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The Effect of Adding Alumina to Diatomaceous Earth-Based Geopolymers †

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Abstract: This study uses waste materials, specifically diatomaceous earth (DE) that is rich in aluminum and silica, as a sustainable source for aluminosilicate precursors in geopolymers to replace conventional cement in mortar applications. While the use of DE shows promising results, it lacks sufficient alumina content, thereby demanding the introduction of alumina powder. However, the effectiveness of this addition 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

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1. Introduction

In recent decades, the number of studies on sustainable materials has grown due to the massive increase in the consumption of raw materials and energy, ultimately leading to the release of high levels of carbon dioxide into the atmosphere. In 2021, the Portland cement industry emitted nearly 2.9 billion tons of carbon dioxide, which is more than 7% of the global carbon emissions [1,2]. Thus, it has become necessary to create strategies to limit the environmental impact of such industries.

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], three-dimensional structure and properties of aluminosilicates, 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 a 3.5 ratio.

Through an innovative approach, it is possible to harness waste materials rich in aluminum and silica as promising sources of aluminosilicates. This will promote a circular

economy and encourage the production of sustainable alternatives to replace Portland cement. Among the solid wastes, diatomaceous earth can be used as an aluminosilicate precursor in geopolymers. DE is used in the wine industry, and it is commonly thrown away after wine production. Hence, using this spent diatomaceous earth (SDE) as a component of a geopolymer to replace cement on mortars has the potential 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 into DE-based geopolymers and assessed its performance in the geopolymerization process.

2. Materials and Methods

2.1. Raw Materials

Table 1 shows the chemical composition of SDE as a potential geopolymer precursor. The SDE samples were supplied by Caves Campelo. The 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 the Geopolymers

Firstly, the alkaline solution was prepared by mixing sodium hydroxide (NaOH) solution with sodium silicate for 10 min in a magnetic stirrer. Next, SDE and aluminum oxide were mixed until a homogeneous powder was obtained. Then, this solid solution was mixed with an 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), finally obtaining the geopolymers. The NaOH concentration and the Si/Al ratio desired for each geopolymer are described in Table 2.

Table 2. Sample specification of the geopolymers.

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

2.3. Characterization of the Geopolymer Properties

To examine the geopolymers' 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.

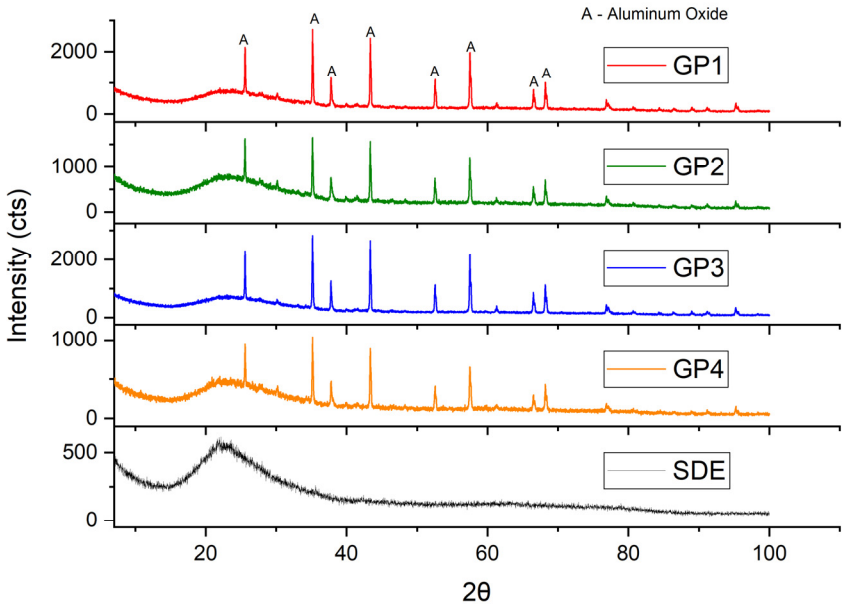

Figure 1. XRD results of SDE and GPs.

The appearance of crystalline peaks is more frequently observed in the XRD analysis of geopolymers compared to that of diatomaceous earth. The major peaks in all four GPs are associated with the aluminum oxide phases at 25.57°, 35.14°, 37.77°, 43.35°, 52.54°, 57.48°, 66.51°, and 68.20° [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; it can be seen that the resulting geopolymers do not have all the peaks present in the raw material as the ones at 41.61°, 46.18°, 59.77°, 70.36°, 74.27°, 85.19° and 90.66°, thereby confirming a certain degree of consumption of alumina in the geopolymerization reaction [10].

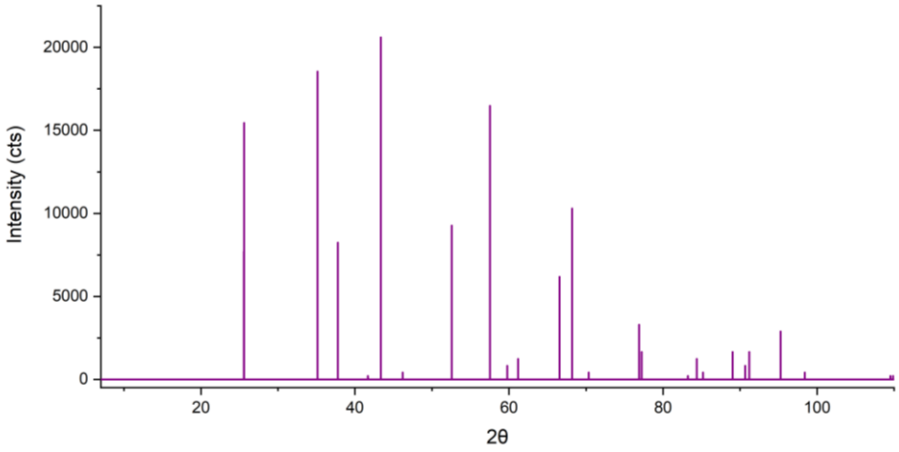

Figure 2. XRD pattern of alumina.

However, the prominent peaks persisted, although with significantly reduced intensity, thereby indicating the presence of partially unreacted crystalline material. This suggests that Al_2O_3 did not 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 aluminum 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 geopolymers were compared based on their Si/Al ratio, it was 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 the presence of a higher amount of alumina 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 $2\theta = 20–30^\circ$ 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 is 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 the same can be assumed 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 balance the negative charge of the $Al(OH)^-$, respectively. If the amount of aluminum exceeds the maximum level for the reaction, a lesser amount of NASH gel is generated, and more unreacted Al remains in the solution [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 ratio of 2.5, so the amount of aluminum oxide powder added to the precursor was higher, thereby causing an excess of Al. This also aligns with the levels of unreacted aluminum described by the intensity of the crystalline peaks.

This can indicate the presence of crystalline phases of zeolite, which could not be detected by XRD due to their 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 can be assumed that the chemical composition and structure of NASH gel are similar to the zeolites, and the latter 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. The GP1 and GP3 samples, with the same Si/Al ratio of 2.5, exhibited irregular shapes and sizes of a flocculent morphology covered with delicate powder spheres [12]. These spheres must have emerged due to the higher quantity of alumina powder added to the samples to achieve the desired Si/Al ratio [13]; they did not react, thereby reinforcing the results of the XRD analysis. These images also exhibited smaller pores and more compact structures.

Meanwhile, the GP2 and GP4 samples mainly presented 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 induce a small amount of poor crystalline phases of zeolite in the sample [12,14], which is in line with the XRD analysis.

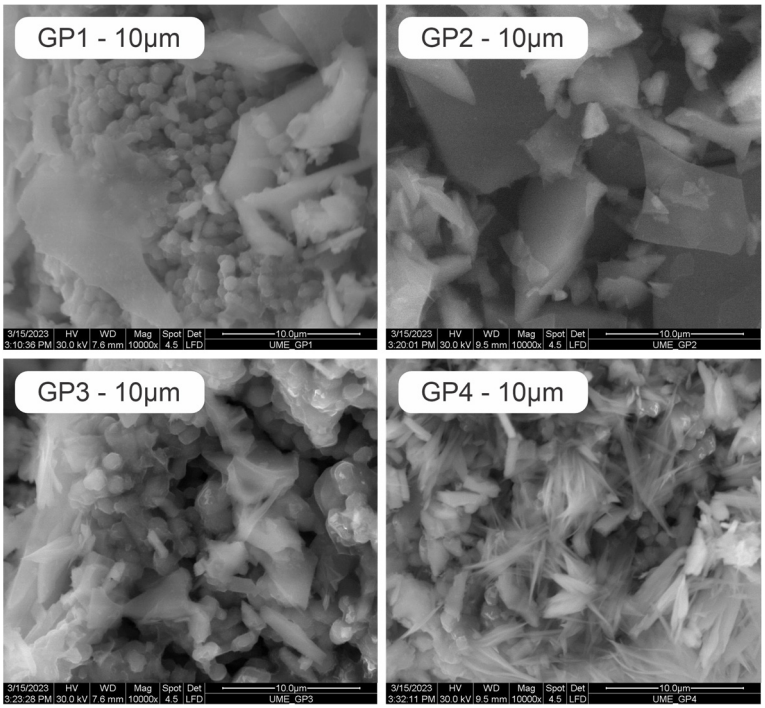

Figure 3. SEM images of GPs.

4. Conclusions

Based on the comprehensive analysis, it can be concluded that SDE is a viable silica source for geopolymer precursors, thereby demonstrating that it is possible to produce geopolymers from SDE. However, it is important to note that SDE lacks sufficient alumina content. To address this deficiency, alumina powder was introduced. Regrettably, this addition proved to be 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 with 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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References

1. Habert, G.; Miller, S.A.; John, V.M.; Provis, J.L.; Favier, A.; Horvath, A.; Scrivener, K.L. Environmental impacts and decarbonization strategies in the cement and concrete industries. *Nat. Rev. Earth Environ.* **2020**, *1*, 559–573. [CrossRef]
2. Friedlingstein, P.; Jones, M.W.; O'sullivan, M.; Andrew, R.M.; Bakker, D.C.; Hauck, J.; Le Quéré, C.; Peters, G.P.; Peters, W.; Pongratz, J.; et al. Global Carbon Budget 2021. *Earth Syst. Sci. Data* **2022**, *14*, 1917–2005. [CrossRef]
3. Tan, T.H.; Mo, K.H.; Ling, T.-C.; Lai, S.H. Current development of geopolymer as alternative adsorbent for heavy metal removal. *Environ. Technol. Innov.* **2020**, *18*, 100684. [CrossRef]
4. Davidovits, J. Geopolymers and geopolymeric materials. *J. Therm. Anal.* **1989**, *35*, 429–441. [CrossRef]
5. Papa, E.; Medri, V.; Amari, S.; Manaud, J.; Benito, P.; Vaccari, A.; Landi, E. Zeolite-geopolymer composite materials: Production and characterization. *J. Clean. Prod.* **2018**, *171*, 76–84. [CrossRef]
6. Rowles, M.; O'Connor, B. Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite. *J. Mater. Chem.* **2003**, *13*, 1161–1165. [CrossRef]
7. He, P.; Wang, M.; Fu, S.; Jia, D.; Yan, S.; Yuan, J.; Xu, J.; Wang, P.; Zhou, Y. Effects of Si/Al ratio on the structure and properties of metakaolin based geopolymer. *Ceram. Int.* **2016**, *42*, 14416–14422. [CrossRef]
8. Swanson, H.E. *Standard X-ray Diffraction Powder Patterns*; United States Department of Commerce National Bureau of Standards: Washington, DC, USA, 1960.
9. Feret, F.R.; Roy, D.; Boulanger, C. Determination of alpha and beta alumina in ceramic alumina by X-ray diffraction. *Spectrochim. Acta Part B At. Spectrosc.* **2000**, *55*, 1051–1061. [CrossRef]
10. Kouamo, H.T.; Elimbi, A.; Mbey, J.A.; Sabouang, C.J.N.; Njopwouo, D. The effect of adding alumina-oxide to metakaolin and volcanic ash on geopolymer products: A comparative study. *Constr. Build. Mater.* **2012**, *35*, 960–969. [CrossRef]
11. Han, W.; Lv, Y.; Wang, S.; Qiao, J.; Zou, C.; Su, M.; Peng, H. Effects of Al/Na and Si/Na Molar Ratios on the Alkalinity of Metakaolin-Based Geopolymer Pore Solutions. *Materials* **2023**, *16*, 1929. [CrossRef] [PubMed]
12. Yang, J.; Li, D.; Fang, Y. Synthesis of Nanoscale CaO-Al_2O_3-SiO_2-H_2O and Na_2O-Al_2O_3-SiO_2-H_2O Using the Hydrothermal Method and Their Characterization. *Materials* **2017**, *10*, 695. [CrossRef] [PubMed]
13. Tanhaei, B.; Ayati, A.; Lahtinen, M.; Sillanpää, M. Preparation and characterization of a novel chitosan/Al_2O_3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorption. *Chem. Eng. J.* **2015**, *259*, 1–10. [CrossRef]
14. Çelikten, S.; Işıkdağ, B. Strength Development of Ground Perlite-Based Geopolymer Mortars. *Adv. Concr. Constr.* **2020**, *9*, 227–234. [CrossRef]