

Characterization of Coal Ash and Rice Husk for Use in Sustainable Constructions

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Abstract: Most of the ashes generated by power plants is disposed of in landfills and the remainder is used, primarily, as admixtures in construction materials. The reuse of these residues needs quantitative information on ash composition, mineralogy and amorphism. Typically, compositions are reported as elemental concentrations, but this data does not indicate the mineral or amorphous phases in which the elements are contained. Based on these aspects, this paper aims to investigate the mineral composition and to quantify the amorphism of residual power generation ashes, from mineral coal (FA-1 and FA-2) and rice husk (RHA), to be used as pozzolans, by X-Ray Diffraction (XRD) technique. The percentual amorphism estimation was determined by a simple area separation method. The mineralogy of ashes includes proportions of quartz. Only coal fly ashes contain calcite and hematite, which is related to the nature of the material. Using the simple area separation method, the percentages of amorphism for FA-1, FA-2 and RHA were 65.08%, 35.49% and 77.52% respectively.

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

1. Introduction

The reuse of by-products such as coal ash (CV) and rice husk ash (CCA) in construction is in line with the concept of sustainable construction, which aims to reduce waste and the environmental and social impacts of the construction sector (Farid and Zaheer, 2023). Sustainable buildings are, in practice, projects that aim to reduce the environmental impact of buildings and promote the responsible use of natural resources. This definition is in line with the concept of sustainability described in the United Nations (UN) Sustainable Development Goals (SDGs), which are a global call to eradicate poverty, preserve the environment and climate and ensure that people can enjoy peace and prosperity (UN, 2023).

VC and CCA are produced in large volumes in thermal power plants and, when disposed of inappropriately, can generate environmental impacts such as contamination of surface and groundwater and soil through the process of leaching (Kumar et al., 2023). Leaching occurs when the compounds present in the ash dissolve and are transported to bodies of water. To mitigate these problems, various studies have been carried out with the aim of finding effective ways of reusing ash. In the construction industry, for example, ash can be used as a substitute for Portland cement, provided it has pozzolanic characteristics (Nijland et al., 2022).

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. According to Medeiros (2022), pozzolan is a siliceous or siliceous-aluminous material, usually in powder form, which can be natural or artificial. When mixed with cement and water, it reacts with the calcium hydroxide released by the hydration of cement to form calcium silicate hydrate (C-S-H), which is essential for the strength and durability of concrete.

The physical and chemical properties of ash are generally influenced by factors such as combustion temperature, fineness and chemical composition. In addition, for VC, the composition of the coal and the type of processing (Mušanić, 2024). The amorphous silica (SiO_2) content is crucial for pozzolanic activity, so according to NBR 12653 (ABNT, 2014) the sum of the amounts of silica (SiO_2), alumina (Al_2O_3), and hematite (Fe_2O_3) must be greater than 70% and the amount of sulfur trioxide (SO_3) must be less than 5%. The presence of unburned carbon, which is common in CCA, can be detrimental to the strength of the concrete, requiring control steps during combustion.

The study by Madhav and Kothari (2023) provides a comprehensive overview of pozzolanic materials and their interactions with cement. It details how pozzolans, being finely divided siliceous or siliceous-aluminous materials, react with the calcium hydroxide released during cement hydration to form hydrated calcium silicate. The study analyzes the chemical and physical effects of these interactions, modifying the microstructure of the cement and influencing its final properties.

Lopes (2020) showed that an amorphous CV contributed to gains in mechanical strength, reduced water absorption by capillarity and improved workability due to the physical effect of the particles on the particle size distribution of the system. The author stressed that the amorphous structure, characterized by the absence of long-range crystalline ordering, was crucial for pozzolanic reactivity.

As mentioned above, the amorphous content of pozzolans is an indicator of their reactivity. An increase in the proportion of amorphous components indicates greater reactive potential. SiO_2 can exist in various polymorphic forms, including quartz, cristobalite and tridymite. Each of these forms has different physical and chemical properties, which influences its reactivity. This polymorphism affects their ability to react with $\text{Ca}(\text{OH})_2$ to form additional cementitious compounds (Williams and Schiller, 2023). With this in mind, knowledge of transformations and polymorphisms is important for the use of pozzolans in the cement industry. The treatment and grinding of SiO_2 can transform its structure and therefore its reactivity. Materials with a higher proportion of amorphous silica and more reactive polymorphic forms can be more effective as pozzolanic additions, providing better performance and durability to cement and concrete (Ghosh and Dhir, 2022).

The quantification of amorphism is based, in practice, on indirect methods of quantifying the reactive potential, which means that although it is possible to analyze the chemical composition, the kinetics of the reaction in a cementitious system is complex and influenced by various factors. This requires reliance on indirect methods which, despite their limitations, provide information for the selection of suitable pozzolanic mineral additions. The different methods, despite their limitations, are capable of supporting the selection of pozzolanic mineral additions (Moreno and Hernández, 2021).

X-ray diffractometry (XRD) is a technique used to characterize materials and allows the identification of SiO_2 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 shows how the crystalline (Ac) and amorphous (Aa) areas are identified and separated (Carolino, 2017 apud Stern; Segerman, 1968).

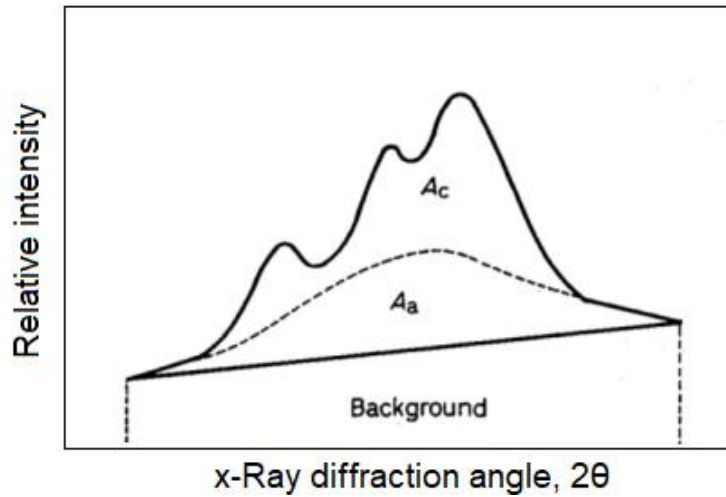


Figure 1. Separation of crystalline and non-crystalline areas (Lopes, 2020).

From an XRD spectrum, Simple Separation of Areas (SSA) can be used to estimate the percentage of crystallinity, and consequently amorphism, in a material. The method consists of subtracting the area of the halo referring to the non-crystalline contribution from the total area of the diffractogram in a diffraction interval. Crystallinity is estimated by integrating the crystalline peaks and the amorphous band. The calculation is carried out using Equation (1).

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

Where Cr corresponds to the percentage of crystallinity, A_c is the crystalline area and A_a is the amorphous area.

Based on the aspects presented, the aim 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, in conjunction with quantitative analyses of amorphous minerals, can be used as a parameter for evaluating the pozzolanic potential of waste ash and, in this context, enable the development of sustainable building materials with an emphasis on waste management in buildings, water saving, less use of natural resources and the use of environmentally friendly products and technologies.

2. Materials

Two VCs (VC-1 and VC-2) generated in Thermal Power Plants (TPPs) located in the Campanha Gaúcha region, in the city of Candiota, were analyzed. The coals have different origins, processing and burning conditions. A burned CCA without temperature control was also analyzed. Figure 2 shows images of the ash analyzed in this study.



Figure 2. Ash used in the research.

3. Methodology

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

4. Results and Discussion

The diffractograms of the ash are shown in Figure 2a-c. The peaks were identified using HighScore Plus software.

As shown in Figure 3 (a-b), CV-1 identified silica, aluminosilicates (mullite) and hematite. In CV-2, silica, hematite and calcite. Calcite is probably related to the oxidation of calcium from residual calcium sulphate from the desulphurization of flue gases (Ledesma, 2018; Lacerda, 2015; Silva, 2009). As the peaks are narrower, it is assumed that the SiO₂ identified in CV-2 is in crystalline form.

Qualitative XRD analysis showed that CCA contains amorphous silica, as indicated by the halo in the diffractogram shown in Figure 2c. The presence of amorphous (pozzolanic) or crystalline (inert) silica is directly linked to the temperature and method of obtaining the ash (Mwangi et al., 2021).

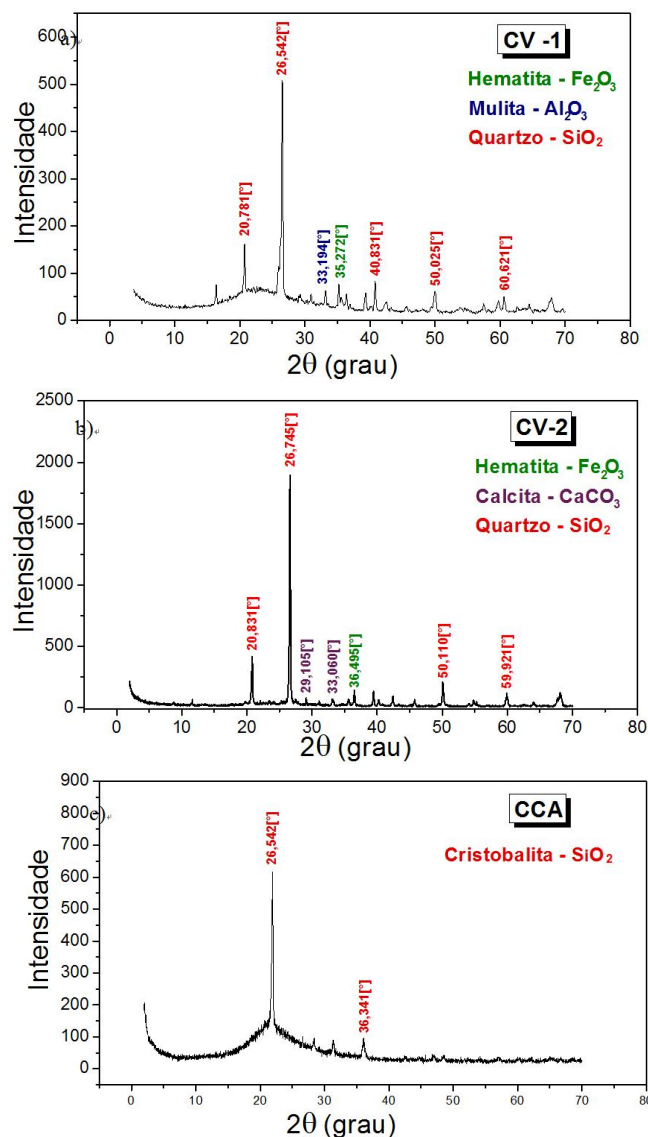


Figure 3. Difratogramas (a) CV-1, (b) CV-2 and (c) CCA.

With regard to the quantification of amorphous material, by calculating the SSA, the crystallinity percentages were estimated (Equation 1) for the three ashes, as shown in Figure 4a-c.

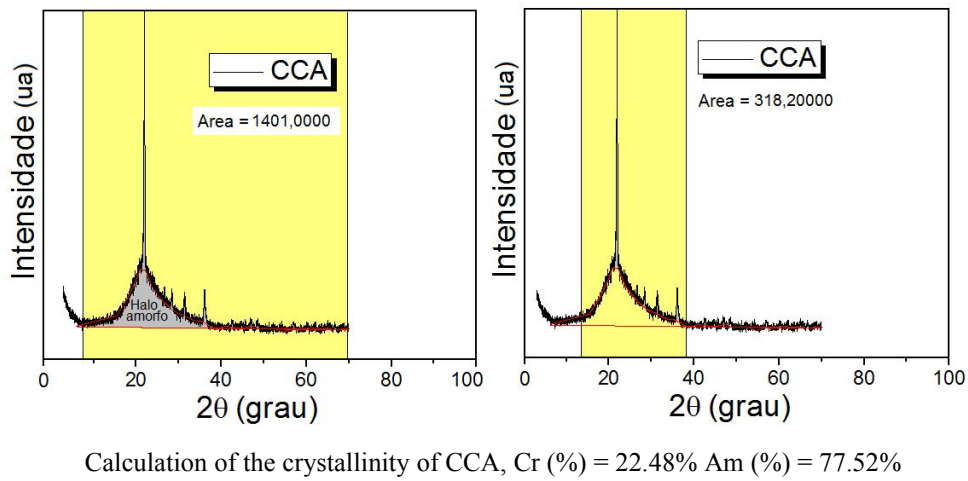
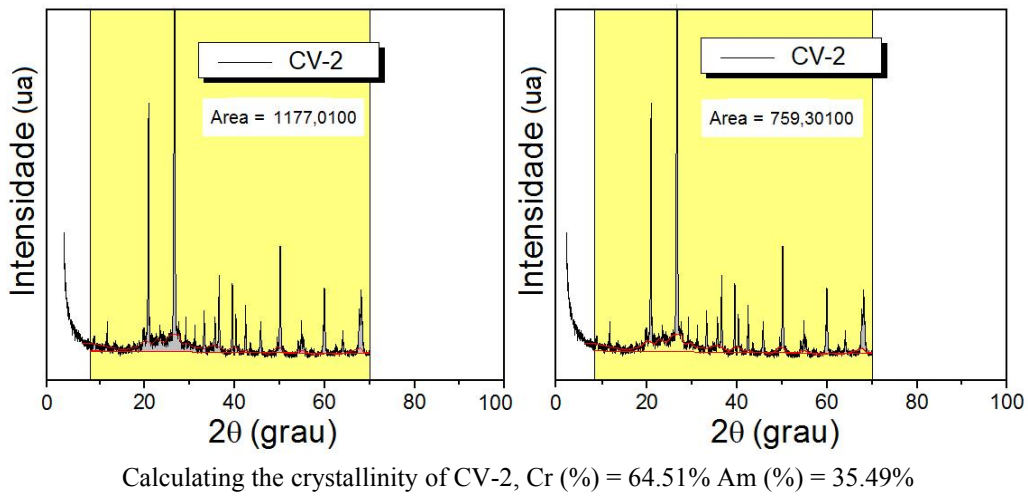
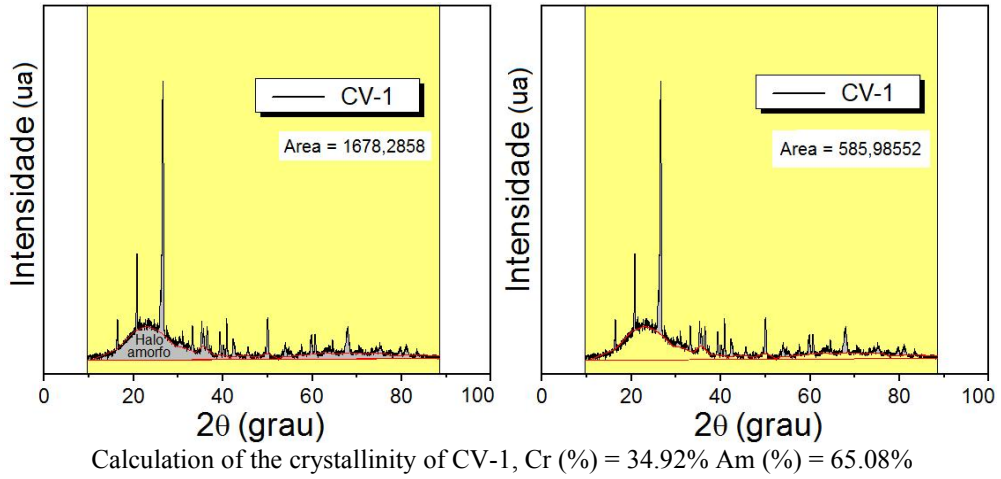


Figure 4. Simple area separation of ash.

This showed that the variability of coal processing can influence the pozzolanic activity of the VCs, as well as the control of burning temperature in the case of CCA. The results showed that the amorphism index can be used as a control parameter for residual ash, since ash with a higher percentage of amorphism has good pozzolanicity.

However, even if a material has a large number of crystalline peaks and is initially unsuitable because it does not have enough amorphous silica to promote pozzolanic reactions, it is still possible to produce cementitious matrices that comply with NBR12653 (ABNT, 2014) and C618 (ASTM, 2012). Otherwise, quartz filler (inert) can be used as an inert material.

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

5. Conclusion

This research involved two stages: (i) analysis of the phases present in the ash samples using X-ray diffraction and (ii) calculation of crystallinity using the SSA method. XRD showed that the ash has an amorphous behavior pattern and a siliceous nature, which makes it suitable for incorporation into cementitious matrices.

The analysis of the estimated results of the crystallinity percentages showed that both CV-1 and CCA are mainly composed of amorphous materials, demonstrating the quantification of reactive phases in the ash. The SSA method can be used as a parameter to evaluate the pozzolanic potential. The determination of the amorphism index using this technique was found to be practical and rapid.

The use of bottom ash in sustainable construction not only minimizes improper disposal, but also helps reduce construction costs by reducing the use of cement. It thus plays an important role in reducing carbon emissions. It is therefore beneficial to the environment, the economy and social welfare.

Conflicts of Interest

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

References

- [1] ABNT - Associação Brasileira De Normas Técnicas. NBR 12653: Materiais Pozolânicos: Requisitos. Rio de Janeiro, 2014.
- [2] ASTM – Specifications for Concrete and Aggregates. C 618: Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete. Annual Book of ASTM Standards Concrete and Aggregates, 2012; v.4. n.4.02 pp. 335-8.
- [3] Carolino, A.S. Estimativa do percentual de cristalinidade de polímeros semicristalinos derivados da anilina através dos padrões de difração de raios X. Dissertação – Universidade Federal do Amazonas, Manaus, 2017.
- [4] Cordeiro, L.N.P.; Masuero, A.B.; Dal Molin, D.C.C. Análise do potencial pozolânico da cinza de casca de arroz (CCA) através da técnica de Refinamento de Rietveld. *Revista Matéria*, v.19, n.02, pp 150-158, 2014.
- [5] Farid, S. A.; Zaheer, M. M. Production of new generation and sustainable concrete using Rice Husk Ash (RHA): A review. *Materials Today: Proceedings*, 2023.
- [6] Ghosh, S. A. K.; Dhir, K. S. Silica in cement and concrete. Cham: Springer, 2022.
- [7] Kumar, P.; Mishra, R. K.; Agrawal, R. S. Sustainable management of coal ash and rice husk ash: environmental impacts and reuse applications. *Journal of Cleaner Production*, v. 310, pp. 127-140, 2023. DOI: 10.1016/j.jclepro.2021.127140.
- [8] Lacerda, L. V. Síntese e caracterização de zeólita tipo sodalita obtida a partir de cinzas volantes de carvão mineral utilizado na usina termelétrica de Candiota-RS. Dissertação de Mestrado em Engenharia - Escola de Engenharia, Universidade Federal do Rio Grande do Sul, Porto Alegre, 2015.
- [9] Ledesma, R. B. Cinzas volantes e zeólitas sintéticas na composição da pasta de cimento classe G e degradação por CO₂ em condições de armazenamento geológico de carbono. Dissertação de Mestrado. PUC-RS. 2018.

- [10] Lopes, D. F. Avaliação das propriedades de argamassas armadas com adição de resíduos da geração termelétrica. Qualificação de Mestrado – Programa de Pós graduação em Ciência e Engenharia de Materiais, Universidade Federal do Pampa, Bagé – RS. 2020.
- [11] Medeiros, A. M. Pozolanas e suas aplicações na construção civil. *Revista Brasileira de Engenharia de Construção*, v. 19, n. 3, pp. 45-58, 2022. DOI: 10.1590/0100-4466.2022.19.03.0045.
- [12] Moreno, A. M.; Hernández, A. Recent advances in sustainable concrete. Cham: Springer, 2021.
- [13] Mwangi, J. M.; Otieno, M.; Diang'a, G. Rice husk ash as a pozzolanic material in concrete. Cham: Springer, 2021.
- [14] Organização Das Nações Unidas (ONU): Como as Nações Unidas Apoiam os Objetivos do Desenvolvimento Sustentável no Brasil. Disponível em: <https://brasil.un.org/pt-br/sdgs>.
- [15] Madhav, V.; Kothari, A. Pozzolanic materials and their role in cement hydration: a comprehensive review. *Journal of Building Materials and Structures*, v. 15, n. 4, pp. 122-135, 2023. DOI: 10.1016/j.jbms.2023.04.001.
- [16] Mušanić, S. M. Ash properties and environmental impact of coal and its blend with patent fuel for climate sustainability. *Sustainability*, v. 16, n. 11, pp. 4413, 2024. Disponível em: <https://doi.org/10.3390/su16114413>.
- [17] Nijland, T. G.; García, R. A.; Zakaria, M. Utilization of industrial by-products in construction: a review of current practices and future directions. *Construction and Building Materials*, v. 343, pp. 127-138, 2022. DOI: 10.1016/j.conbuildmat.2022.127138.
- [18] Silva, D. F. F. Influência da cinza volante na pasta de cimento. Dissertação de Mestrado. Universidade Federal do Pará – Belém, 2009.
- [19] Stern, P.G.; Segerman, E. On the structure of polypropylene fibres. *Polymer*, Elsevier v.9, n.322, p. 471-477, 1968.
- [20] Williams, I. P.; Schiller, E. M. Pozzolanas: properties, characterization, and use. Hoboken: John Wiley & Sons, 2023.