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The Effect of Adding Alumina as an Aluminum Source to the Diatomaceous Earth-Based Geopolymer

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Abstract: This study uses waste materials, specifically Diatomaceous Earth (DE), rich in aluminum and silica, as a sustainable source for aluminosilicate precursors in geopolymers to replace conventional cement in mortar applications. While DE shows promise, it lacks sufficient alumina content, demanding the introduction of alumina powder. However, this addition's effectiveness is limited, as unreacted alumina particles were observed in the X-ray diffraction and SEM analyses. This could potentially impact various geopolymer properties due to the incomplete achievement of the desired silicon/aluminum (Si/Al) ratio. Achieving the appropriate Si/Al balance remains crucial for geopolymers to realize their potential as environmentally friendly alternatives to Portland Cement.

Keywords: Geopolymer; Alumina; Diatomaceous Earth

1. Introduction

Over the last few decades, the number of studies about sustainable materials has increased once we are facing a consumption of a massive amount of raw materials, energy and releasing high levels of carbon dioxide into the atmosphere. In 2021, the Portland cement industry emitted nearly 2.9 billion tons of carbon dioxide, more than 7% of the global carbon emissions [1, 2]. In this way, it is necessary to create strategies to limit this environmental impact.

One of the alternatives to PC is the formulation of new binders, such as geopolymers, with enhanced mechanical strength and the ability to withstand elevated temperatures and chemical attacks by acids and acid salts [3]. Geopolymer is an inorganic polymer produced with an aluminosilicate precursor reacted with an alkaline solution, which results in an amorphous three-dimensional network structure of silicon-oxygen tetrahedron $(SiO4)^{4-}$ and aluminum-oxygen tetrahedron $(AlO4)^{5-}$ connected through bridge oxygens [4].

According to Davidovits [4] and PAPA et al. [5], aluminosilicates' three-dimensional structure and properties, such as mechanical properties, are determined by the silicon/aluminum molar ratio. Rowles and O'Connor [6] achieved excellent compressive strength with a 2.5 ratio, while He P et al. [7] attained excellent mechanical properties with 3.5.

Introducing an innovative approach, it's possible to harness waste materials rich in aluminum and silica as promising sources of aluminosilicates. This promotes a circular economy and encourages the production of sustainable alternatives to replace Portland cement. Among the solid waste, Diatomaceous Earth can be used as an aluminosilicate

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precursor in geopolymers. This earth is used in the wine industry, and it's commonly thrown away after wine production. So, using this spent diatomaceous earth (SDE) as a component of a geopolymer that will be used to replace cement on mortars can be a possibility to reduce environmental impacts.

Moreover, since the material in question is waste, attaining the desired Si/Al ratios essential for generating geopolymers may necessitate the incorporation of supplementary sources of aluminum or silicon. This research examined the impact of introducing alumina and assessed its performance in the geopolymerization process.

2. Materials and Methods

2.1 Raw Materials

Table 1 shows SDE's chemical composition as a geopolymer precursor. Caves Campelo supplied it. Once Si/Al ratios of 2.5 and 3.5 were chosen for this study. The precursor had a ratio of 6.08; it required the addition of aluminum oxide powder (Al_2O_3 – 99.7% pure) to increase the proportion of aluminum and bring the Si/Al ratio to an appropriate level. The alkaline solution consisted of sodium hydroxide (10M and 12M) and sodium silicate (Na_2O:10.6% and SiO_2:26.5%).

Table 1. Chemical composition of Spent Diatomaceous Earth (wt.%).

Si	Al	K	Fe	Ca
42,1	7,4	3,5	0,6	0,6

2.2 Synthesis of Geopolymer

First, the alkaline solution was prepared by mixing sodium hydroxide (NaOH) solution with sodium silicate for 10 minutes in a magnetic stirrer. Later, the SDE and the aluminum oxide were mixed until a homogeneous powder was obtained. Then, this solid portion was mixed with the alkaline solution and water in a standardized paddle mixer. After that, the fresh geopolymer was placed in a silicone mold and subsequently cured for four days at 40 °C and then at room temperature (25 °C), obtaining a final geopolymer. The NaOH concentration and the Si/Al ratio desired for each geopolymer are described in Table 2.

Table 2. Geopolymers Samples Specification.

Samples	Si/Al Ratio Desired	NaOH Concentration
GP1	2.5	10M
GP2	3.5	10M
GP3	2.5	12M
GP4	3.5	12M

2.3 Characterization of Geopolymer Properties

To examine the geopolymer's properties, such as phase composition and structure, X-ray diffraction (XRD) analyses were performed. These analyses were performed in a PANalyticalX'Pert PRO equipped with an X'Celerator detector and secondary monochromator (Cu Kα λ = 0.154 nm; data recorded at a 0.017◦ step size). To examine and analyze the microstructural properties of solid GPs, Scanning Electron Microscopy with energy-dispersive X-ray Spectroscopy (SEM/EDS) analysis was conducted. The samples analyzed in this study were collected in powder form and were examined at scales of 100, 20, and 10 μm.

3. Results and Discussion

3.1 X-Ray Diffraction (XRD)

Figure 1 shows the diffractogram of diatomaceous earth and geopolymers with different NaOH concentrations and Si/Al ratios.

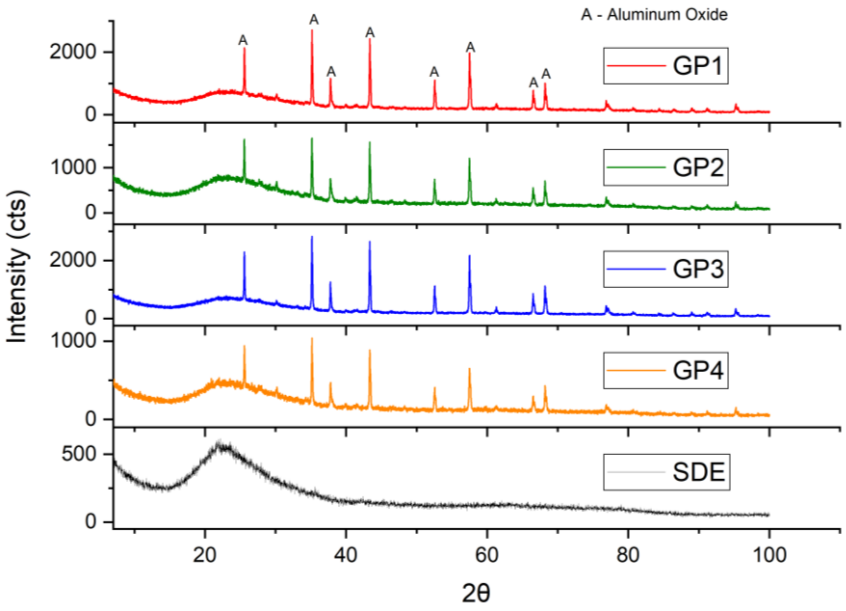

Figure 1. XRD results for SDE and GPs.

The appearance of crystalline peaks is observed in the XRD analysis of geopolymers compared to that of diatomaceous earth. The major ones are associated with the aluminum oxide phase at 25.57º, 35.14º, 37.77º, 43.35º, 52.54º, 57.48º, 66.51, and 68.20º in all four GPs [8, 9]. These peaks originate from the alumina added to the precursor, some of which are repeated in the diffractogram of the geopolymers. The alumina pattern is shown in Figure 2, and it can be seen that the resulting geopolymers do not have all the peaks present in the raw material, as the ones at 41.61º, 46.18º, 59.77º, 70.36º, 74.27º, 85.19º and 90.66º, confirming a certain degree of consumption of this alumina in the geopolymerization reaction [10].

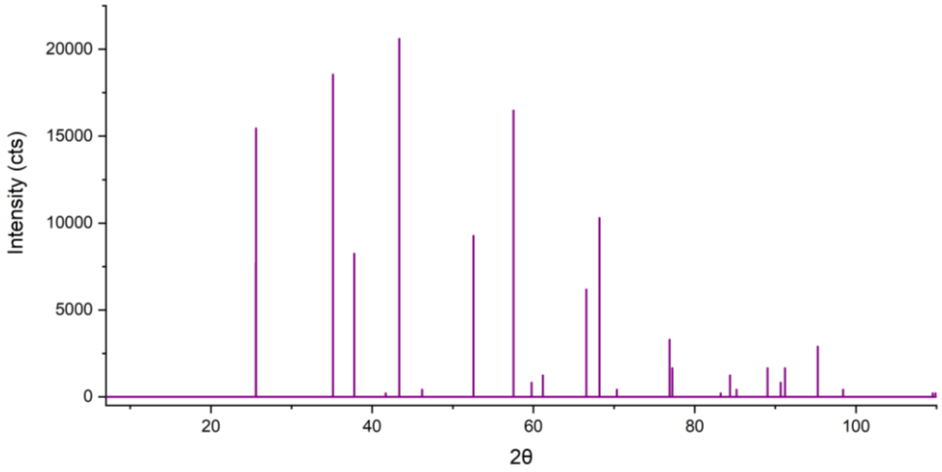

Figure 2. XRD Pattern for Alumina.

However, the prominent peaks persisted, although with significantly reduced intensity, indicating the presence of partially unreacted crystalline material. This suggests that Al_2O_3 didn't completely dissolve in the alkaline solution, which may have an impact on the geopolymerization reaction since the alumina added to compensate for the low level of it in the diatomaceous earth should promote the polymerization process by producing a significant amount of $Al(OH)^4$ when reacting with the alkaline solution [10].

When comparing geopolymers based on their Si/Al ratio, it can be observed that GP1 and GP3 exhibit more pronounced peaks of aluminum oxide compared to GP2 and GP4. This can be attributed to the fact that GP1 and GP3 have Si/Al ratios of 2.5, which indicates a higher amount of alumina present in the geopolymer, in contrast to GP2 and GP4, which have Si/Al ratios of 3.5. The higher alumina concentration in GP1 and GP3 likely contributes to the observed differences in aluminum oxide peaks between these materials and GP2 and GP4.

A broad and diffuse halo centered at approximately 2θ = 20-30° is observed in the SDE, indicating the presence of an amorphous phase. In the diffractograms of the four GPs in Figure 1, a similar halo is observed at approximately the same position but with varying intensities. When compared with the diffractogram of the SDE, the intensity of the halo in the GPs has increased, which indicates a more considerable amount of the amorphous phase. This, in turn, suggests a greater quantity of the geopolymer phase present in the samples [10], especially in GP2. In the literature, this amorphous phase described by the halo usually indicates the NASH structure (sodium alumino-silicate hydrate) gel formation [11, 12], so it's possible to assume the same in this work.

The geopolymerization process is influenced by the amount of alkaline solution and its concentration once the amount of OH^- and Na^+ is sufficient to dissolve the aluminum from the precursor and to balance the negative charge of the $Al(OH)^-$, respectively. If there is more aluminum than the maximum for the reaction, less NASH gel is generated, and more unreacted Al is presented [11]. This is a possible explanation for why the amorphous halos of GP1 and GP3 are less intense than GP2. The first and the third samples have a Si/Al of 2.5, so the amount of aluminum oxide powder added to the precursor was higher, causing an excess of Al. This also goes according to the conclusion of unreacted aluminum described by the intensity of the crystalline peaks.

It can be a sign of a few crystalline phases of zeolite that XRD couldn't detect due to its small quantity. In GP4, however, it can be noticed that the crystalline peaks and the amorphous halo have lower intensities than the other samples. It's possible to assume this once the chemical composition and structure of NASH gel are similar to the zeolites, and this last one has a greater tendency to be formed in high concentrations, which is the case of GP4 (12M) [12].

3.2 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy

Figure 3 presents the SEM images of the produced GPs. GP1 and GP3 samples, with the same Si/Al ratio of 2.5, exhibited the irregular shapes and sizes of a flocculent morphology covered with delicate powder spheres [12]. These attached spheres can be due to the higher quantity of alumina powder added to these samples to achieve the desired Si/Al ratio [13]; they didn't react, reinforcing the XRD analysis. These images also exhibited smaller pores and more compact structures.

Meanwhile, GP2 and GP4 samples presented mainly a flocculent morphology with more prominent pores and a less compact structure. Also, needle-like structures were detected in GP4. This type of structure is similar to zeolitic-fibrous phases, which can propose a small amount of a poor crystalline phase of zeolite in the sample [12, 14], going according to what was analyzed in XRD.

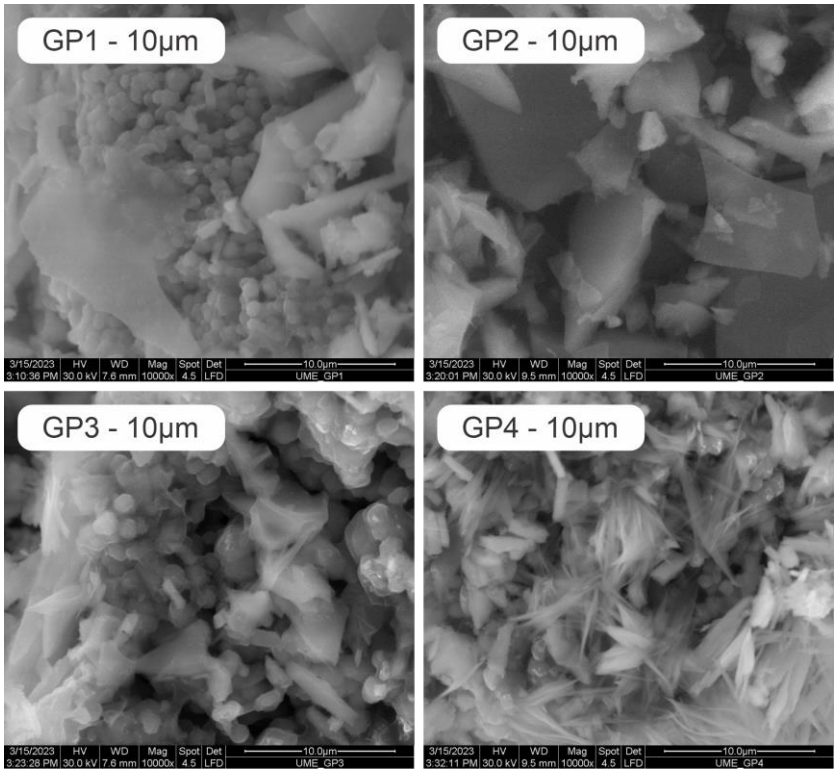

Figure 3. SEM images of GPs.

4. Conclusions

Based on the comprehensive analysis, it can be concluded that SDE is a viable silica source for geopolymer precursors, demonstrating that it is possible to produce geopolymers from SDE. However, it's important to note that SDE lacks sufficient alumina content. To address this deficiency, alumina powder was introduced. Regrettably, this addition proved ineffective, as unreacted alumina particles were detected in both XRD and SEM images. This can potentially impact various properties of the geopolymers, primarily because the desired Si/Al ratio was not achieved as intended.

Although the geopolymerization reaction involves the creation of intricate three-dimensional structures, imparting specific properties like mechanical and flexural strength, these properties are intricately linked to the silicon/aluminum molar ratio. An improper balance between aluminum and silicon may result in the formation of weaker or incomplete structures.

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Conflicts of Interest: The authors declare no conflict of interest.

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