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OPTIMIZATION OF THE CALCIUM SILICATE HYDRATED COMPOUNDS SYNTHESIS FROM THE RECYCLING OF MATERIAL DERIVED FROM COAL INDUSTRY WASTE

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ABSTRACT

The intensification of society's consumption and population growth are the main aspects that most contribute to negative impacts on living beings and environmental management due to the generation of large quantities of waste generated daily by industrial production processes. As a result, the valorization of these industrial by-products has been highlighted with the aim of obtaining value-added materials. The concepts of reuse and recycling are presented as a new production model aiming at more sustainable processes.**:** In the present work, the optimization of the synthesis of calcium silicate hydrated compounds was carried out from sulfated coal ash generated in the flue gas desulfurization process in a thermoelectric plant using the two-stage method (alkaline fusion followed by hydrothermal treatment). The studied parameters that influenced the synthesis were fusion time, agitation time, volume of water for the hydrothermal treatment of the samples, and two types of agitators (rod with blade-type propeller and shaking table). XRF and XRD characterized the ash and products. According to the characterization results, the highest crystallinity of calcium silicate hydrated compounds was identified in the product synthesized under the following conditions: fusion time of 3 h; volume of water for hydrothermal treatment of 100 mL; agitation time of 2 h agitator equipped with rod and blade-type propeller.**:** It can be concluded that sulfated ash is viable as a starting material for the formation of hydrated calcium silicate compounds, following the principles of environmental sustainability and the objectives of the circular economy.

Keywords: *FGD ash; C-S-H compounds; Industrial waste; Circular economy; Sustainability*.

1. INTRODUCTION

Production processes significantly impact the environment. The Circular Economy proposes sustainable closed-loop processes to improve resource use and waste reuse (Unep, 2024; Kanwal et al., 2023).

Coal industries generate large amounts of coal ash. In Brazil, flue gas desulfurization in thermoelectric plants reduces NOx emissions by 70-80%, operating at 750-900°C. This process generates sulfated ash or FGD ash (Bibiano, 2021), which contains high sulfur and calcium levels that can harm ecosystems if improperly disposed of (Grosche, 2019).

The cement industry also contributes significantly to greenhouse gas emissions. Portland cement production emits approximately one ton of CO2 per ton of cement, representing 7% of global CO2 emissions (Arachchige et al., 2019; IEA, 2018).

Calcium silicates hydrated (C-S-H) compounds comprise 75% of hydrated Portland cement and show high cation immobilization potential (Tang et al., 2021). Tobermorite (TOB), structurally similar to C-S-H, can be obtained through alkaline hydrothermal treatment and may improve cement matrix properties (Kremleva et al., 2020).

TOB synthesis depends on various parameters, including Ca/Si ratio, temperature, and pH (Majdinasab and Yuan, 2020). Studies have explored TOB as a cement additive (Land and Stephan, 2015) and contaminant removal agent (Berg et al., 2006), using various sources like newspaper ash (Coleman and Brassington, 2003) and quartz sand (Galvánková et al., 2018).

This work aimed to obtain C-S-H

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compounds from sulfated coal ash through alkaline fusion and hydrothermal treatment as an alternative for supplementary cementitious material production.

2. MATERIALS AND METHODS

2.1. Materials

The Porto provided the sample of FGD ash do Pecém coal power plant located in São Gonçalo do Amarante City, State of Ceará, Brazil. Sodium hydroxide (Synth, P.A. 100 %), shaking table (Quimis - modelo Q-225M), agitator equipped with rod and blade-type propeller, oven and muffle (Fanem) and quantitative filter paper (Nalgom 3400, diâmetro = 150 mm) were used. X-ray fluorescence (Philips - Malvern Panalytical, Venus-Zetium model) and X-ray diffraction (Rigaku multiflex diffractometer with Cu anode using Co Kα radiation at 40 kV and 20 mA over the range (2 θ) of 5–60 ° with a scan time of 0.5 °/min) were performed to characterize the prepared materials.

2.2. Methods

The characterization of FGD ash was the first step defined in this study, with the aim of evaluating the chemical composition of the precursor material to see if it is favorable for the development of C-S-H compounds. Therefore, the characterization of the FGD ash and the products obtained were characterized by XRF and XRD.

For the synthesis of the compounds, the two-step method was evaluated, which consists of first fusing the ash mass with solid NaOH mass and then subjecting the fused mass to hydrothermal synthesis. First, the NaOH mass was ground and homogenized with the ash mass (ash:NaOH = 1/1.2). After grinding, the sample was fused at 600 °C in a muffle furnace. After the fusion time, the sample was cooled to room temperature and then ground again until a fine material was obtained. Right after, the volume of bidistilled water was added to the sample and agitated in two types of agitators: one equipped with a rod and blade-type propeller and a shaking table. After agitation, the sample was heated in an oven for 24 h at 100 °C. After the heat treatment, the suspension was filtered with quantitative filter paper, washed with bidistilled water, and then dried in an oven for 12 h at 100 °C.

Table 1 shows the samples and their respective synthesis parameters.

The products obtained were named as: SPF-1, SPF-2, SPF-3, SPF-4, SPF-5, and SPF-6. The arbitrary criterion used to evaluate the synthesis results was the comparison of the relative intensity of the main TOB peak (2 Θ ~ 8 °) present in the products obtained.

Table 1. Parameters of the synthesis of CSH compounds

Sample	T_{Fusion}/h	V_{H2O}/mL	t_{Agit}/h
1^1	1	100	18
2^1	3	100	18
3^2	1	100	2
4^2	3	100	2
5^2	1	200	6
6^2	1	100	6

(*) 1: table; 2: rod and blade-type propeller

3. RESULTS AND DISCUSSION:

3.1. Results

3.1.1. Characterization of FGD ash

According to the XRF results (in mass %), the main chemical constituents of FGD ash are SiO_2 (31.4); CaO (22.1); Al_2O_3 (12.4); SO_3 (11.9) and Fe_2O_3 (6.22). From the results of the XRD analysis (not shown), it was confirmed that the mineralogical content of the FGD ash is mainly calcite and quartz, with a smaller fraction of mullite and magnetite.

3.1.2. Synthesis of C-S-H compounds

XRD analyzed the results of the synthesis of C-S-H compounds using the two-step method, which is shown in Figure 1.

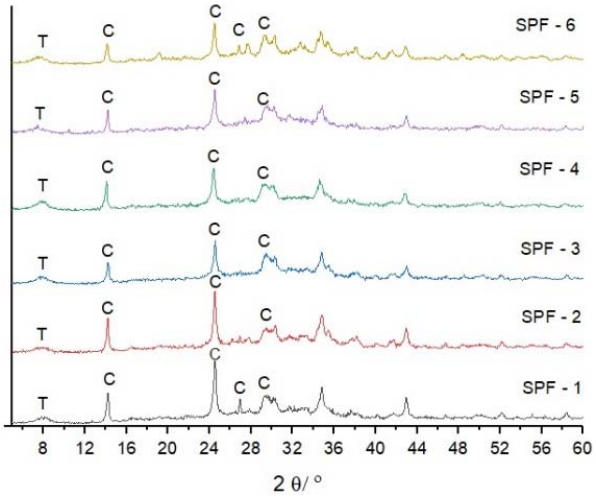

Figure 1. Diffractograms of the C-S-H compounds (T = Tobermorite;C = calcium silicate hydrated compound)

3.2. Discussion

3.2.1. Characterization of FGD ash

It was found that calcium and silicon, which

are the main elements for the formation of C-S-H compounds, are present in larger quantities (Tang *et al*., 2021). It is also possible to observe the presence of a high content of SO_3 (11.9) originating from the desulfurization process.

3.2.2. Synthesis of C-S-H compounds

From the analysis, it is possible to observe that the C-S-H and TOB phases were formed in all synthesized products. During the process of formation of C-S-H gels, there is an intermediate and unstable phase with free calcium and silicon ions, and it is in this phase that TOB is formed (Smalakys, 2021).

Figure 2 shows the arbitrary comparison of the relative intensities in the 8° region at 2 Θ obtained from the products.

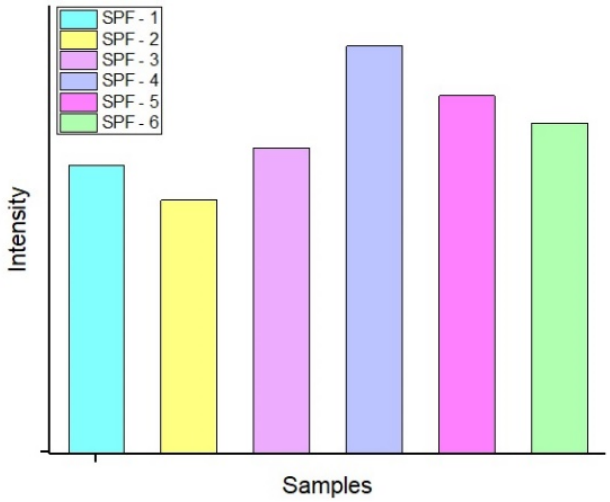

Figure 2. Comparison of the relative intensities of the samples in the region of 2Θ = 8º.

From the comparison of the relative intensities of the samples, it was possible to define that the SCF-4 sample has the highest crystallinity of the product, for which the following parameters were used: melting time – 3 h; volume of water for TH – 100 mL; stirring time – 2 h; and agitator equipped with rod and blade-type propeller.

The 3 stages of synthesis of CSH compounds in this study consist of: 1 - fusion, is the stage in which the compounds containing Si^{4+} and Ca^{2+} present in the FGD ash dissolve, forming the molten C-S-H compound, which is soluble in water; 2 - through contact of the molten sample with water under agitation, the condensation of silicate and calcium ions occurs in an alkaline solution to form CSH and TOB gel; and 3 - TH in an oven, which is the stage in which the gel crystallizes, producing crystalline C-S-H compounds.

According to the results, a longer fusion time provided a greater formation of TOB and C-S-H compounds. It can also be concluded that the formation of C-S-H compounds and TOB decreases with the increase in the value of the water-to-solid ratio. This fact was observed in the literature (Galvánková *et al*., 2018; Kikuma et al., 2011).

Agitation in water helps dissolve the molten compounds, form the initial gel formation, and maintain a homogeneous gel. The use of a rod instead of a stirring table facilitates the breaking of the $CaSO_2$/$CaSO_3$ and Si-O bonds in the ash. Consequently, this results in a faster dissolution rate of these compounds in the alkaline solution during aging with water. The complete dissolution of the C-S-H compounds and the formation of a homogeneous gel make the raw material available for the growth of TOB crystals. Since the agitation is efficient, the TOB formed in the last stage is purer, more crystalline, and has a higher yield (Rosa, 2024).

4. CONCLUSIONS:

This study showed that industrial waste, sulfated coal ash from coal-fired power plants, is an efficient material for obtaining calcium silicate hydrated compounds through alkaline fusion followed by hydrothermal treatment. According to the characterization of the materials and the optimization of the synthesis process, the greatest crystallinity of the products was observed under the following conditions: fusion time of 3 h; volume of water in the agitation of 100 mL; agitation time of 2 h; and agitator equipped with rod and blade-type propeller. Therefore, this study demonstrates the possibility of managing waste from the coal industry following the principles of the circular economy and Sustainable Development Goal (SDG) number 12, specifically in item 12.5: “By 2030, substantially reduce waste generation through prevention, reduction, recycling and reuse”.

5. DECLARATIONS

5.1. Acknowledgements

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5.2. Open Access

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