the method cannot be use because it is not a silicon, aluminum or silica alumina material, in other words, without the possibility to be considered as pozzolana due to its chemical composition.

Raverdy et al. [28] studied the calcium fixation by samples of pozzolana obtaining the minimum indicator value of 330 mg CaO/g sample or 436 mg $Ca(OH)_2$/g sample] for a material to be considered as potentially pozzolanic.

**Table 5** Chapelle test, determined by NBR 15895/2010

| Material | Content $Ca(OH)_2$ fixed (mg $Ca(OH)_2$/g specimen) | Increase in reactivity with fineness (%) |
|---|---|---|
| Rice husk ash | 1336 | – |
| Ceramic material 0.5 h | 454 | – |
| Ceramic material 1.0 h | 516 | 14.0 |
| Ceramic material 1.5 h | 537 | 18.0 |

In this study, tests were executed using proportion 1:1 (CaO:pozzolana).

Recently, the Brazilian and French standards, respectively, NBR 15,895/2010 [25] and NF P18.513/2012 [29] were reviewed and incorporated a significant change by adopting the proportion of 2:1 (CaO:pozzolana), with gain in the efficiency of the test and the result started to be expressed in mg $Ca(OH)_2$/g pozzolana.

The reactivity of RCW in the different finesse, determined by NBR 15,895/2010 [27], indicated, base id in the minimum limit proposed by Raverdy et al. [28] (436 mg $Ca(OH)_2$/g pozzolana), that the analyzed samples have some reactivity, with values near the minimum limit. It is worth to highlight that milling incremented the consumption of lime of the RCW, despite the specific surface area BET not varying considerably with the comminution.

The result of $Ca(OH)_2$ fixed by the rice husk ash was more than twice the one of red ceramic waste, indicating the high pozzolanic activity of this type of residue.

#### 3.2.2 Index of Pozzolanic Activity with lime

Results of the Index of Pozzolanic Activity (IPA) with lime for limestone filler, for rice husk ash and for ceramic material are in Fig. 2. Relation water/bonding materials (sodium hydroxide + mineral addition) of mortar with limestone filler was 0.54, in the case of rice husk ash it was 0.66; while for RCW, independently of the fineness, the relation was 0.38. Mortar with inert mineral addition, had compressive strength below the minimum of 6.0 MPa recommended by NBR 12,653/2012 [30]. If fact, this predictable behavior evidences that there is no significant chemical activity between calcium hydroxide and limestone filler and, this way, this addition is not classified as pozzolana. Mortars with addition of ceramic material, independently of milling time, also have compressive strengths below the minimum recommended by the standard, indicating, by this methodology, that such addition, independently of the levels of fineness used in this work, cannot be classified as pozzolana. Those results are compatible with the ones obtained by Oliveira et al. [6] regarding the classification of pozzolanic activity; however, they are against the results presented by Garcia et al. [31]. In the case of rice husk ash, this addition was classified as a pozzolana, despite the result being in the pozzolanicity threshold, which is a contradictory result with data obtained in the modified Chapelle Test (according to NBR 15,895/2010) [27] indicating high Pozzolanicity of this material.

#### 3.2.3 Index of Pozzolanic Activity with Portland cement

The test according to NBR 5,752/2012 [26] (IPA with Portland cement) demands that mortars have available, in fresh state, a pre-established consistency (225 ± 5 mm), resulting in varied volumes of kneading water as a function of the physical–chemical characteristics of mineral additions. Standard NBR 12,653/2012 [30] establishes as limit an additional of 10 to 15% over the water volume of mixture of the reference mortar, impacting in the compressive strength of the mortar. Figure 3 has the demand of water of mortars after the partial substitution of cement by limestone filler, rice husk ash or RCW with the different finenesses. The reference mortar, with cement only, was molded in water/cement relation equal to 0.48 (150 grams of water). Limestone filler increased in 6% the demand by water compared with the reference mortar, while red ceramic, with the different finesses, reduced the demand, in average for a proportional of 75%

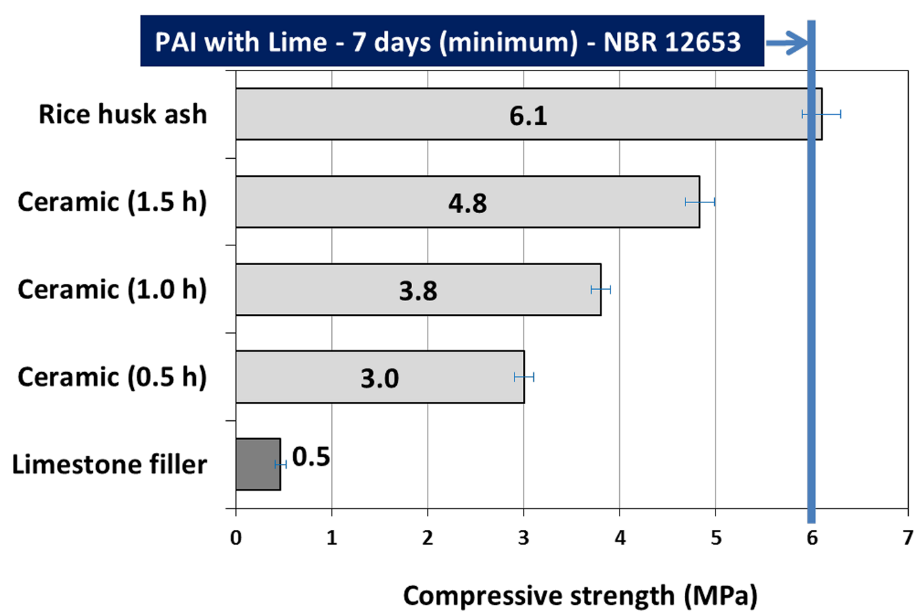


**Fig. 2** Pozzolanic activity index (PAI) with lime cal

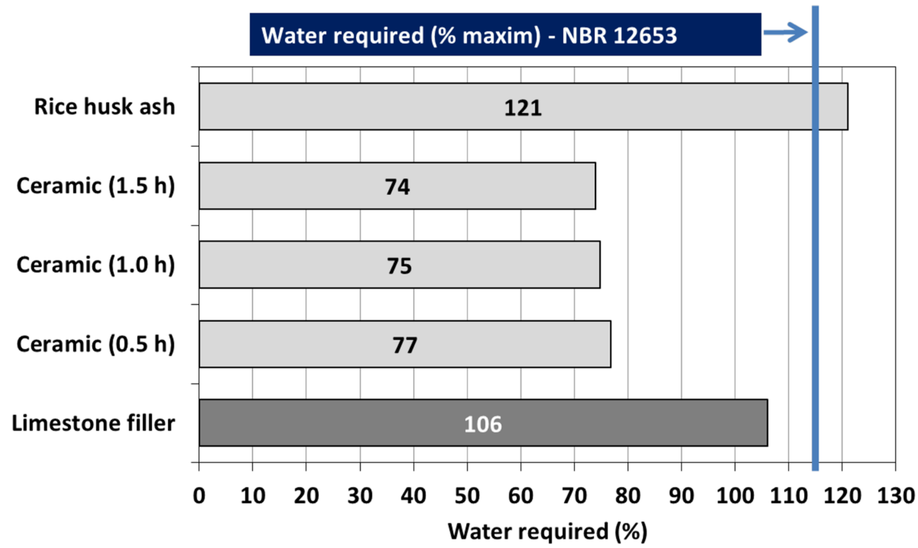


**Fig. 3** Demand percentage of mixing water of Portland cement mortars containing mineral additions compared to the reference mortar

and rice husk ash increased the demand of water to 121% of the water required for the reference series. In fact, the decrease of water demand by red ceramic potentiates the compressive strength of the mortar, to be evaluated next.

Figure 4 shows data of the compressive strength of Portland cement mortars with and without the limestone filler, with rice husk ash and with ceramic materials. The reference mortar reached, in average, compressive strength of 41.1 MPa, while the substitution of 35% of the volume of cement by limestone filler reduced resistance for approximately 23.2 MPa. Standard NBR 12,653/2012 [30] establishes a minimum percentage of 75% of compressive strength to the reference mortar in order to attribute pozzolanic potential to the mineral addition tested. Thus, for the studied cement, mortars with mineral additions must reach a minimum resistance of 30.8 MPa, which did not happen with mortar containing limestone filler, neither with samples having ceramic material. Therefore, they are not considered as pozzolana, this result being according to the test of IPA with lime. For rice husk ash the average value was 38.8 MPa, in other words, it was classified as pozzolanic addition with some slack.

It is worth to highlight that ceramic ground during 1.5 h reached compressive strength near the limit for classification as pozzolana. This behavior is related, mainly, to the smaller demand of mixing water for reaching the consistency pre-established in the normative methodology, although according to results from modified Chapelle test it is evident that there is influence of the chemical interaction of red ceramic with portlandite. As the variation in the demand of mixing water in the three mortars with red ceramic is very small, which is according with results from the BET specific surface area, the increment in compressive strength has to be associated with the greater interaction of the particles of the addition with calcium hydroxide, with consequent formation of a greater amount

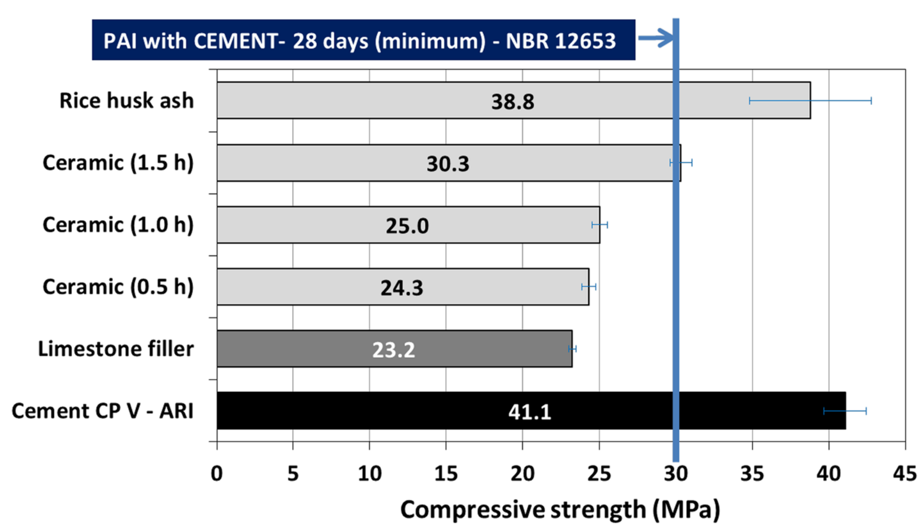


**Fig. 4** Pozzolanic activity index (PAI) with Portland cement

of hydrated calcium silicate, directly responsible by the carrying capacity of the material.

Figure 5 shows the X-ray diffratogram of the limestone filler. Using data from the International Centre for Diffraction Data (ICDD) for identifying constituents of this addition, characteristic peaks were found, indicating presence of calcite ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$) and quartz ($SiO_2$). In the sample of ceramic (diffractogram of Fig. 6) were found typical peaks revealing the existence of quartz ($SiO_2$), illite ($K \cdot Al_2 \cdot (Si_3.Al) \cdot O_{10} \cdot (OH)_2$) and hematite ($Fe_2O_3$).

In limestone filler there is no evidence of the presence of Amorphous halo in the diffractogram, evidencing that such addition has a high degree of crystallinity. Despite that, due to the fineness of this material, it may be used as filling material, improving the packaging of particles in mixtures and contributing for a better densification of cementitious composites. Red ceramic has a tenuous amorphous halo, coherent with its restrict capacity of reaction with lime, forming hydrated compounds, such as verified by Chappele's test [29] and also in IPA with lime [27] and in IPA with cement [28].

Chemical analysis of rice husk ash shows that practically 89% of this material is formed by silica ($SiO_2$), however, the determining factor of pozzolanic reactivity of a material depends on the degree of amorphicity of the silica compounding it. Figure 7 shows the X-ray diffractogram of this material, indicating that the silica of this ash is mostly in vitreous state and a small amount is organized as cristobalite, one of the polymorphic shapes of silicon dioxide. The main indication of the amorphous character of this material is the presence of the amorphous halo highlighted in Fig. 7. It must be verified that the size of the amorphous halo of the rice husk ash (RHA) is much more insinuated than the one presented by red ceramic waste (RCW), this being a determining factor to explain the fact that RHA had results much above the minimum limit in the test of IPA with cement.

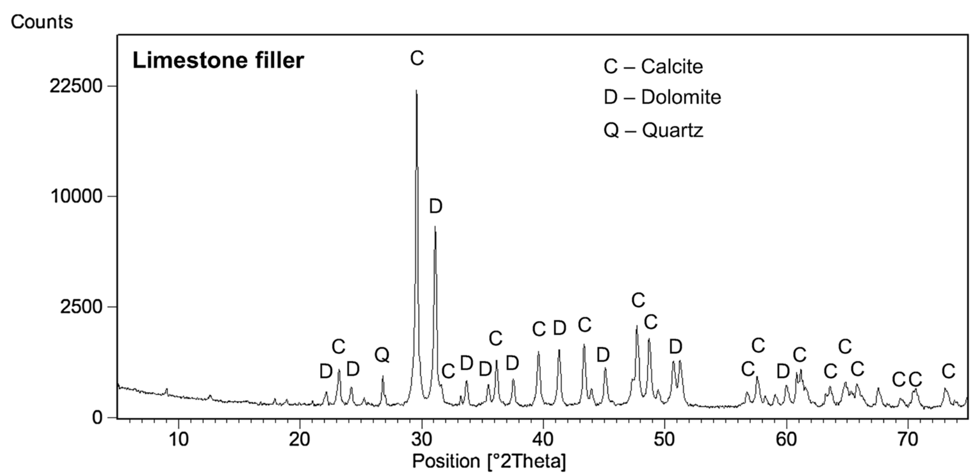


**Fig. 5** Diffractogram of X-ray limestone filler

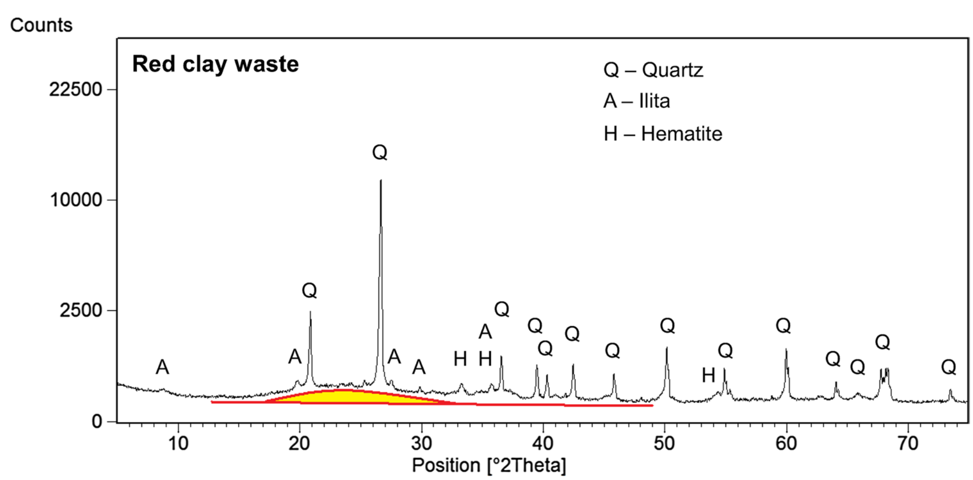


**Fig. 6** Diffractogram of X-ray red clay waste

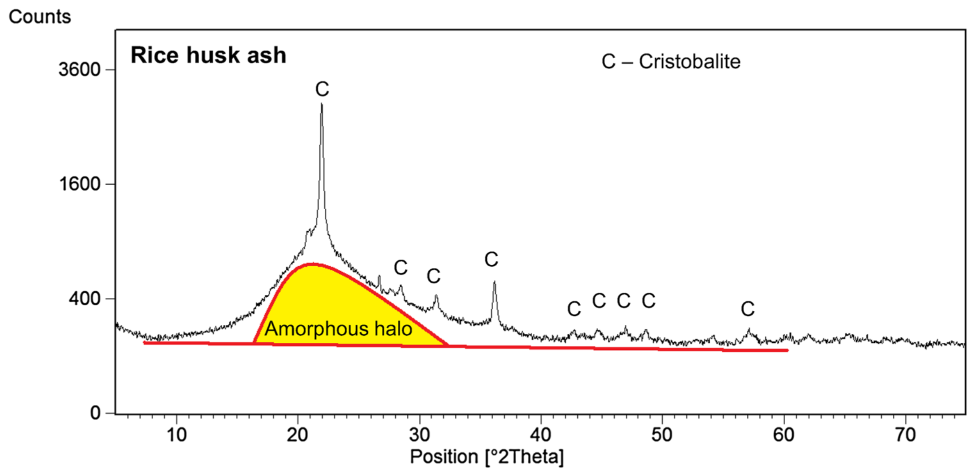


**Fig. 7** Diffractogram of X-ray rice husk ash

### 3.3 Alkali silica reaction

The evolution of the expansion of mortar bars due to the alkali silica reaction along 66 days is displayed in Fig. 8. The mortar of cement CP V—ARI, considered as the standard cement according to recommendations of NBR 15,577-4/2008 [21], was used for classifying, according to NBR 15,577-1/2008 [32] criteria, the innocuous or reactive potential of the aggregate used in this experiment. As expansion at 30 days (0.15%) was below the limit expansion of 0.19% established in the mentioned standard, the aggregate would be classified as potentially innocuous to be used in concrete. It is worth to highlight that the aggregate used in this experiment has a history of having ASR in a dam construction in Brazil, whose name is not authorized to be used in this document. NBR 15,577-1/2008 [32] indicates that in cases where there is history of ASR, the aggregate must be considered as potentially reactive, thus this is the effective classification of the aggregate.

Besides, Tiecher [20] and Valduga [19] by means of standard ASTM C 1260/2007 [20] also attributed 65reactive potential to this same aggregate. According to this american standard, it must be considered the possibility of this aggregate having alkali silica reaction due to expansion, at 14 days, being in the region of uncertainty established by the american standard[1], demanding, preventively, the adoption of mitigating measures.

The influence of the mineral additions of this work for mitigating the expansion of mortars, according to recommendations of NBR 15,577-1/2008 [32], must be evaluated at the age of 16 days, when expansion must be under 0.10%. In this study, besides the age recommended by the standard, it was opted by monitoring the behavior of mortars in greater ages, in order to better evaluate the influence of RCW and rice husk ash (Fig. 8), where are also displayed results of the

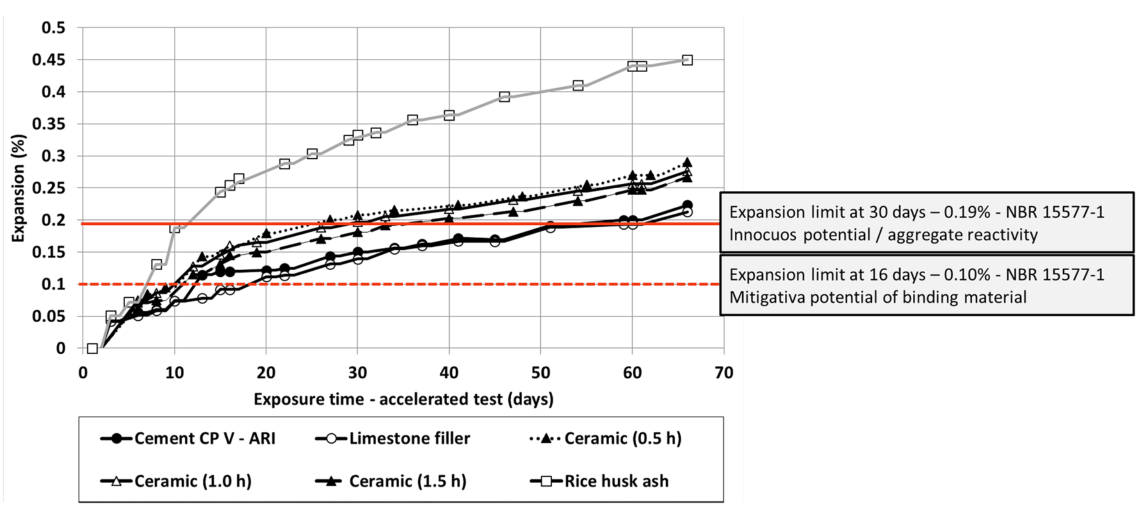


**Fig. 8** Alkali-silica reaction—evolution of the average expansion of mortar bars 100% cement compared to 10% replacement of cement mineral additions

expansion, at 16 days, of mortars containing the different bonding materials. As a matter of fact, cement CP V—ARI, used was standard, resulting in a system with expansion over the limit recommended by the standard.

The use of limestone filler in the composition of the bonding material apparently attributed mitigating potential to these additions, although, statistically, the result may be considered as identical to the limit value of 0.10%. Physical effects of limestone filler interfere in the microstructure of the hydrated matrix, which propitiated the expansion of mortar. Despite being classified as pozzolanic addition, the test represented in Fig. 8 show that rice husk ash increased, sharply, the expansion by RAS.

Red Ceramic Waste (RCW), independently of fineness, besides not mitigating the alkali silica reaction, propitiated the expansion of mortar to values over the one observed in reference. The greater milling time of red ceramic waste tended to reduce mortar expansion.

The general analysis, along 66 days, shows that the expansive behavior of mortar with limestone filler tends to equate the one of the reference series after 20 days, keeping this tendency along the studied period. The series containing RCW, in different finenesses, had a tendency to a greater expansion when comparing with the reference series, for the evaluated ages. As a matter of fact, the greater expansion always happens in the sample of red ceramic waste with less milling time.

It is worth to highlight that the use of RCW, with milling times of 0.5 and 1.0 h, attributed reactive potentiality to the respective mortars, because they overcome the expansion limit of 0.19% at 30 days. The mortar having residue milled during 1.5 h had expansion near the limit of the standard for the age in reference, attributing to this mineral addition uncertainty about its suitability for mitigating the alkali silica reaction. Summarizing, the red ceramic waste potentiates the expansion of mortar when there is presence of alkalis in the aqueous solution of the pores of the hydrated matrix.

## 4 Conclusions

The focus of this work was investigating the effect of incorporating RCW and rice husk ash for execution of concretes and mortars of Portland cement submitted to favorable conditions for occurrence of RAS. Results obtained in tests allow the following conclusions:

- RCW was classified as pozzolanic mineral addition when evaluated by means of the modified Chapelle test, besides results from indirect tests for evaluating pozzolanic activity (IPA with lime and IPA with cement) not attributing pozzolanicity to ceramic material, independent of fineness. The greater milling time of RCW incremented the use of lime by pozzolanic activity and the compressive strength of lime or cement mortars.
- The pozzolanic potentiality of RCW demands proper comminution of the material so that this also fulfils the classificatory requirements regarding compressive strength. This trend was evident in results of IPA with lime and IPA with Portland cement.
- The greater milling time of RCW increases the packaging of particles and, consequently, the compressive strength of the mortar.
- Based in data from laser granulometry, it is concluded that the greater the milling time of RCW is, the thinner is the material, indicating that the time of reduction of milling efficiency reported by Luz et al. [33] and Bristot [34] was not reached. This is the limit of milling time where, even increasing the time of operation of the mill, the granulometric curve of the powder produced does not indicate increase in the amount of thinner grains.
- Limestone filler did not reduce significantly ASR effects, despite promoting decrease of portlandite and alteration in the level of particles packaging. Generally, it can be considered that the series with limestone filler and the reference series are equivalent.
- In the case of RCW, expansion values by ASR, in all cases, were superior to the ones presented by the reference series, indicating that this material is not recommended to be used in concretes used together with reactive aggregate.
- Rice husk ash had proved pozzolanic activity in all tests of pozzolanicity, however, in ASR test it had increase of expansion, against the general consensus that the addition of pozzolans tends to be a way of mitigating ASR. This result shows that the mitigating capacity of ASR depends on the pozzolana to be used, demanding specific tests for each case of field application.
- Finally, the evaluating time of the accelerated tests proposed in ASR standards may be very short, because at more advanced ages, results indicate different and more conclusive trends when compared with results obtained in ages established in the respective standards.

**Acknowledgments** The authors thank for the support from the "Programa de Pós-graduação em Engenharia de Construção Civil da Universidade Federal do Paraná (DCC-PPGECC-UFPR)", from "Universidade Estadual de Ponta Grossa (UEPG)", from "Universidade Federal do Oeste da Bahia (UFOB)", from the "Instituto de Pesquisas Tecnológicas do Estado de São Paulo (IPT)" and from the "Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq)".

## References


1. Lucas D, Benatti C (2008) Utilização de resíduos industriais para a produção de artefatos cimentícios e argilosos empregados na construção civil. Rama: Revista em Agronegócio e Meio Ambiente 1:405–418
2. Senthamarai RM, Manoharan PD (2005) Concrete with ceramic waste aggregate. Cement Concr Compos 27:910–913
3. Senthamarai RM et al (2011) Concrete made from ceramic industry waste: durability properties. Constr Build Mater 25:2413–2419
4. Cabral A et al (2009) Desempenho de concretos com agregados reciclados de cerâmica vermelha. Cerâmica 55:448–460
5. Brito J et al (2005) Mechanical behaviour of non-structural concrete made with recycled ceramic aggregates. Cement Concr Compos 27:429–433
6. Oliveira L et al (2012) The potential pozzolanic activity of glass and red-clay ceramic waste as cement mortars componentes. Constr Build Mater 31:197–203
7. Reig L, Tashima MM, Soriano L, Borrachero MV, Monzo´ J, Paya J (2013) Alkaline activation of ceramic waste materials. Waste Biomass Valor 4:729–736
8. Matias G, Faria P, Torres I (2014) Lime mortars with ceramic wastes: characterization of components and their influence on the mechanical behavior. Constr Build Mater 73:523–534
9. Medeiros MHF, Souza DJ, Hoppe Filho J, Adorno CS, Quarcioni VA, Pereira E (2016) Resíduo de cerâmica vermelha e fíler calcário em compósito de cimento Portland: efeito no ataque por sulfatos e na reação álcali-sílica. Revista Matéria 21(2):282–300
10. Asensio E, Medina C, Frías M, Rojas MIS (2016) Characterization of ceramic-based construction and demolition waste: use as pozzolan in cements. J Am Ceram Soc 99(12):4121–4127
11. Castro AL, Santos RFC, Gonçalves KM, Quarcioni VA (2017) Caracterização de cimentos compostos com resíduo da indústria de cerâmica vermelha. Cerâmica 63(365):65–76
12. Geraldo RH, Ouellet-Plamondon CM, Muianga EAD, Camarini G (2017) Alkali-activated binder containing wastes: a study with rice husk ash and red ceramic Cerâmica 63:44–51
13. Cordeiro G et al (2009) Influência da substituição parcial de cimento por cinza ultrafina da casca de arroz com elevado teor de carbono nas propriedades do concreto. Ambiente Construído (Online) 9:37–49
14. Rodrigues M, Beraldo A (2010) Caracterização física e mecânica de argamassas à base de cimento Portland e cinza de casca de arroz residual. Engenharia Agrícola (Impresso) 30:193–204
15. Isaia G et al (2010) Viabilidade do emprego de cinza de casca de arroz natural em concreto estrutural. Parte I: propriedades mecânicas e microestrutura ISSN 1678-8621. Ambiente Construído (Online) 10:37–49
16. Zerbino R, Giaccio G, Isaia GC (2011) Concrete incorporating rice-husk ash without processing. Constr Build Mater 25:371–378
17. Zerbino R, Giaccio G, Batic OR, Isaia GC (2012) Alkali–sílica reaction in mortars and concretes incorporating natural rice husk ash. Constr Build Mater 36:796–806
18. Associação Brasileira de Normas Técnicas. NBR 15.577-5 (2008) Reação álcali-agregado. Parte 5: Determinação da mitigação da expansão em barras de argamassa pelo método acelerado. Rio de Janeiro
19. Associação Brasileira de Normas Técnicas. NBR 11.578 (1991) Cimento Portland composto. Rio de Janeiro
20. Tiecher F (2005) Reação álcali-agregado: avaliação do comportamento de rochas do sul do Brasil quando se altera o cimento utilizado. Exame de qualificação para obtenção do título de Mestre—Faculdade de Engenharia Civil, Universidade Federal do Rio Grande do Sul, Porto Alegre
21. Valduga L (2007) Influência das condições de ensaio da ASTM C 1260 na verificação da reação álcali-agregado. Tese (Doutorado em Engenharia Civil)—Escola de Engenharia, da Universidade Federal do Rio Grande do Sul, Porto Alegre
22. ASTM C-1260/07 (2007) Standard test method for potential alkali reactivity of aggregates (mortar-bar method). Philadelphia, Section 4 (Construction), v. 04.02 (Concrete and aggregates), pp. 647–650
23. Associação Brasileira de Normas Técnicas. NBR 15.577-4 (2008) Reação álcali-agregado. Parte 4: Determinação da expansão em barras de argamassa pelo método acelerado. Rio de Janeiro
24. Associação Brasileira de Normas Técnicas. NBR NM 23 (2001) Cimento portland e outros materiais em pó—Determinação da massa específica". Rio de Janeiro
25. Associação Brasileira de Normas Técnicas. NBR 5.751 (2012) Materiais pozolânicos—Determinação da atividade pozolânica—Índice de atividade pozolânica com cal—Método de ensaio". Rio de Janeiro
26. Associação Brasileira de Normas Técnicas. NBR 5.752 (2012) Materiais pozolânicos — Determinação do índice de desempenho com cimento Portland aos 28 dias. Rio de Janeiro
27. Associação Brasileira de Normas Técnicas. NBR 15.895 (2010) Materiais pozolânicos—Determinação do teor de hidróxido de cálcio fixado—Método Chapelle modificado. Rio de Janeiro
28. Raverdy M et al. (1980) Appréciation de l' ativité pouzzolanique des constituants secundaries. In: Congrés Internacional de la Chimie des Ciments, Paris, 7ª e., v.II e IV
29. Association Française de Normalisation. NF P 18-513 (2012) "Métakaolin, addition pouzzolanique pour bétons"—Définitions, specifications, critères de conformité
30. Associação Brasileira de Normas Técnicas. NBR 12.653 (2012) Materiais pozolânicos—Requisitos. Rio de Janeiro
31. Garcia E et al (2014) Resíduo de cerâmica vermelha (RCV): uma alternativa como material pozolânico. Revista Cerâmica Industrial 19(4):31–38
32. Associação Brasileira de Normas Técnicas. NBR 15.577-1 (2008) "Agregados—Reatividade álcali-agregado. Parte 1: Guia para avaliação da reatividade potencial e medidas preventivas para uso de agregados em concreto. Rio de Janeiro
33. Luz A et al. (2004) "Tratamento de Minérios". *CETEM: 4ed*, Rio de Janeiro
34. Bristot V (2008) Ferramental para prensagem hidráulica de esferoides de alumina. Dissertação (mestrado)—Escola de Engenharia da Universidade Federal do Rio Grande do Sul, Porto Alegre