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Amorphism and mineral composition estimation of residual ashes for reuse as additives in construction materials

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Abstract: The ash generated in thermoelectric plants, originating from both coal and rice husk combustion, can be used in civil construction as sustainable additives, thus minimizing improper disposal. However, for this application, it is important to understand the characteristics of the materials. The chemical composition and amorphism are fundamental to understanding the reactive properties of ash when used as additives in construction materials. Based on these aspects, this study analyzed the mineral composition and estimated the amorphism of two coal fly ashes (CV-1 and CV-2) and one rice husk (RHA), using the X-ray diffraction (XRD) technique. The amorphism was estimated using the simple area separation method. Mineralogical analysis of the ash revealed that CV-1 and CV-2 contain quartz, calcite and hematite, while RHA is predominantly composed of quartz. The degree of amorphism was quantified at 65.08% for CV-1, 35.49% for CV-2 and 77.52% for CCA. The greater amorphism of CV-1 and CCA indicate more pozzolanic activity and, in turn, can be used as additives in construction materials replacing cement.

Key words: coal ash; rice husk ash; pozzolan; XRD

1 Introduction

Coal and rice husk ash, byproducts of burning for heat generation, are wastes generated in large volumes whose improper disposal can cause environmental problems, since improper disposal can contaminate surface and groundwater and soil through leaching (Canul et al., 2016). Therefore, research has been carried out with the aim of reusing these byproducts. In civil construction, for example, ash can replace Portland cement, in adequate proportions, as long as this material has pozzolanic characteristics (Tashima 2012).

According to the prescriptions of NBR 12653 (ABNT, 2014), to present pozzolanic activity the sum of the quantities of silica (S_iO_2), alumina (Al_2O_3), and hematite (Fe_2O_3) must be greater than 70% and the quantity of sulfur trioxide (SO_3) must be less than 5%.

The physical and chemical properties of ash from coal combustion are influenced by several factors, such as the composition of the coal used; the degree of coal processing and grinding; the type, design and operation of the boiler and the ash extraction and handling system (Sabedot et al., 2011).

According to the Brazilian Association of Technical Standards NBR12653 (ABNT, 2014), ash from the combustion of coal in Thermoelectric Power Plants (UTEs) is classified as class C pozzolans and CCA is classified as super pozzolan.

Paiva et al. (2016) report that pozzolans are finely divided siliceous or siliceous-aluminous materials that, once added to cement, provide chemical and physical interaction with the clinker hydration products, modifying the material's microstructure. The chemical effect refers to the reaction capacity of the mineral addition with calcium hydroxide, generated during cement hydration, to form hydrated calcium silicate.

NBR 12653 (ABNT, 2014) defines pozzolans as siliceous or silicoaluminous materials with little or no cementing properties, but when finely divided and in the presence of water, they are capable of reacting with the calcium hydroxide released during the cement hydration process, combining with it and fixing it at room temperature.

In cement-based matrices, pozzolans can contribute to increased mechanical strength, reduce water absorption by capillarity and improve workability due to the physical effect of the particles on the system's granulometric distribution. However, for this to happen, the ash needs to be amorphous (Lopes, 2020).

In terms of sustainability, the use of ash combined with new construction technologies contributes to reducing CO_2 emissions, the main environmental liability of the cement industry. In this scenario, Brazil has stood out with the use of this residue in cement matrices (Altherman et al., 2017).

The characterization of pozzolans is based, in practice, on indirect methods of quantifying the reactive potential. The different methods, despite their limitations, are capable of supporting the selection of pozzolanic mineral additions (Filho et al., 2017).

The reactivity of a pozzolan is related to the amorphous content. In the case of silica, the reactivity is related to the polymorphism of silicates; basic knowledge of these transformations becomes interesting for the commercial use of CV as a pozzolanic material (Cordeiro et al., 2014).

X-ray diffractometry (XRD) is a technique used in the characterization of materials and allows the identification of silica polymorphs, as well as the identification of minerals (Cordeiro et al., 2014).

What differentiates the crystalline and non-crystalline (amorphous) phases is the intensity of the crystalline dispersion, which is concentrated in the reflections, forming narrower peaks, and for the non-crystalline dispersion, in the amorphous halo and background. Figure 1 exemplifies how the crystalline (Ac) and amorphous (Aa) areas are identified and separated (Carolino, 2017 apud Stern; Segerman, 1968).

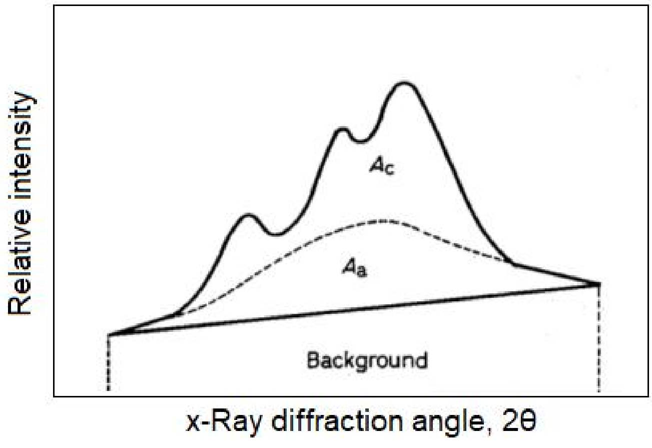


Figure 1. Separation of crystalline and non-crystalline areas

Source: Stern (1968), apud Carolino (2017).

From an XRD spectrum, by Simple Area Separation (SSA), it is possible to estimate the percentage of crystallinity and, consequently, of amorphism, of a material. The method consists of subtracting the halo area corresponding to the non-crystalline contribution from the total area of the diffractogram in a diffraction interval. The crystallinity estimate is performed by integrating the crystalline peaks and the amorphous band. The calculation is performed using Equation (1).

$$\%Cr = 100\frac{A_c}{A_c + A_a} \quad (1)$$

Where cr corresponds to the percentage of crystallinity, Ac to the crystalline area and Aa to the amorphous area. Based on the aspects presented, the objective of this work is to present the quantification of the amorphous phases of the three ashes. The research aims to demonstrate that mineralogical characterization by XRD, together with quantitative analysis of amorphous minerals, can be used as a parameter for the evaluation of the pozzolanic potential of residual ashes.

2 Materials

Two fly ashes (CV's) generated in thermoelectric power plants located in the Campanha Gaúcha region, in the city of Candiota, were analyzed. The coals have different origins, processing methods, and burning conditions. A rice husk ash burned without temperature control was also analyzed. The coal samples were identified as CV-1 and CV-2, and the rice husk ash was identified as CCA. Figure 2 shows images of the ashes analyzed in this study.

Figure 2. Ashes used in the research

Source: Prepared by the Authors (2023).

3 Methodology

The characterization of the ashes consisted of determining the mineralogical composition by XRD. The analysis was performed in a Rigaku diffractometer model ULTIMA IV with Bragg-Bretano geometry under the following conditions: copper ka line radiation, 0.05°/s step and 40 kV and 20 mA. The determination of the percentage of amorphism was performed based on the diffraction spectra.

4 Results and discussion

The ash diffractograms are shown in Figure 2a-c. Peak identification was performed using HighScore Plus software.

As shown in Figure 3 (a-b), silica, aluminosilicates (mullite) and hematite were identified in CV-1. While silica, hematite and calcite were identified in CV-2. Calcite is probably related to the oxidation of calcium from residual calcium sulfate from the desulfurization of flue gases (Ledesma 2018; Lacerda 2015; Silva 2009). The results were compared with literature standards. Because it presents narrower peaks, it is assumed that the S_iO_2 identified in CV-2 is in crystalline form.

Qualitative XRD analysis showed that CCA contains amorphous silica, indicated by the halo present in the diffractogram shown in Figure 2c. The presence of amorphous (pozzolanic) or crystalline (inert) silica is directly linked to the temperature and the method of obtaining the ash.

The burning of rice husk produces a significant amount of ash with pozzolanic characteristics, which can be in a crystalline or amorphous state, depending on the temperature control during burning, with amorphous ash generally being more reactive (Tashima 2012).

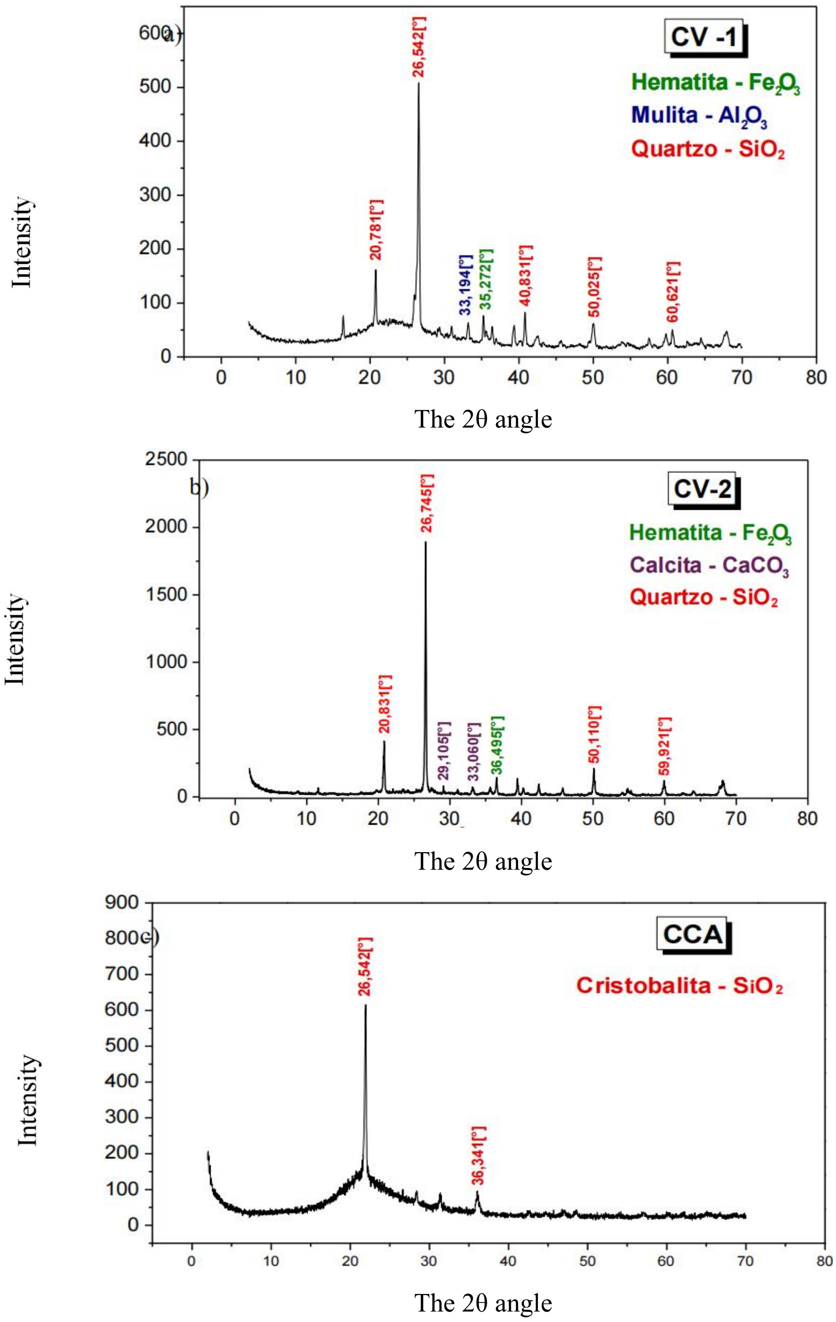
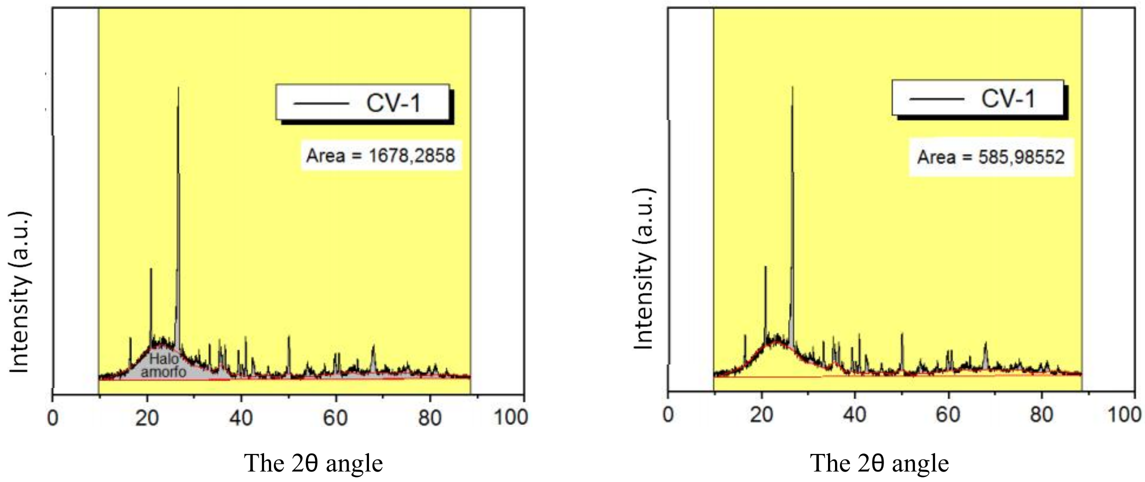


Figure 3. Diffractograms a) CV-1, b) CV-2 and c) CCA

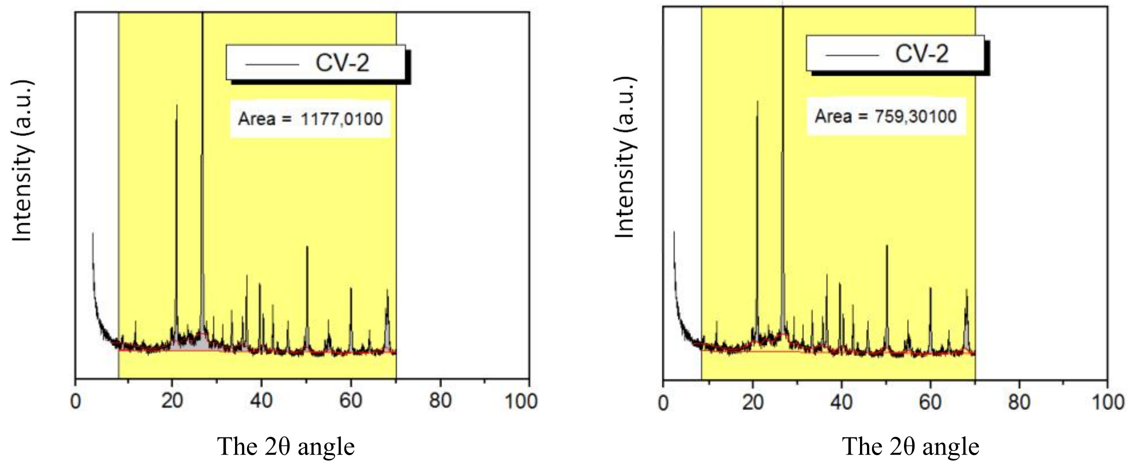
Source: Prepared by the Authors (2023).

Regarding the quantification of amorphous material, the crystallinity percentages (Equation 01) were estimated for the three ashes by calculating the SSA, as shown in Figure 4a-c.



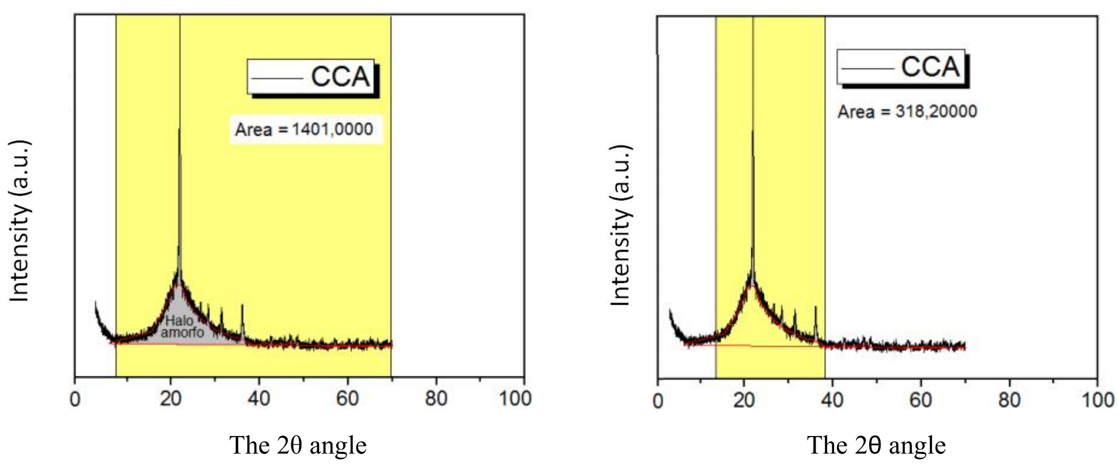
Calculation of crystallinity of CV-1

Cr (%) = 34.92% Am (%) = 65.08%



Calculation of crystallinity of CV-2

Cr (%) = 64.51% Am (%) = 35.49%



Calculation of crystallinity of CCA

Cr (%) = 22.48% Am (%) = 77.52%

Figure 4. Simple Separation of Ash Area

Source: Prepared by the Authors (2023).

Thus, it was shown that the variability of coal processing can influence the pozzolanic activity of CVs, as well as the control of burning temperature in the case of RHA. The results demonstrated that the amorphousness index can be used as a parameter for controlling residual ash, since ash with a higher percentage of amorphousness presents good pozzolanicity.

However, even if a material presents a large amount of crystalline peaks and is unsuitable, at first, because it does not have enough amorphous silica to promote pozzolanic reactions, it is still possible to produce cementitious matrices that meet NBR12653 (ABNT, 2014) and C618 (ASTM, 2012). Otherwise, quartzose filler (inert) can be used as the inert material.

The ashes analyzed in this work could, for example, replace, in adequate quantities, Portland Cement in cementitious matrices. However, CV-1 and CCA in Portland Cement (CP) type IV (pozzolanic) and CV-2 in CP type II are as quartzose filler (inert).

The reuse of ash from thermal power plants as additives in construction materials represents a step forward in terms of sustainability and efficiency in waste management. The results of this study are fundamental to understanding how the intrinsic characteristics of ash, such as mineral composition and degree of amorphism, directly influence its effectiveness as additives in construction materials. Ashes with a higher degree of amorphism, as observed in CV-1 and CCA, demonstrate greater pozzolanic activity, which means that they can chemically react with lime to form compounds that improve the strength and durability of concrete matrices. This reactivity not only reduces the need for cement, one of the largest emitters of CO_2 in the construction industry, but also valorizes waste that would otherwise be disposed of in landfills.

Furthermore, the inclusion of ash as an additive can improve the physical and chemical properties of building materials, such as compressive strength and durability, while aligning with sustainable construction practices. By utilizing industrial waste products such as coal ash and rice husk ash, construction companies can contribute to the circular economy by promoting the efficient use of resources and reducing the environmental footprint of their projects. Thus, insights into the mineral composition and amorphism of ash not only provide a scientific basis for its practical application, but also encourage innovation in the development of more sustainable and economically viable building materials.

5 Conclusion

Based on the proposed objectives, it was concluded that XRD analysis revealed that the ashes have a predominantly amorphous behavior and a siliceous nature, characteristics that make them ideal for incorporation into cementitious matrices. This is particularly relevant for the construction industry, since the presence of amorphous materials in the ashes indicates a high potential for pozzolanic reactivity, an essential factor in the partial replacement of conventional cement.

The estimated amorphousness percentage results confirmed that both CV-1 and CCA are composed mainly of amorphous materials, effectively quantifying the reactive phases present in the ashes. This aspect is crucial, since the high reactivity of ashes can significantly improve the mechanical and durability properties of construction materials. The SSA methodology proved to be a practical and efficient tool in determining the amorphousness index, offering a rapid approach to assess the pozzolanic potential of waste. Thus, the findings of this research not only reinforce the feasibility of ash reuse in construction materials, but also provide a robust scientific basis for the implementation of more sustainable and innovative practices in the industry.

Conflicts of interest

The author declares no conflicts of interest regarding the publication of this paper.

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