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Evaluation of the Pozzolanic Activity of Glass Powder in Three Maximum Grain Sizes

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The addition of pozzolans has a potentially important role in the cement industry since using waste from other industries has important environmental benefits, including reduced CO_2 emissions from cement production. This study evaluates the pozzolanic activity of the glass powder in three different particle sizes (150 µm, 75 µm, and 45 µm, upper limits) and compares the results with those of other added pozzolans and technical standards found in the literature. Pozzolanicity was determined by four methods: Pozzolanic Activity Index (PAI) with lime, Performance Index (PI) with Portland cement, electric conductivity, and modified Chapelle. The results of the Chapelle and electrical conductivity trials indicated the pozzolanic activity of glass powder in all three particle sizes studied. The results of PAI with lime revealed pozzolanic activity of the 45 µm fraction while the performance index with cement showed the pozzolanicity of the 75 µm and 45 µm fractions according to ASTM C 618-05 (2005). It is concluded that the smallest glass fractions provided better reaction rates due to larger contact surfaces and are, therefore, considered pozzolans.

Keywords: *additions, pozzolanic activity, glass powder.*

1. Introduction

Pozzolans are inorganic, siliceous or silico-aluminous materials that alone exhibit little or no binding property, but finely ground and in the presence of water and calcium hydroxide, they react and form compounds with binding properties[1] at room temperature. Thus, these materials may be incorporated during the Portland cement production to form other cement types or added during the mixing of concrete and mortar.

Pozzolanic activity is the ability of certain materials to react with calcium hydroxide, a by-product of the cement and water reaction, to form compounds with cementitious properties. In the presence of water, Portland cement gives off calcium hydroxide as a by-product of hydrating silicates, offering a limited contribution to the strength and durability of hydrated cement paste when compared to C-S-H[1,2].

The pozzolanic reaction causes calcium hydroxide to combine with pozzolanic material, forming secondary C-S-H, which further improves the mechanical properties and durability of the hydrated cement paste[2].

Thus, the technical advantage of adding pozzolans to the mixture is to consume the portlandite formed to produce an additional C-S-H[3], outlined in the following reactions.

$$\begin{aligned} &Portland\ cement + water \rightarrow CSH + Ca(OH)_2 \\ &Ca(OH)_2 + Pozzolans + water \rightarrow CSH \end{aligned} \quad (1)$$

The pozzolanic activity is a measure of the degree of reaction between the active pozzolanic materials and portlandite in the presence of water over time. It is defined by two parameters, the maximum amount of portlandite with which a pozzolanic material can be combined and the process reaction rate. Both parameters depend on the nature of the pozzolanic material and, more specifically, on the quality and quantity of the active phases. Because pozzolans are a heterogeneous family and hydration is a complex phenomenon, it becomes difficult to define a single pozzolanic activity model and, therefore, only general effects can be identified[4].

The effect of adding pozzolans can be characterized by direct and indirect methods. The indirect methods do not provide information on the pozzolan itself but resort to measuring the performance properties and the material reactivity in the cementitious composite over time[5]. Therefore, the performance index (PI) with Portland cement at 28 days and pozzolanic activity index (PAI) with hydrated lime at

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seven days are measured following the NBR 5752: 2014[6] and NBR 5751: 2015[7], respectively. The classification following these indirect methods is based on evaluating the compression strength of the mortar after adding the potential pozzolan. Also, measuring pozzolanicity using electrical conductivity is highlighted as an indirect method.

On the other hand, the direct methods use analytical means to evaluate the ability of pozzolans to fix lime to form hydrated compounds which, despite being more precise compared to indirect methods, have more restricted use due to high specialization[5]. Modified Chapelle, Frattini method and classic chemical titration are a few direct methods used to assess pozzolanicity.

Classified as a group of the ceramic material family, traditional glasses result from the fusion of a mixture of minerals and inorganic compounds, which after controlled cooling become a hard, homogeneous, stable, inert, amorphous, and isotropic material[8,9].

Zanotto and Mauro[10] seeking to clarify the solid and liquid concepts, reviewed several glass definitions previously published, and proposed the following definition, "glass is a non-equilibrium, non-crystalline, condensed state of matter that exhibits a glass transition. The structure of the glasses is similar to that of their parent super-cooled liquids (LSR/SCL), and they spontaneously relax toward the SCL state. The ultimate fate, in the limit of infinite time, is to crystallize".

Based on the composition, glass can be classified into several categories, but soda-lime glass, also called soda-lime-silica glass, is the most widely used for several purposes, such as producing containers (packaging, flasks), household glass (glasses, crockery) and flat glasses (buildings and automobile windows). Since it is the most commonly used, most research and publications focus on recycling soda-lime glass as cement supplement material in concrete[9,11,12].

Glass, in its simplest chemical form, may consist of pure silica and is called "quartz glass". However, the production of pure amorphous silica glass is a highly energy-intensive process that requires temperatures of about 1900 °C. Thus, quartz glass, considered a special glass type, is produced only when the application requires high chemical resistance. That said, the raw material of soda-lime glasses is either sodium carbonate or soda (Na_2CO_3), which is added as a Na_2O source to decrease the silica melting point to about 1500 °C. However, because adding soda increases glass solubility and, therefore, corrosion in water, calcium oxide or lime (CaO), magnesium oxide (MgO), and aluminum oxide (Al_2O_3) are added to improve chemical durability. Thus, soda lowers the temperature at which the silica melts and softens while lime acts as a stabilizer. Soda-lime glass is cheap, chemically stable, reasonably hard, and highly sustainable because it can be recycled several times, if necessary[11].

Glass waste is an environmental problem around the world, occupying huge areas of landfills while causing environmental pollution due to non-biodegradable nature. Additionally, the lack of space for new landfills is a problem faced by densely populated cities in different countries around the world. Therefore, the best solution to overcome the environmental impact of glass waste is to reuse it[13]. Although glass is already recycled on a large scale, different colored glasses are often mixed during recycling and become more difficult to be processed since the new resulting glass has a color that is difficult to control during the recycling process[14]. To this end, the Business Commitment for Recycling (Compromisso Empresarial para Reciclagem, CEMPRE)[15] reports that Brazil recycles on average only 47% of 980 thousand tons of the produced glass waste.

Given the above, using glass in the construction industry is among the most attractive options to value this waste since significant amounts of these materials can be used, without requiring very high quality[13,16].

The concept of using glass waste in concrete is not new and research on crushed glass used as a partial substitute for aggregates goes back a few decades. However, these attempts were unsatisfactory since the strong reaction between the alkalis present in the cement and the reactive silica in the glass interfered with cement mechanical properties. Nevertheless, as a fine powder with particle sizes less than 300 μm, glass performs well as a pozzolanic material in concrete and can mitigate the alkali-silica reaction[17-20].

In another study on the feasibility of including residual glass as a partial replacement of cement in cementitious systems[21], the authors suggest that glass particle size must be at least as fine as that of cement powder for evident pozzolanic activity in the short term.

The present study investigates the pozzolanic activity of finely ground glass for three different grain sizes defined by the upper limits of 150 μm, 75 μm, and 45 μm, passing through the #100, #200, and #325 mesh sieves, respectively.

Besides, adding glass to cementitious composites is an important sustainable practice since the added glass particles originate from residues of other industries that, probably, would be discarded in large quantities in inappropriate places, generating contamination risks to the soil and water sources. Nowadays, sustainability in civil construction has become an imperative for all agents of society, such as governments, consumers, investors, builders, and associations[22].

In this research, the pozzolanic activity of finely ground glass was determined by PAI with hydrated lime, PI with Portland cement, and electrical conductivity as indirect methods and the modified Chapelle method, as the direct method. The objective is to classify and rank the glass powder grain sizes according to the parameters established by these methods and to compare the obtained results with those reported in the literature and the available technical standards. However, although used in other pozzolan addition studies, the literature on the electrical conductivity evaluation method lacks data on its application in glass mixtures.

2. Materials and Methods

2.1. Glass processing

The glass powder used is soda-lime from amber-colored bottles. The bottles were carefully washed to remove dirt, labels, and glue, then crushed into pieces in a concrete mixer with steel balls while the obtained shard was ground in a ball mill. The 14-hour-grinding was performed using a mill coated with flint (silicate sedimentary rock) and balls of the same material. The steps of the process for obtaining the glass powder are shown in Figure 1.

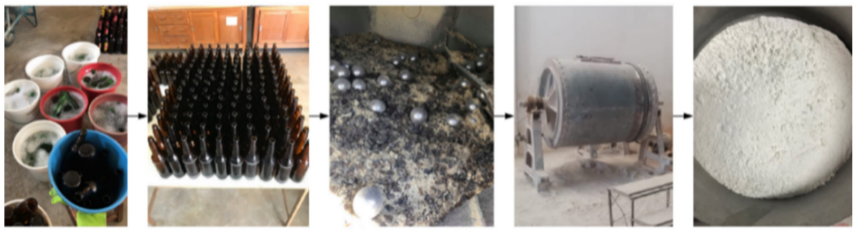


Figure 1. a) Washing to clean and remove the labels of the used bottles; b) Air drying of bottles; c) Crushing the bottles into pieces in a concrete mixer with steel balls; d) Final grinding in a ball mill; e) Final product after grinding.
Source: Freitas et al.[23]

Table 1. Proportions of components in the mortar mixtures used for PAI with lime.

Mortars	Mass of materials (g)				Water/binders ratio[2] (g/g)	Consistency[3] (mm)
	Lime	Brazilian standard Sand[1]	Glass powder	Water		
#100	104.00	936.00	248.04	205.00	0.58	225.00
#200	104.00	936.00	248.04	205.00	0.58	226.00
#325	104.00	936.00	251.00	228.00	0.64	226.00

[1]Brazilian standard sand according to NBR 7214:2015[27]: 234 g of each grain fraction. [2]Water/binders ratio: water mass divided by the calcium hydroxide and glass powder masses in the mortar: $m_{water}/(m_{calcium\ hydroxide} + m_{glass\ powder})$. [3]Consistency index obtained by the flow table test, according to NBR 7215:2019[28].

The obtained glass powder was separated into three fractions with different grain sizes defined by the following upper limits, <150 µm (#100 mesh sieve), <75 µm (#200 mesh sieve), and <45 µm (#325 mesh sieve). Average yields of 92, 65 and 18% were recorded for the #100, #200 and #325 sieves, respectively. The final sifting was carried out in the Materials and Components Laboratory (LMC) of the Federal University of São Carlos (UFSCar). Initially, the glass powder was dried in an oven at (110 ± 5) °C for 24 h, then sieved in a Ro-Tap W. S. TYLER sieve shaker in the three fractions. All samples were prepared following the same procedure and using the same equipment.

The grain sizes of the three fractions were determined in the ANALYSETTE 22 NanoTec laser granulometer, FRITSCH, Germany. The glass powder morphology was determined using the Inspect F50 FEI scanning electron microscopy (SEM), in the dry particulate state[24].

The density of the samples was determined by the Le Chatelier volumetric flask method according to NBR 16605: 2017[25]. The glass powder fineness was determined by the air permeability method (Blaine method) according to NBR 16372: 2015[26].

The chemical composition was determined in glass powder samples passing through the #200 mesh using plasma with optical emission, X-ray fluorescence spectrometry (XRF).

X-ray diffraction (XRD) analyses were used to determine the crystalline phases of the materials in #200 mesh fraction samples, using a Rigaku RU200B Rotaflex, with a 2θ nominal scanning between 3° and 120°, 0.02° step, scanning speed of 2°/min, 40 kV and 60 mA voltage, and copper anode.

2.2. Determining the Pozzolanic Activity Index (PAI) with lime

The PAI with lime was determined according to NBR 5751: 2015[7]. The mortars used in the specimens were prepared by mixing LABSYNTH calcium hydroxide (95.0% purity), water, added glass powder fraction of the studied grain sizes with Brazilian standard sand fractioned into four-grain sizes (coarse, #16; medium coarse, #30; medium fine, #50; and fine, #100), processed and produced by the Institute of Technological Research of the State of São Paulo (IPT) as established by NBR 7214: 2015[27].

To determine the PAI with lime, the evaluated mortar had a fixed calcium hydroxide mass (104 g) whereas the amount of added pozzolan corresponded to twice the calcium hydroxide volume. The pozzolan (glass powder) mass, m, in grams for the mixture is given by Equation 2.

$$m = 2 \cdot \frac{\delta_{poz}}{\delta_{cal}} \cdot 104\,\text{g} \quad (2)$$

Where,
δ_{poz} *density of pozzolan,*
δ_{cal} *density of calcium hydroxide.*

For the compressive strength test, the mortar used in the specimens must present, in the fresh state, a consistency index of (225 ± 5) mm, thus requiring mixing water at varying volumes, according to the physical-chemical characteristics of the added pozzolans[5]. Table 1 shows the proportions of the components used in the mortar mixtures, the water/binder ratios, and the consistency of each mixture.

Table 1 shows the mixture ratios according to the NBR 5751: 2015[7] for molding three cylindrical specimens of 50 mm x 100 mm (diameter x height) for each particle size fraction. To improve the precision of the results, the material quantities established by the standard were doubled, so the mortar was enough to produce six specimens for each grain fraction. The specimens were submitted to the compressive strength test after seven days.

It is noteworthy that the same amount (248.04 g) of glass powder was used from the #100 and #200 fractions while a slightly larger amount (251 g) was used from the #325 fraction. In this experiment, the pozzolan amount must correspond to twice the volume of calcium hydroxide[7], therefore, the weight difference compensates the 2.57 g/cm^3 glass powder density of the #325 fraction that is slightly higher than the 2.54 g/cm^3 of both #100 and #200 fractions.

The specimens were cured in their molds, kept closed at room temperature in the first 24 h, and then placed in an oven at 55 ± 2 °C.

Figure 2 shows some steps of the molding process of the specimens for the PAI test with lime.

2.3. Determining Performance Index (PI) with portland cement

The performance index with Portland cement was determined according to NBR 5752: 2014[6]. As recommended in the standard, the Portland CP II-F-32 cement, the Brazilian standard sand, water, and the added glass powder fraction of the three-grain sizes studied were mixed to produce two mortars, a reference (without added pozzolan) while the second had added glass powder fraction.

This experimental step requires mortars prepared using specific dosages. The reference mortar contains only cement, Brazilian standard sand, and water while in the second mortar, 25% by weight of CP II-F-32 cement was replaced with the pozzolan.

Table 2 shows the mix proportions of materials required for molding six specimens for testing the reference mixture and the mixture with added glass powder in the three grain sizes.

The NBR 5752: 2014[6] states that a superplasticizer additive must be added when the standard consistency index of the mortar with added pozzolan is equal (± 10 mm) or less than that of the reference mortar, otherwise the additive is not necessary (the case here with added glass powder of three different grain sizes).

For each prepared mortar, six cylindrical specimens of 50 mm x 100 mm were molded and subjected to the compressive strength test after 28 days, during this time they were cured with lime saturated water following the NBR 7215: 2019[28], except for the first 24 h, when they were placed still in the molds in a humid chamber.

Figure 3 shows some steps of the molding and curing process of the specimens for the performance index test.

2.4. Modified Chapelle

The Modified Chapelle test was performed according to NBR 15895: 2010[29]. In this trial, pozzolanicity is determined as the material ability to fix lime by pozzolanic action to form hydrated compounds in an accelerated test. For this, the material is kept in aqueous calcium oxide (CaO) suspension for (16 ± 1) h at (90 ± 5) °C, under constant agitation.

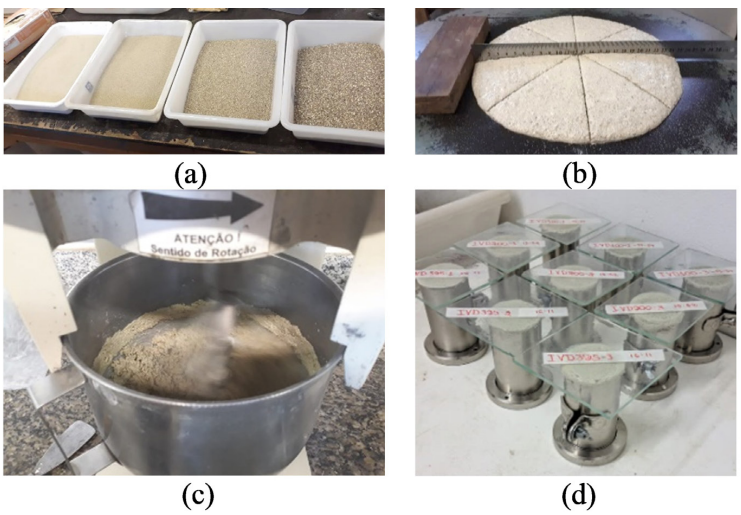


Figure 2. a) Grain fractions of the Brazilian standard sand used; b) Checking mortar consistency; c) Mixing process; d) Curing process of the specimens in the first 24 h.

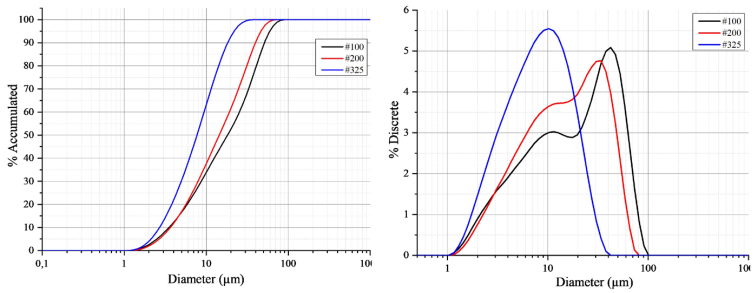
Table 2. Mix proportions of materials in the mortar used for molding the specimens to determine the performance index with the Portland cement.

Mortars	Mass of materials (g)				Water/binders ratio[2] (g/g)	Consistency index[3] (mm)
	Portland cement	Brazilian standard sand[1]	Glass powder	Water		
Reference	624.00	1872.00	-	300.00	0.48	156.00
#100	468.00	1872.00	156.00	300.00	0.48	154.30
#200	468.00	1872.00	156.00	300.00	0.48	151.00
#325	468.00	1872.00	156.00	300.00	0.48	150.00

[1]Brazilian standard sand according to NBR 7214:2015[27]: 234 g of each grain fraction. [2]Water/binders ratio: water mass divided by the masses of cement and glass powder in the mortar: $m_{water}/(m_{calcium\ hydroxide} + m_{glass\ powder})$. [3]Consistency index obtained by the flow table test, according to NBR 7215:2019[28].

(a) (b) (c)

Figure 3. a) Determining the consistency index; b) Measuring the spreading diameter; c) First 24 hours of curing of the specimens.



(a) (b)

Figure 4. Grain size distribution of the glass powder: a) Accumulated; b) Discrete.

The mixture consists of adding (1.00 ± 0.001) g mineral addition and (2.00 ± 0.001) g calcium oxide in 250 mL of water in a plastic Erlenmeyer. The solution is titrated with HCl and the result is expressed as the amount of calcium hydroxide fixed per gram of mineral added. Glass powder samples of all three-grain sizes were tested.

2.5. Pozzolanicity by electrical conductivity

In this test, pozzolanicity is measured as the variation in electrical conductivity, represented by the Relative Loss of Conductivity over time. There is an evident correlation between the decreasing electrical conductivity and the formation of hydrates during the pozzolanic reaction. According to literature[30-33], conductivity decreases significantly due to the early fixation of calcium by amorphous silica in the initial moments of the reaction between pozzolan and lime (CH).

According to Luxán et al.[33], Raask and Bhaskar[34] were the first to develop a method to evaluate pozzolanic activity by measuring electrical conductivity while investigating the pozzolanic activity of pulverized fuel ash using hydrosulfuric acid as a dispersant to measure the amount of dissolved silica. This quick method represented an advance compared to the previous ones and was adjusted to be applied to fly ash of power plants.

Luxán et al.[33] established a correlation between the pozzolanicity of natural materials and their electrical conductivity. These authors observed a good correlation between decreasing conductivity and the formation of hydrates during the pozzolanic reaction.

The electrical conductivity of a glass powder and deionized water solution was measured to assess the contribution to the total conductivity of Na^+, K^+, Mg^{2+} and other minor ions that could be present in the finely ground glass. Subsequently, the electrical conductivity of calcium hydroxide, deionized water and glass powder solution was measured. In the second case, 250 ml of deionized water were heated to 80 °C in Erlenmeyer, then 200 mg of $Ca(OH)_2$ was added to obtain an unsaturated solution. The mixture was homogenized for 1 h to dissolve all $Ca(OH)_2$[31], then the solution temperature was lowered to 60 °C. Upon reaching this temperature, the electrical conductivity was measured using a conductivity meter. Next, 5.25 g of glass powder was added to the heated solution while the data for calculating the Relative Loss of Electrical Conductivity (RL), according to Equation 3, were collected over a 24 h period.

$$RL(\%) = \frac{C_0 - (C_{pa})}{C_0} \cdot 100 \quad (3)$$

Where,

C_0 is the electrical conductivity of the unsaturated $Ca(OH)_2$ solution before adding the pozzolan (glass powder). The measurement is expressed as microsiemens per centimeter (µs/cm);

C_{pa} is the absolute loss of electrical conductivity at a given time t (s).

After the calculations, the relative loss of electrical conductivity (RL%) x time data were plotted to analyze the results. The pozzolanicity by electrical conductivity was evaluated for all three-grain sizes of the glass powder.

3. Results and Discussion

3.1. Characterizing the glass powder

Figure 4 shows the cumulative and discrete particle size distributions of finely ground glass for all three-grain sizes studied.

The plot shows that the lagest particle size, 90 µm, is found in the fraction of the #100 sieve (largest mesh analyzed). Additionally, the smallest particle size of approximately

1 µm is the same for all three-grain size curves. The median diameters (d_{50}) of 7.7, 14.4, and 18.1 µm were determined for glass powder sifted through #325, #200, and #100 mesh, respectively.

Figure 5 shows the micrographs of the glass powders for all three different particle sizes obtained by scanning electron microscopy (SEM).

Figure 5 evidences the different particle sizes of the glass powders for all three-grain fractions while demonstrating the similar morphology of the glass particles to that of cement, such as defined edges and angular shapes. Mineral additions incorporated in the concrete mixture can be classified, according to their shape, into three different morphological categories: spherical, lamellar, and irregular[35]. Thus, the micrographs allow identifying the irregular morphology of the glass powder.

Table 3 shows glass powder densities and Blaine fineness for all three particle sizes analyzed. The glass powder chemical composition is shown in Table 4.

The glass powder had a large amount (74%) of silicon dioxide (SiO_2), as well as sodium (11.0%), calcium as CaO (9.1%), aluminum (3.7%), and iron (0.42%) oxides, among others (Table 4). In view of the material chemical composition, the recommendations of NBR 12653: 2014[1] for pozzolanic materials are valid, since this standard determines that the summation of SiO_2, Al_2O_3 and Fe_2O_3 oxides must be greater than 70% for pozzolan classes N and C: volcanic materials, calcined clays, fly ash.

Zheng[20] reported that aluminum plays an important role in reducing the alkali-aggregate reaction, combining with the reactive silica of the aggregates, preventing its dissolution

Table 3. Glass powder densities and Blaine fineness.

Mesh	Density (g/cm^3)	Blaine fineness (cm^2/g)
#100	2.54	2860
#200	2.54	3930
#325	2.57	7420

Table 4. Glass powder chemical composition.

Components	% mass
Calcination loss (PPC)	0.58
Al_2O_3	3.7
CaO	9.1
Fe_2O_3	0.42
K_2O	0.56
MgO	0.74
Na_2O	11.0
SiO_2	74.0
SrO	0.039
Rb_2O	0.016

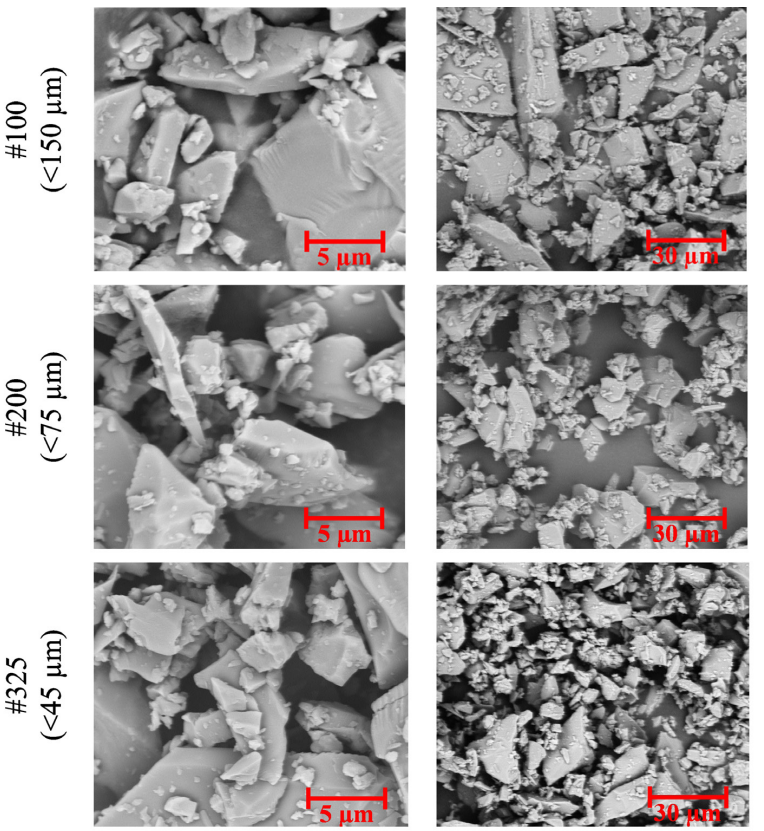


Figure 5. SEM Micrographs of glass powder of three grain sizes (<150 µm; <75 µm; <45 µm).

in the cementitious matrix while avoiding its reaction with the cement alkalis. The author states that the aluminum may come from the glass itself, especially from the dissolution of the monosulfate, formed during the hydration of the cement, but apparently decomposed in environments rich in sodium (Na) and silica (Si) (a large sodium amount is provided by the glass) and low in calcium (Ca) because the pozzolanic reaction consumes a large amount of $Ca(OH)_2$.

The XRD diffractogram of Figure 6 shows the test results where the peaks indicate the presence of a crystalline phase.

The graph shows that the material is predominantly amorphous, with a SiO_2 peak between the angles 2θ (°) 25 and 30. The SiO_2 peak may be explained by material contamination during the dry grinding process of the samples using flint balls, indicating the wear of the mill and the SiO_2-rich balls. However, the effect of this contamination was considered not significant.

The crystalline peak is understood to be contamination since glass, by nature, always presents amorphous diffractometry. In this case, the material can be associated with quartz (crystalline silica). The crystalline silica contamination is not a reactive load with the other compounds present and should behave as an aggregate in smaller dimensions, in the same way as a filler, and not interfere with the cement hydration reaction.

Likewise, Elaqra and Rustom[36] identified similar contamination of the glass powder with cement that originated from remnants of the material present in the equipment during grinding.

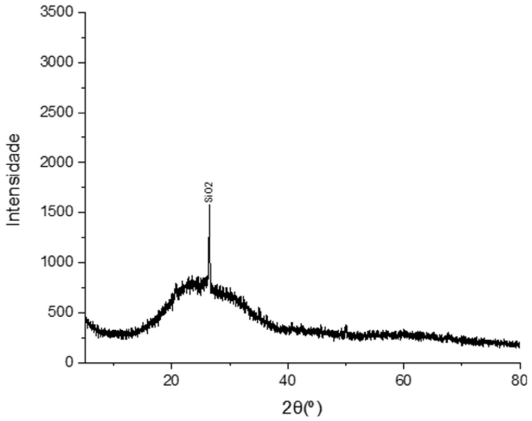


Figure 6. Diffractogram of the glass powder.

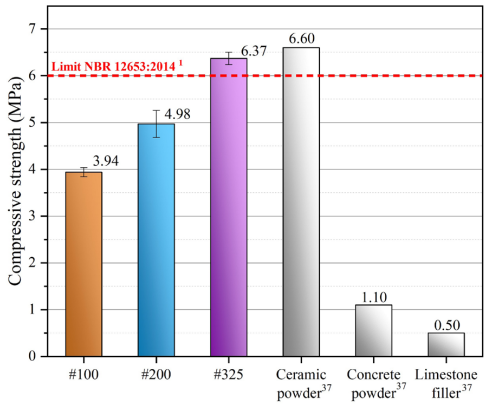


Figure 7. Compressive strength results of PAI tests with lime for the studied grain sizes of glass powder and comparison with ceramic and concrete waste powders, as well as limestone filler[37].

3.2. Evaluation of pozzolanic activity/ pozzolanicity

The method of indirect investigation of the reactive potential standardized by NBR 5751: 2015[7] is based on determining the ultimate compressive strength of specimens molded with a fixed volumetric proportion of solid materials and variable water volume, to obtain a pre-established consistency index of (225 ± 5) mm in fresh mortars.

Thus, the results of compressive strength for different pozzolans cannot be compared, but rather correlated with an arbitrary minimum value. The conditions recommended by the standard interfere directly with the compressive strength parameter since changing the water volume in the mixture while keeping the particle volume constant changes the mixture porosity, affecting the compressive strength of the hardened material specimen[5].

Thus, NBR 12653: 2014[1] states that for the pozzolanic activity index test with lime, mortars containing the addition being studied must reach a minimum compression of 6.0 MPa to be classified as pozzolanic materials that can be incorporated into the composition of composite Portland cement or pozzolanic[5,37].

Figure 7 shows the results of PAI with lime for mortars with added glass powder in the three-grain sizes studied and compares to those of Brekailo et al.[37]. These authors evaluated the reactive potential of red ceramic waste powder (d_{50} = 30 µm), concrete waste powder (d_{50} = 25 µm), and limestone filler (d_{50} = 20 µm) as a reference.

Figure 7 reveals that, after 7 days, only the glass powder of the #325 fraction achieved the minimum compressive strength of 6 MPa required by the standard NBR 12653: 2014[1]. Additionally, the results show that the pozzolanic activity of the glass powder increases with decreasing grain size (increasing fineness). Likewise, the analyzed results of the work in the literature[37] show that only the ceramic powder achieved the minimum compressive strength of 6.0 MPa required in the standard. Furthermore, it is noteworthy that the filler material, which is expected to have low reactivity had, in fact, the lowest resistance.

The NBR 5752: 2014[6] states that the pozzolanic activity index with cement is defined as the ratio between the average compressive strength of the cylindrical specimens with pozzolans and the reference specimens containing only cement, Equation 4. The maximum relative deviation cannot exceed 6%[28].

$$I_{cement} = \frac{f_{cVD}}{f_{cREF}} \cdot 100 \quad (4)$$

Where,

I is the performance index with Portland cement at 28 days. Result expressed as (%);

f_{cVD} *is the average resistance of specimens molded with cement and 25% glass powder, expressed as MPa;*

f_{cREF} is the average resistance of reference specimens molded with cement only (MPa).

Figure 8 shows the performance index results with Portland cement and added finely ground glass in the three-grain sizes studied and comparison with data for ceramic and concrete powders, as well as limestone fillers from Brekailo et al.[37].

At 28 days, the performance index of specimens molded with Portland cement and added materials of three different grain sizes did not reach the 90% performance index required by NBR 12653: 2014[1] for being classified as pozzolans (Figure 8).

On the other hand, the American standard ASTM C 618-05[38] requires a minimum performance index of 75% to classify a material as a pozzolan. In this context, the #200 and #325 glass fractions fulfill the American standard requirement. Similarly, Cordeiro et al.[39] also compared the Brazilian and American standards while studying the pozzolanic activity and the filler effect of ash from sugarcane bagasse.

As observed with the #325 glass powder fraction in the present study, Brekailo et al.[37] reported the best performance index for mortars with Portland cement and added red ceramic powder. The #100 glass fraction and the limestone filler had the lowest performance indexes and, therefore, a low pozzolanic activity.

Even with a poorer performance confirming the material inert character, the limestone filler result is close to the requirement of the American standard[38]. This seeming contradiction is explained by the fact that even inert materials mixed with cement can significantly affect the hydration of the clinker phases, the so-called filler effect[40].

The physical effect, known as the filler effect, corresponds to the pore refinement process: the hydration reaction products fill the large capillary spaces quite efficiently while increasing system resistance and reducing permeability[35].

Two main mechanisms contribute to the filler effect: a) The first is related to **extra space**: as the filling material does not produce hydrates, in the same water/solids ratio, the higher water/clinker ratio allows more space for hydration products of the clinker phases; b) the second mechanism is related to the **nucleation effect** in which the thin surface of the supplementary cementitious material acts as nucleation sites for the hydration products of the clinker phases, causing a refinement of the hydrated matrix pores[40].

The result of the modified Chapelle test is expressed by the lime content fixed by the pozzolanic activity of the studied mineral. Lime consumption is indicative of the pozzolanic potential of mineral addition.

Proposed by Raverdy et al.[41], the modified Chapelle method states that 330 mg CaO/g mineral addition (equivalent, by stoichiometric calculation to 436 mg $Ca(OH)_2$/g addition) is the minimum consumption established for classifying the added mineral as a pozzolan.

Figure 9 shows the results for the consumption of Ca $(OH)_2$/g glass powder in the three analyzed particle sizes. Regarding the comparison with the study in the literature[37], the modified Chapelle test was performed only for the added red ceramic powder because the other two added materials (concrete powder and limestone filler) had a large amount of calcium in their composition, not being recommended to quantify the remaining[37].

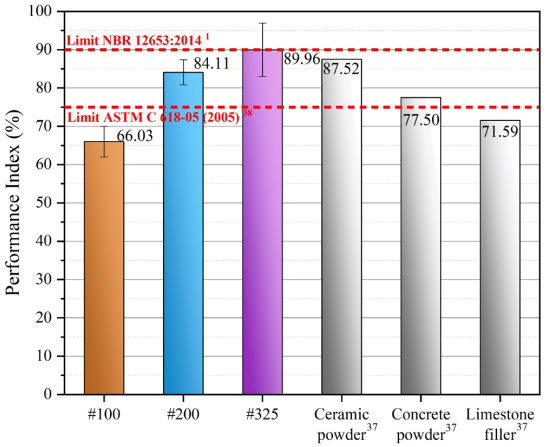


Figure 8. Performance Index with Portland cement and added glass powder of three different grain sizes and comparison with ceramic and concrete waste powders, as well as limestone fillers[37].

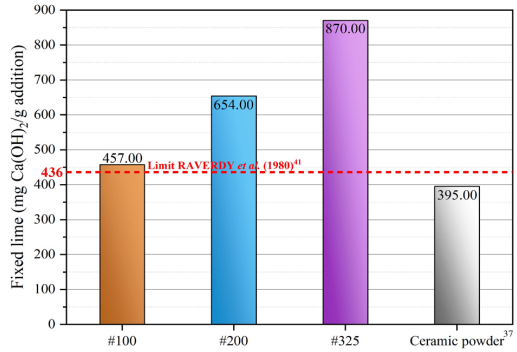


Figure 9. Modified Chapelle Test.

Figure 9 shows that all three size fractions of the glass powder reached the minimum requirement of 436 mg $Ca(OH)_2$/g mineral addition, but the pozzolanic performance increases remarkably with decreasing particle size (finer glass particles). Indeed, the #325 glass powder fraction reached 870 mg of lime fixed per gram of glass powder, well above the minimum requirement.

Another important point is that the NBR 15894-1: 2010[42] establishes that the Chapelle pozzolanic activity index should be greater than or equal to 750 mg $Ca(OH)_2$/g for metakaolin (a pozzolan intended for use with Portland cement in concrete, mortar, and paste). And, in this study, the smallest size of the glass powder exceeded the reference value for metakaolin.

Unlike the red ceramic powder, which provided a value of 395 mg $Ca(OH)_2$/g, below the minimum required and cannot be classified as pozzolan according to this test.

The pozzolanic activity results, indicated by the varying electrical conductivity of the solution, are given by the Relative Loss of Electrical Conductivity (Pr) over the reaction time (s). Figure 10 shows the resulting curves for the glass powder in the three particle sizes studied.

To complement the analysis, Table 5 compares the electrical conductivity pozzolanicity of glass powder to that of porcelain residue (PR), metakaolin (MK), and rice husk

Table 5. Relative loss of electrical conductivity (%) over time (s) for different mineral additions.

Time (s)	#100 glass fraction	#200 glass fraction	#325 glass fraction	PR[31]	MK[31]	RHS[31]
100	2.40	6.15	7.94	5	63	27
1000	6.16	10.39	13.21	14	69	46
10000	44.86	56.97	65.00	45	80	48
100000	83.87	81.82	80.92	83	74	58

Table 6. Summary of the results of the pozzolanic activity tests performed with glass powder.

Grain sizes of glass powder	PAI with lime	Performance index with cement (limit NBR 12653:2014[1])	Performance index with cement (Limit ASTM C 618-05[38])	Modified Chapelle	Pozzolanicity by electrical conductivity
#100 (150 µm)	⊗	⊗	⊗	✓	✓
#200 (75 µm)	⊗	⊗	✓	✓	✓
#325 (45 µm)	✓	⊗	✓	✓	✓

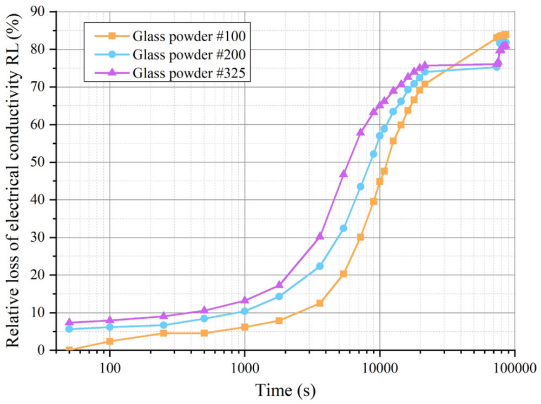


Figure 10. Relative loss of electrical conductivity over time (s) for CH and glass powder solutions in the three particle sizes studied.

silica (RHS), already known as traditional pozzolans used in mortars and concrete, determined by Fernandes et al.[31].

Figure 10 shows that the low initial RL values of the glass powder occur because the material was still being dissolved at the beginning of the reaction. The stabilizing trend of the curves observed after 20000 seconds, indicates a reduction of chemical activity and the time when the reaction between amorphous silica and calcium to form hydrated calcium silicate (C-S-H) is practically finished. Thus, as the pozzolan consumes $Ca(OH)_2$, the calcium hydroxide concentration in the solution decreases and forms insoluble products while the lower Ca^{2+} causes the electrical conductivity to decrease[31].

At the initial times, the glass powder in the smallest particle size (#325) fraction provided the highest percentages of the relative loss of conductivity, indicating a better reactivity at this studied size compared to the other two particle sizes.

Table 5 shows the relative loss of conductivity results for the glass powder in the three particle sizes studied, as well as the PR, MK, and RHS. MK and RHS had a higher RL in the initial times due to a greater chemical affinity with the calcium present in the solution. At 1000 seconds, the MK value stands out compared to the other materials analyzed. Indeed, this material is known for its high pozzolanicity[31]. Also, despite the initial slow reaction, after 10000 seconds, the three particle sizes of the studied fine glass powder reach values (80%) similar to those reported for metakaolin.

Table 6 summarizes the results of the pozzolanic activity tests performed in this study to evaluate glass powder of three particle sizes.

The results of all performed tests indicate that the finely ground glass of the smallest particle size yielded the best pozzolanic activity performance. Likewise, Khmiri et al.[16] studied the pozzolanic activity and the compressive strength of mortars with 20% glass powder (different grain sizes) replacement proportion in relation to cement, and these authors concluded that the smallest particle size studied (<20 µm) exhibited better pozzolanic behavior. Other authors have also linked a better pozzolanic behavior with the smaller particle sizes of finely ground glass[18,19] while pointing out that when used as supplementary cementitious material, as the glass particle size decreases, occurs a control of the alkali-silica reaction rates (RAS) in cementitious composites.

Given the above, the varying physical-chemical characteristics of the mineral additions and several other factors affect the interaction with lime to form cementitious components. These characteristics shape the complexity of quantifying the pozzolanic activity of a given material and make it difficult to standardize a normative methodology for characterizing and raking these materials. The compatibility between the application and the development of the reactive potential of the mineral additions require scientific rigor to assign appropriate physical and mechanical characteristics to the cement matrix, thus, different evaluation methodologies must be employed to investigate the performance of the pozzolans[5].

The RILEM TC 267-TRM (Tests for Reactivity of Supplementary Cementitious Materials) has been established to evaluate existing reactivity tests and develop a pre-normative recommendation for rapid reactivity tests that can be adopted as standard methods. Researchers recommend that testing methods should be simple and robust, provide results faster than standard compressive strength tests while not requiring expensive equipment or advanced training of the techinicians performing it[43].

Li et al.[43] investigated 10 different reactivity tests and 11 supplementary cementitious materials (SCMs), covering

the main classes of materials in use. These authors used different methods seeking to correlate the compressive strength of standard mortar specimens with a 30% SCM replacement compared to 28-day-old cement and concluded that calorimetry tests are the best to estimate the pozzolanicity of the materials. Furthermore, they reported that methods such as Chapelle and Frattini did not show acceptable correlations in all analyzed materials.

According to Snellings et al.[44], the several existing methods of testing reactivity for SCMs often fail in one or more of the main requirements of an adequate test (especially the scope, practicality, reproducibility, and relevance of the results). A Rapid, Robust and Relevant (R3) chemical reactivity test applicable to a wide range of SCMs would serve not only as a global benchmark but would also remove current ambiguities regarding classification.

The basic principle of the R3 test methods is to use a simplified model system to separately measure the SCM reaction, seeking to avoid interference and overlap with the clinker hydration reactions that occur in a cement mixing system. Besides, the use of laboratory chemicals instead of local Portland cement types avoids much of the variability related to the material. Examples of tests that use the R3 methodology: calorimetry, bound water, chemical shrinkage, portlandite consumption[43,44].

4. Conclusions

This study investigated the pozzolanic activity of finely ground soda-lime glass of three different grain sizes, aiming at understanding the correlation between this material pozzolanic behavior and the different grain sizes of fractions sifted through #100, #200, and #325 mesh sieves (150, 75 and 45 μm, respectively). The three indirect evaluation methods used were PAI with lime, performance index with Portland cement and pozzolanicity by electrical conductivity, in addition to the direct method, the modified Chapelle.

The results of the modified Chapelle and electrical conductivity methods determined pozzolanic activity for the glass powder of all three particle sizes. However, the results of PAI with lime indicated pozzolanicity only for the #325 glass fraction. The performance index with cement does not indicate pozzolanic activity for any grain size according to the requirements of the Brazilian standard. However, according to the American standard, the results of the performance index with Portland cement indicate pozzolanic activity for the #200 and #325 glass fractions. Furthermore, the chemical composition of the soda-lime glass used in this study fulfills the requirements for pozzolanic materials, since the sum of oxides (SiO_2, Al_2O_3, and Fe_2O_3) is greater than 70%. The XRD analysis indicated a predominance of amorphous material with reactive potential.

The results obtained revealed that larger contact surfaces provide better reaction rates since the pozzolanic activity became more evident with decreasing grain size. Furthermore, all measurement methods indicate pozzolanic activity for the smallest particle size studied (smaller than 45 μm).

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