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Optimizing Alkaline Activation of Natural Volcanic Pozzolan for Eco-Friendly Materials Production: An Investigation of NaOH Molarity and Na₂SiO₃-to-NaOH Ratio

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Abstract: The production of Portland cement is energy-intensive and polluting. As a result, the search for ecological and economical alternatives has become a global priority. Geopolymers are among the most promising ecological alternatives to Portland cement. Their properties depend on the nature and concentration of the activators. This study investigates the effect of Na₂SiO₃/NaOH ratio and NaOH molarity on the alkaline activation of natural volcanic pozzolan. The physico-mechanical and microstructural properties of the investigated geopolymer were evaluated using compressive strength, density, porosity, water absorption, X-ray diffraction, infrared spectroscopy, and scanning electron microscopy. The results indicate that the optimal parameters for activation are a NaOH molarity of 8 mol/L and Na₂SiO₃/NaOH ratio of 1.2. These parameters enhance the dissolution of the volcanic pozzolan and the formation of a N-A-S-H geopolymer gel, resulting in a dense, less porous matrix with good resistance.

Keywords: Portland cement; polluting; ecological alternatives; geopolymers; volcanic pozzolan



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1. Introduction

Natural pozzolans, also known as volcanic pozzolans, are a type of volcanic aluminosilicate [1]. Natural volcanic pozzolans are pyroclastic rocks resulting from the accumulation of lava debris thrown into the atmosphere following explosive volcanic eruptions. During explosive volcanic eruptions, the pressure decreases, resulting in the formation of a microporous structure due to the release of gases which were previously dissolved in the magma elements. Additionally, the rapid cooling process contributes to the formation of the material's glassy pozzolan structure [2].

Pozzolans were first used by the Romans (fifth century BC to fourth century AD) for the production of building blocks in the city of Pozzuoli in Italy, from which the name pozzolan derives [2]. Due to its morphostructural properties, pozzolan is widely used in several industrial fields such as filtration, abrasion, agriculture, etc. [3]. Additionally, due to its chemo-mineralogical composition, volcanic pozzolan is considered as one of the most used materials in the field of ecological construction, as it presents advantages in terms of cost reduction and improved durability [2]. Owing to its pozzolanic properties, it can be used to partially replace Portland cement, the production of which is energy-intensive and polluting [4]. Several research works have been conducted on the replacement of Portland cement with finely ground pozzolan and have succeeded in replacing up to 20% of the cement. According to Omrane and Rabehi [5], pozzolan, with its aluminosilicate

composition and amorphous phase content, reacts with excess portlandite released by cement hydration and forms calcium silicates and/or hydrated calcium aluminosilicates, thereby increasing the long-term mechanical properties of the cement [6]. This partial replacement of Portland cement with natural pozzolan has reduced energy consumption and CO₂ emissions associated with the replaced portion, resulting in partially eco-friendly building materials [7].

Although partially replacing cement with volcanic pozzolan reduces the energy-intensive and polluting nature of construction materials, the large remaining portion of cement poses an environmental and economic problem. This has led several researchers, internationally, to develop more economical and eco-friendly substitutes for Portland cement, such as geopolymers [8–12]. Due to their lower negative impact on the environment and superior physico-mechanical properties (high compressive strength, minimal shrinkage, rapid setting, and low thermal conductivity), these new materials have gained attention as a possible substitute for conventional Portland cement [13]. They correspond to a new class of semi-crystalline aluminosilicate materials that can be synthesized at room temperature by a chemical reaction between a source containing amorphous alumina, silica, and an acid or alkaline activator solution [14].

Natural pozzolan, according to the required criteria for geopolymerization, is a material that could potentially be used for the synthesis of geopolymers due to its chemo-mineralogical composition, wide availability in nature (124 million hectares) [15], and low cost associated with extraction [16]. However, according to Firdous et al. [2], the geopolymerization of volcanic pozzolan is not always easy, especially when it has a relatively high degree of crystallization. In this sense, several researchers have tried to activate volcanic pozzolans from various regions of the world by adding calcium and/or alumina mineral admixtures, or by thermally treating the geopolymers at relatively high temperatures [1,17–19]. Djobo et al. [17] used from 5% to 25% metakaolin as the source of alumina with pozzolan from Cameroon. Elmahdoubi et al. [1] added 20% of metakaolin clay to the Moroccan natural pozzolan. Haddad, R. H et al. [18] and Juhyuk Moon et al. [19] obtained good results after thermally activating their pozzolan at a temperature of 100 °C for 48 h.

In this study, an investigation of the activation of volcanic pozzolan using sodium hydroxide and sodium silicate-based activator solutions is presented. The geological context and the chemical, mineralogical, and microscopic characterization of pozzolan rock are presented and discussed. The effect of the molarity of the NaOH solution and the Na₂SiO₃-to-NaOH mass ratio is studied and optimized. The performance of the synthesized geopolymers is analyzed in terms of mechanical, mineralogical, and microstructural properties and is discussed in light of previous works.

2. Raw Material and Experimental Techniques

2.1. Volcanic Pozzolan

In the current study, the volcanic pozzolan was sourced from the Moroccan volcanic province of the Middle Atlas (Figure 1a) and specifically obtained from the Jbel Hebri quarry situated between the cities of Azrou and Timahdite (33.112934° N, −5.758614° W) (Figure 1b). The sampling strategy employed in this study aimed to gather pozzolan fragments from various sections of the investigated volcano. After collection, the pozzolan samples were washed with distilled water and then subjected to a drying process for 24 h at 105 °C using an oven. Subsequently, the cleaned volcanic pozzolan fragments (Figure 1c) were milled for 10 min using a Retsch-type ball mill and sifted using a Fritsch-type sieve shaker to obtain a powder with particle sizes of less than 63 µm.

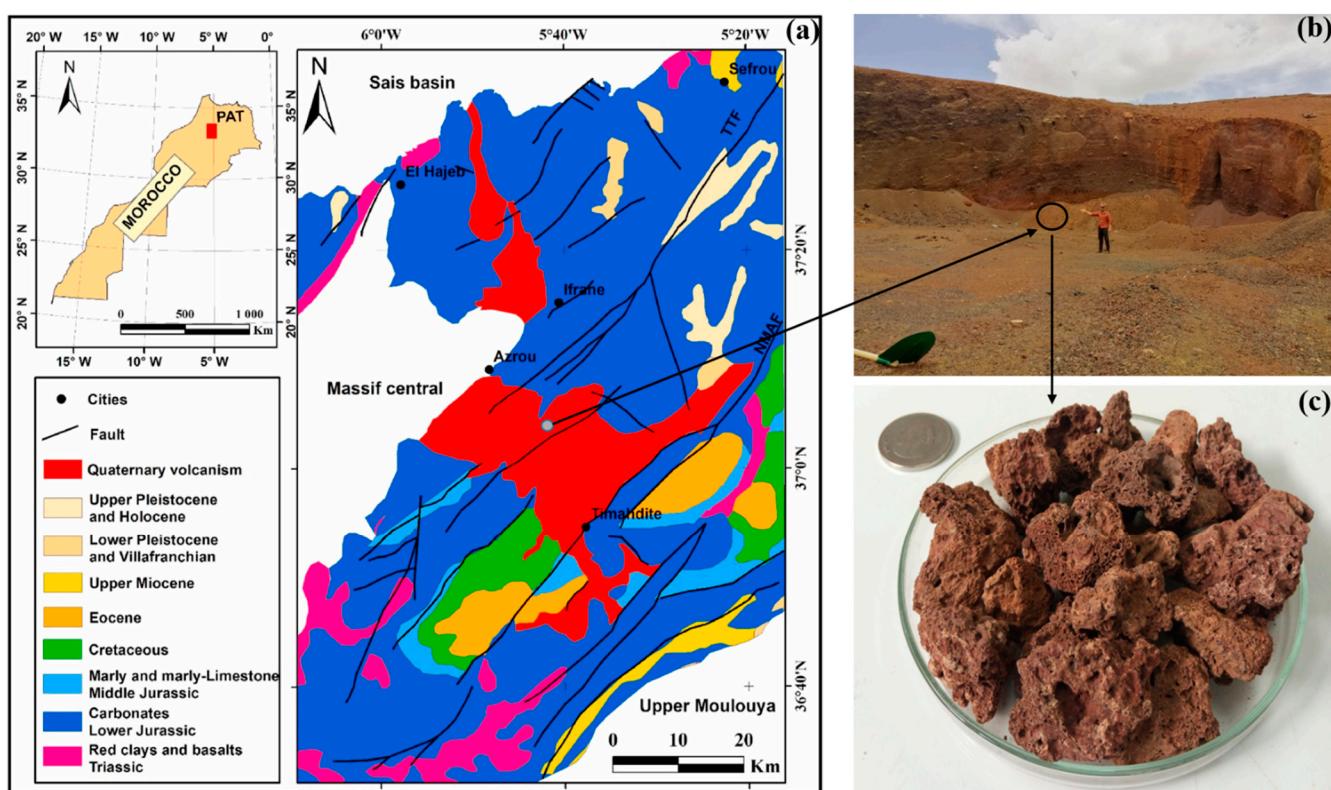


Figure 1. (a) Geological map of the central Middle Atlas; (b) Pozzolan quarry of Jbel Hebri; (c) sampled volcanic pozzolan fragments.

2.2. Alcaline Solution

The alkaline solution used in this work corresponds to the mixture of water, sodium hydroxide, and sodium silicate, provided by CADILHAC Company. Firstly, sodium hydroxide solutions with molarities of 4, 6, 8, 10, and 12 mol L⁻¹ were prepared by dissolving 99% pure NaOH flakes in distilled water. Then, solutions consisting of a mixture of NaOH solution and sodium silicate (25.7% SiO₂, 10.2% Na₂O, and 64.1% H₂O) with a SiO₂-to-Na₂O ratio of 2.6 and a density of 1370 kg·m⁻³ were prepared by varying the Na₂SiO₃/NaOH ratio to 0.9, 1, 1.1, and 1.2. The solutions were prepared 24 h before the manipulations.

2.3. Geopolymers Preparation

The procedure for preparing geopolymers in this work is divided into two series of synthesis (Figure 2a,b). In the first series (a), natural pozzolan was activated by activator solutions at different NaOH molarities (4, 6, 8, 10, and 12 mol L⁻¹) to produce 5 mixes (GP1, GP2, GP3, GP4, and GP5). In the second series, the NaOH molarity was fixed at 8 mol L⁻¹ and natural volcanic pozzolan was activated by activator solutions at different Na₂SiO₃/NaOH mass ratios (0.9, 1, 1.1, and 1.2) to obtain 4 geopolymer formulations (GP6, GP7, GP8, and GP9). Note that the maximum Na₂SiO₃/NaOH ratio is 1.2, since cracks appeared on the surface of the samples beyond 1.2.

The protocol for both series of geopolymers developed in this study is illustrated in Figure 2c. After mixing the pozzolan powder with the activator solution according to the proportions displayed in Table 1, the mixture was blended for 10 min, and the resulting slurry was poured into cubic molds (4 cm on each side). Then, the filled mold was vibrated to expel trapped air inside the slurry. After 24 h of ambient temperature polymerization, the polymerized geopolymers were demolded and placed in plastic bags until the testing age.

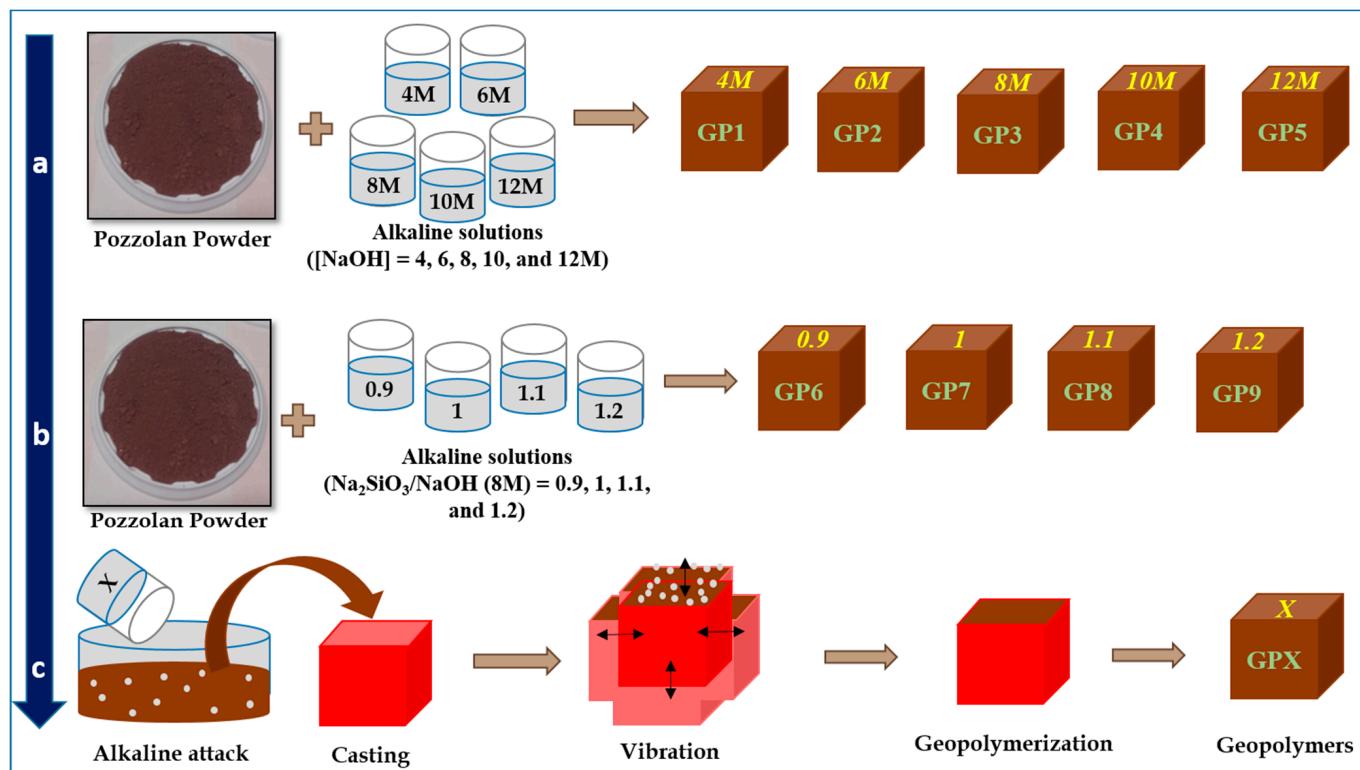


Figure 2. (a) Geopolymer synthesis protocol by varying the molarity of NaOH; (b) Geopolymer synthesis protocol by varying the Na_2SiO_3 -to-NaOH ratio; (c) steps of geopolymer synthesis.

Table 1. Mix proportions of the synthesized geopolymers binders.

Code	Pozzolan (g)	NaOH Molarity	$Na_2SiO_3/NaOH$	Na_2SiO_3 (g)	NaOH (g)
GP1	40	4	0.9	9.48	10.52
GP2	40	6	0.9	9.48	10.52
GP3	40	8	0.9	9.48	10.52
GP4	40	10	0.9	9.48	10.52
GP5	40	12	0.9	9.48	10.52
GP6	40	8	0.9	9.48	10.52
GP7	40	8	1	10	10
GP8	40	8	1.1	10.48	9.52
GP9	40	8	1.2	10.9	9.09

2.4. Characterization Methods

The chemical composition of volcanic pozzolan was determined using an “AXIOS” wavelength dispersion spectrometer in X-ray fluorescence (XRF). For the mineralogical analysis of volcanic pozzolan and geopolymers, which were ground into powder, a Panalytical X’Pert Pro powder diffractometer was utilized to reflect copper K $\alpha 1$ radiation ($\lambda = 1.54 \text{ \AA}$) in X-ray diffraction (XRD).

The infrared spectroscopic analysis of the powdered pozzolan and geopolymers was performed using a BRUKER VERTEX 70 spectrometer in transmittance mode, covering the wavenumber range between 400 cm^{-1} and 4000 cm^{-1} in Infrared Spectroscopy (FTIR).

The water absorption (A), porosity (P), and bulk density (D) were evaluated at the 28-day mark, according to ASTM C642-13 standard, on three cubic samples (40 mm) using the following equations:

$$\text{Bulk density } (g/cm^3) = \frac{W_{ds}}{W_{ss} - W_{ws}}$$

$$\text{Water absorption (\%)} = \frac{W_{ss} - W_{ds}}{W_{ds}} \times 100$$

$$\text{Porosity (\%)} = \frac{W_{ss} - W_{ws}}{W_{ss} - W_{ws}} \times 100$$

where W_{ss} refers to the weight of the sample when saturated in air, W_{ds} refers to the weight of the specimen after being dried for 24 h at $100 \pm 5^\circ\text{C}$, and W_{ws} refers to the weight of the specimen in water.

The compressive strength of the geopolymers was also evaluated on a cubic specimen (40 mm) after 7 and 28 days of curing, using a press type “RP25 ATF” with a compression capacity of 250 kN and a loading rate of 1.6 kN s^{-1} . Three replicate samples of each formulation were tested, and the average mechanical strength was considered as the representative value. Additionally, the morphology of the pozzolan and geopolymers was examined using a “JEOL JSMTT 100” scanning electron microscope coupled with a “JEOL JSMTT 100” energy dispersive spectrometer, with an ultra-thin (2.5 nm) gold layer deposited on an optimal geopolymer fragment using a JEOL JFC2300 HR secondary vacuum metallizer.

3. Results and Discussion

3.1. Characterization of the Raw Materials

3.1.1. Volcanological Analysis

Basaltic volcanism is the most predominant volcanic activity on Earth [20,21]. The most frequent volcanic landforms are Strombolian cones, which are followed by phreatomagmatic tuff rings and cones [22]. Cones are volcanic structures resulting from “dry” Strombolian eruptions. This type of eruption consists of a series of alternative explosions of large gas bubbles at the surface of the magma, ejecting lava packages of all sizes into the air [23,24]. Strombolian deposits are generally highly vesicular, appearing as an alternation between horizons dominated by vesicular scoria ashes, and horizons dominated by bombs and lava blocks. These deposits show variations in texture, sorting, granulometry, density, color, and vesicularity rate according to the distance from the crater [25,26].

The West Hebri pozzolan used in this study is derived from a complex volcano that consists of a partially superimposed cone and maar. It is a small cone, about 20 m high and elongated over nearly 300 m in diameter (NE-SW). Towards the end of the same eruption, the SW part of the cone was removed by the formation of a maar with a diameter of 800 m and a depth of 65 m. The structure of the cone was exploited for the pozzolan progressively from the northeast in a distal position to the southwest flank in a proximal position. Excavation work has left two parallel cut faces that are 20 m high and 150 m wide passing through the center of the volcano. The outcrop represents multi-decimeter horizons of lapilli, intercalated by decimeter levels of bombs. A clear variation in color and granulometry was recorded at the center, dominated by reddish coarse bombs and lapilli, and the periphery, dominated by dark-colored ashes and fine lapilli. The pozzolan collected from the proximal part are represented by weakly vesicular coarse lapilli ($\phi < 45 \text{ mm}$), in rounded shapes and with a reddish tint (Figure 1c).

3.1.2. Chemo-Mineralogical and Morphostructural Analysis

Figure 3a,b depicts the SEM micrographs of the volcanic pozzolan at two different scales, 50 μm and 10 μm , respectively. The electron microscopy characterization of the pozzolan rock reveals a porous morphostructure which is attributed to the gas-rich magma during volcanic eruptions [27]. This porous structure is formed by the trapping of gas bubbles in the magma fragments during volcanic activity. Bubble-like particles are observed on the surface of pozzolan fragments, which can be formed by the rapid cooling of the pozzolan fragments, causing the gas underneath the surface of the pozzolan to be trapped and appear as bubbles. From a chemical-mineralogical point of view, elemental analysis by EDS shows that the pozzolan is composed of silicon, aluminum, oxygen, calcium, iron, and magnesium (Figure 3c). Chemical analysis of major elements by X-ray Fluorescence (XRF) corroborated the EDS analysis and showed that the pozzolan has the composition of

a moderately siliceous ($\text{SiO}_2 = 37\%$), moderately alumina-rich ($\text{Al}_2\text{O}_3 = 14.88\%$), strongly titano-ferromagnesian ($\text{Fe}_2\text{O}_3 + \text{MgO} + \text{TiO}_2 = 28.32\%$), and more calcic than alkaline ($\text{CaO}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) = 6.62$) volcanic rock (Figure 4). Figure 5 shows the mineralogical characterization by X-ray diffraction of the natural volcanic pozzolan. From the X-ray diffractogram, it was determined that the pozzolan used in this work is composed of calcic plagioclase as anorthite, calco-iron-magnesian pyroxene as augite, calcic amphibole as hornblende, magnesian olivine (forsterite), and titanium and iron oxides as hematite and ilmenite. Infrared spectroscopic characterization of the pozzolan revealed the presence of a double absorption band at 464.47 cm^{-1} and 530.32 cm^{-1} , corresponding to the bending vibration of the Si-O-Al and Si-O-Si bonds, respectively [28] (Figure 6). An intense band was noted around 1037.60 cm^{-1} , corresponding to the stretching vibration of the Si-O-Al and Si-O-Si bonds. Bands corresponding to the bending vibration of the H-O-H bond and the stretching vibration of the -OH bond were also detected at 1642.21 cm^{-1} and 3462.82 cm^{-1} , respectively, in the spectra.

Based on the chemo-mineralogical analysis of the pozzolan, it was observed that its composition, which is moderately siliceous and moderately alumina-rich, is conducive to geopolymerisation. However, the presence of minerals such as hematite, augite, and forsterite may have an impact on the pozzolan's reactivity. Furthermore, infrared spectroscopic analysis revealed that the pozzolan contains essential Si-O-Al and Si-O-Si bonds, indicating a potential for geopolymer gel formation.

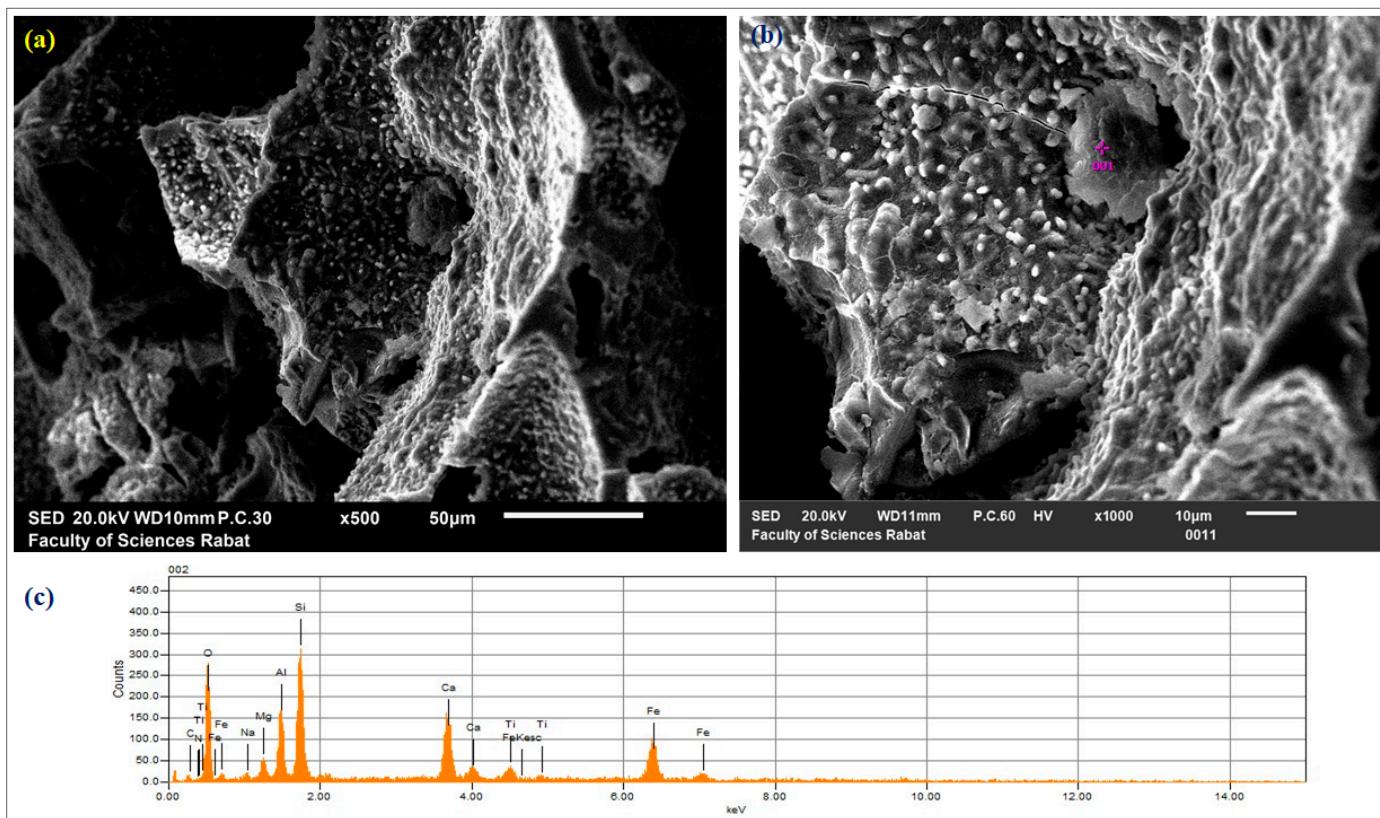


Figure 3. (a,b) Morphology of volcanic pozzolan fragments used in the present study (SEM); (c) chemical analysis of the pozzolan determined by EDS.

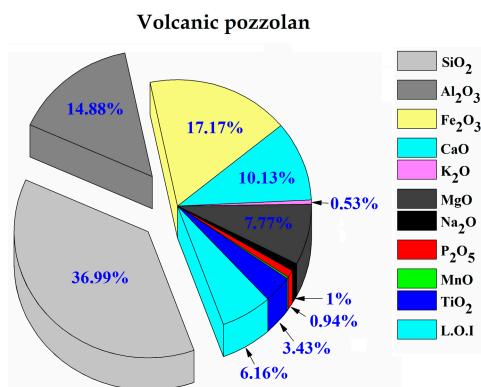


Figure 4. Chemical composition of volcanic pozzolan determined by XRF.

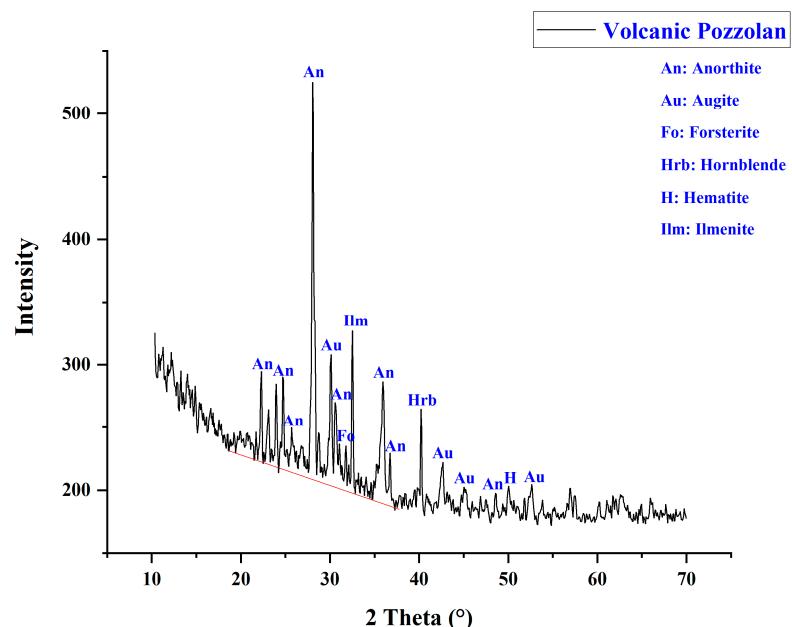


Figure 5. Mineralogical composition of natural volcanic pozzolan determined by XRD.

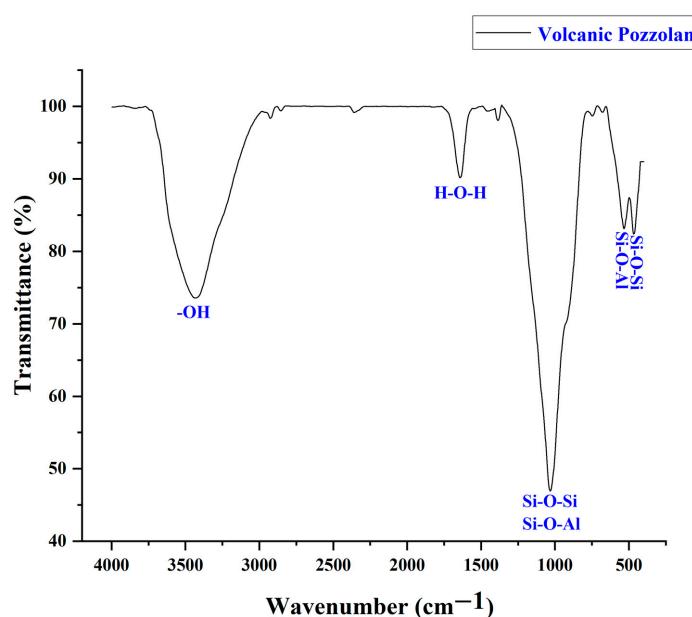


Figure 6. Infrared spectrum of the pozzolan used in this study.

3.2. Geopolymers Characterization

3.2.1. Effect of NaOH Molarity on Physico-Mechanical Properties

Figure 7 depicts the variation in the compressive strength of geopolymers based on natural volcanic pozzolan as a function of NaOH molarity. The compressive strength increased from 2.5 to 5.4 MPa at 7 d and from 4.8 to 11.3 MPa at 28 d, with an increase in molarity from 4 to 8 mol·L⁻¹, followed by a decrease in compressive strength from 5.4 to 4.69 MPa at 7 d and from 11.3 to 9.1 MPa at 28 d, with an increase in NaOH molarity from 8 to 12 mol·L⁻¹. Based on these results, the optimal NaOH molarity in terms of mechanical strength is 8 mol·L⁻¹. The trend of compressive strength variation with NaOH molarity has also been previously reported in the literature [29,30]. The increase in compressive strength with an increase in NaOH molarity from 4 to 8 mol·L⁻¹ is due, according to Ayoub et al. [31] and Nadoushan and Ramezanianpour [29], to the increase in OH⁻ ions concentration in the reaction mixture, which promotes the dissolution of natural volcanic pozzolan and the formation of monomers in the form of aluminates, leading to a dense geopolymeric matrix and high internal cohesion. According to the previous works [29,32], the use of a high concentration of NaOH in the activating solution hinders the dissolution of aluminosilicate precursors, delaying the formation of coagulated structures by limiting the mobility of OH⁻ ions. Thus, the observed decrease in compressive strength after increasing the NaOH molarity from 8 to 12 mol·L⁻¹ is the result of a low ionic mobility of the OH⁻ ions, which is related to the increase in NaOH quantity with molarity increase.

The compression strength results found in this study, as a function of NaOH molarity, corroborate those found in the literature and show that the optimal concentration which ensures good mobility of the hydroxide ions of NaOH is 8 mol·L⁻¹ [29–31]. This concentration favors the reaction of dissolution of natural volcanic pozzolan, and the formation of aluminates and silicates and their polycondensation reaction, thereby allowing for a geopolymer with relatively high mechanical properties. Despite this molarity optimization study, when fixing the Na₂SiO₃/NaOH ratio at 0.9, the compression strength results (11.3 MPa at 8 mol·L⁻¹) appear insufficient. Therefore, a second optimization study of the Na₂SiO₃/NaOH ratio while fixing the molarity at 8 M was launched to study its effect on the physicomechanical and microstructural properties of volcanic pozzolan-based geopolymer.

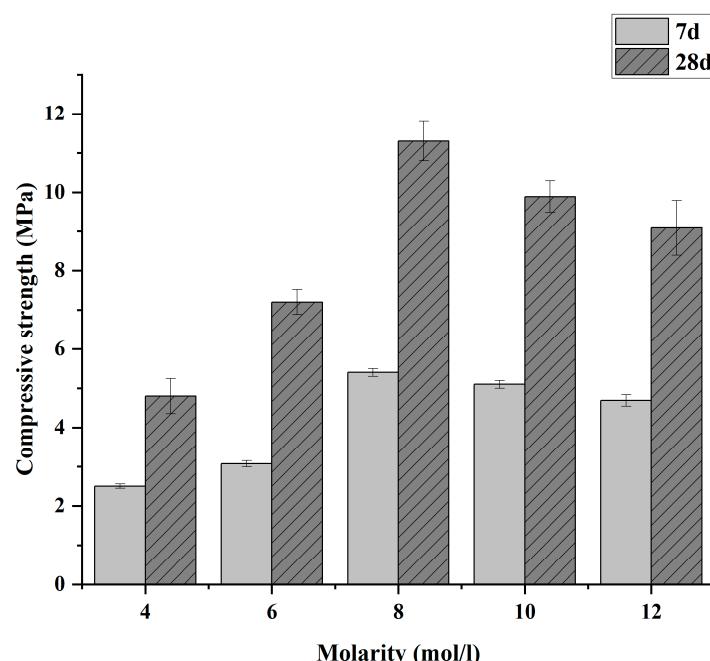


Figure 7. Compressive strength of geopolymers according to the molarity of NaOH used in the activating solution.

3.2.2. Effect of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ Ratio on Physical-Mechanical and Microstructural Properties Compressive Strength

The compression strength of the geopolymers synthesized in this work at 7 and 28 d of curing, as a function of the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ mass ratio, is presented in Figure 8. Generally, the compression strength values increased with increasing age of curing in all $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios. Specifically, increasing the Na_2SiO_3 -to- NaOH mass ratio significantly increases the compression strength of the geopolymers. At 7 days of curing, this improved from 5.4 MPa (ratio of 0.9) to 12.85 MPa (ratio of 1.2), and at 28 days of curing, it improved from 11.3 MPa (ratio of 0.9) to 21.7 MPa (ratio of 1.2). The increase in compression strength of the geopolymers with increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ mass ratio, i.e., increasing the amount of Na_2SiO_3 and decreasing the amount of NaOH , could be due primarily to the presence of a high amount of NaOH in the low $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios which, according to Lee et Van Deventer [32] and Fernández-Jiménez et al. [33], leads to a rapid and premature precipitation of aluminosilicate gel by inhibiting the formation of other monomers. Secondly, this improvement in compression strength could also be due to the increase in soluble sodium silicate concentration in the reaction medium. As reported by Morsy et al. [34], the amount of soluble silicate is a critical factor in the process of geopolymerization because it increases the soluble silicate content in the reaction medium, which acts as an ion, balancing the charge, and releases the soluble silicate species into the reaction medium, initiating oligomer formation and, consequently, polycondensation [35,36]. Thus, increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio in this study triggered the reaction of pozzolan dissolution and the formation of a 3D polymer network, leading to an increase in the mechanical properties of the geopolymers [37].

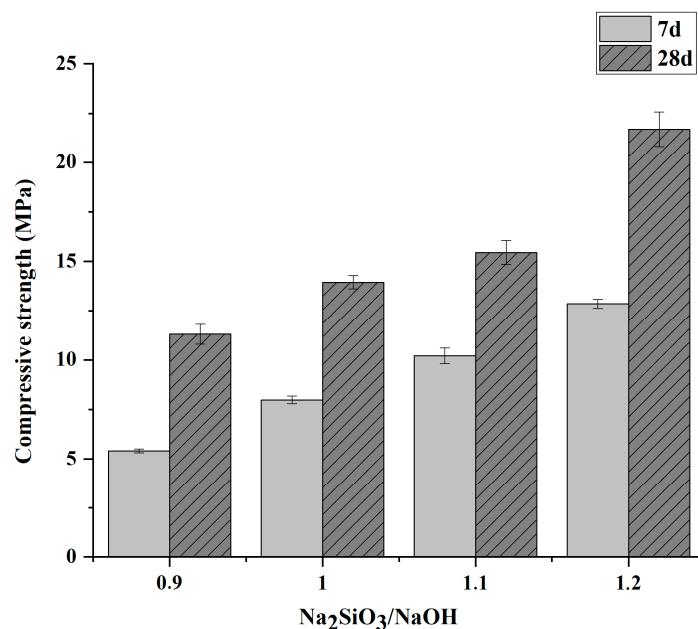


Figure 8. Compressive strength of geopolymers according to the Na_2SiO_3 -to- NaOH ratio used in the activating solution.

Density (D), Porosity (P), and Water Absorption (A)

Figure 9 shows the evolution of D, P, and A, measured at 28 d of curing, according of the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. From this Figure, it can be seen that the bulk density increases with increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio from 1.7 g/cm^3 for a ratio of 0.9 to 1.84 g/cm^3 for a ratio of 1.2. However, with the increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio from 0.9 to 1.2, a decrease in the porosity of the elaborated geopolymers was observed from 24.5% to 21.8%. The same fluctuation was also noted for water absorption, which decreased from 13.85% to 11.96% with the increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio from 0.9 to 1.2. Nur et al. [38] also

observed a similar trend in the variation of bulk density, porosity, and water absorption when using metakaolin as a precursor. The low bulk density and high porosity and water absorption observed at low $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios may be due to the limited amount of soluble silicate in the reaction medium [37], which initiates the dissolution reaction and partially dissolves the aluminosilicate, creating voids in the geopolymers matrix. Increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio results in an increase in soluble silicate content, which promotes the pozzolan dissolution reaction, and the formation of oligomers and their subsequent polycondensation. This leads to the formation of a polymerized and dense matrix without unreacted pozzolan particles [36,38,39]. These results corroborate the compressive strength results that were found to accord with the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, showing a positive correlation between bulk density and compressive strength and a negative correlation with porosity and water absorption.

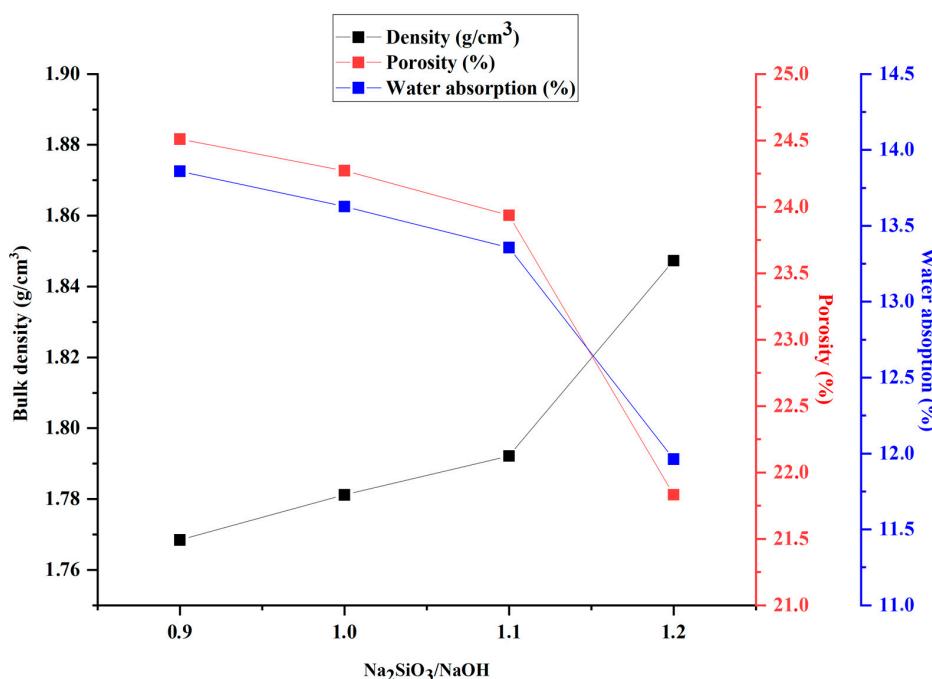


Figure 9. Evolution of bulk density, porosity, and water absorption as a function of the variation in the Na_2SiO_3 -to- NaOH ratio.

FTIR Analysis

Figure 10 illustrates the infrared spectra of pozzolan and the synthesized geopolymers with low (0.9) and high (1.2) $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios. By comparing the spectra of the natural pozzolan with those of the geopolymers, a transformation of the intensities and locations of the vibrational bands was observed after geopolymerization and as a function of the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. An increase in the intensity of the vibrational bands located at 3462 cm^{-1} and 1642 cm^{-1} , characteristic of the bending vibration of the -OH bonds and the stretching vibration of the H-O-H bonds [40], was observed due to the absorption of H_2O molecules in the structural cavities after the geopolymerization reaction [37]. In addition, the appearance of a vibrational band related to the vibration of O-C-O bonds at 1454 cm^{-1} was also reported after the geopolymerization due to the formation of carbonates during geopolymerization by a reaction between alkali hydroxide and CO_2 from the atmosphere [41]. With the increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, an increase in the intensity of the bands located at 464 cm^{-1} and 530 cm^{-1} was observed, which are associated with the bending vibration of Si-O-Al and Si-O-Si bonds, respectively [37]. The most intense absorption band, appearing around 1000 cm^{-1} and associated with the vibration of Si-O-Al and Si-O-Si bonds [42], shifted to lower wavenumbers, and its intensity increased with the increase in the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio. According to Tho-In et al. [43], the change in the

intensity and the shift of this band indicate the formation of the bonds of polysialatesiloxo and polysialatedisiloxo structures in the form of hydrated sodium aluminosilicate gel (N-A-S-H) which was generated by the geopolymerization reaction after the dissolution reaction by adding a silica source. Thus, increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio, in the present work, increased the soluble silica content in the reaction medium by promoting the pozzolan dissolution reaction and the formation of a dense geopolymer matrix with high physico-mechanical properties.

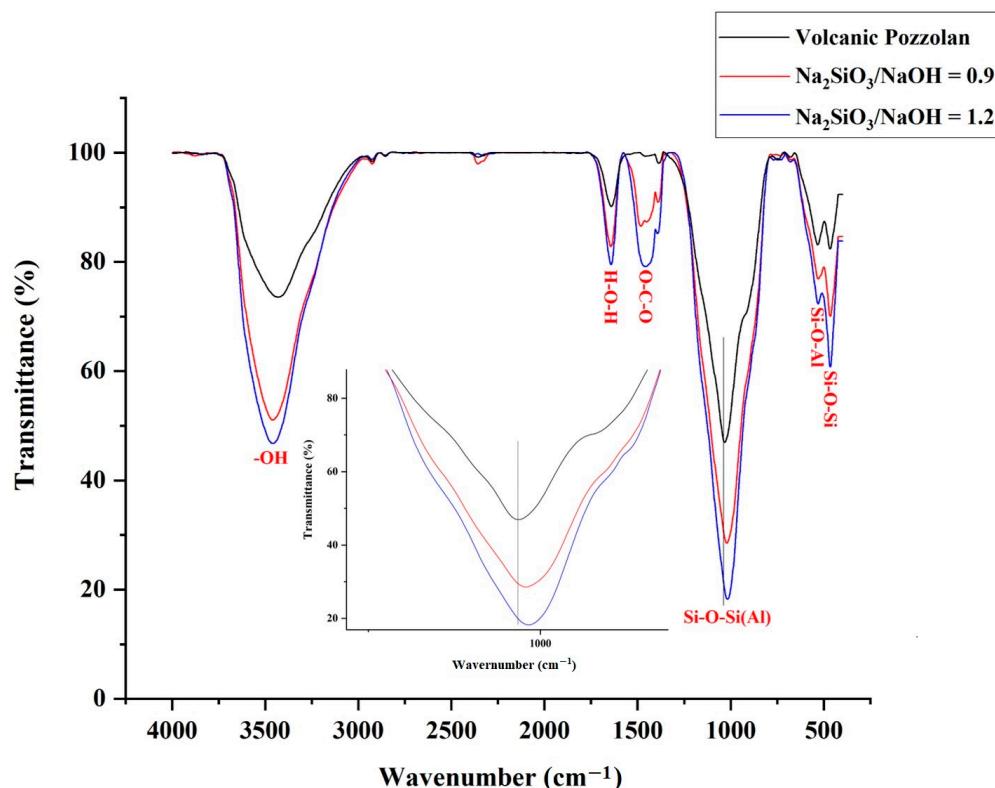


Figure 10. Infrared spectrum of geopolymers synthesized with low (0.9) and high (1.2) ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ compared with that of pozzolan.

XRD Analysis

The mineralogical composition of geopolymers synthesized with low (0.9) and high (1.2) $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios is compared with that of the natural pozzolan in the form of diffractograms in Figure 11. In general, the diffractograms show crystalline peaks and amorphous phase halos of varying intensities. In particular, the peaks corresponding to forsterite, hematite, and augite retain the same intensity after geopolymerization, which, according to Ayoub et al. [44] and Baifa Zhang et al. [45], demonstrates their chemical stability during the geopolymerization reaction of the volcanic pozzolan. A decrease in the intensity of crystalline peaks of ilmenite and anorthite, and the disappearance of hornblende ($2\theta = 40.22^\circ$) and anorthite ($2\theta = 48.50^\circ$) peaks, were observed after the geopolymerization reaction in both ratios (0.9 and 1.2). This is due, according to Taxiarchou et al. [46] and Aziz et al. [28], to the partial dissolution of anorthite and ilmenite and the complete dissolution of hornblende and anorthite in the reaction medium, as they participate in the formation of the amorphous hydrated sodium aluminosilicate gel (N-A-S-H). This is represented by the amorphous phase halo between $2\theta = 17^\circ$ and $2\theta = 36^\circ$ in the diffractograms of the two geopolymers, as shown in Figure 11.

The comparison of the two diffractograms of the geopolymers synthesized with $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios of 0.9 and 1.2 (Figure 11) shows that an increase in the ratio causes a decrease in the intensity of crystalline peaks and the disappearance of some peaks. This is due to the increase in the concentration of soluble sodium silicates in the reaction medium,

which act as a charge-balancing ion and releases soluble silicate species, triggering the dissolution of some of the crystalline and amorphous phases of the pozzolan, leading to the formation of oligomers and polycondensation, and precipitation of the N-A-S-H gel [34,36,37]. These results are consistent with the findings of increased compressive strength (Figure 8) with higher $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratios. This is due to a higher ratio result in a greater amount of amorphous phase in the form of N-A-S-H gel in the synthesized geopolymers, as indicated by the increase in halo intensity between 17 and 36 in 2 Theta (Figure 11), leading to a higher compressive strength of the elaborated geopolymers.

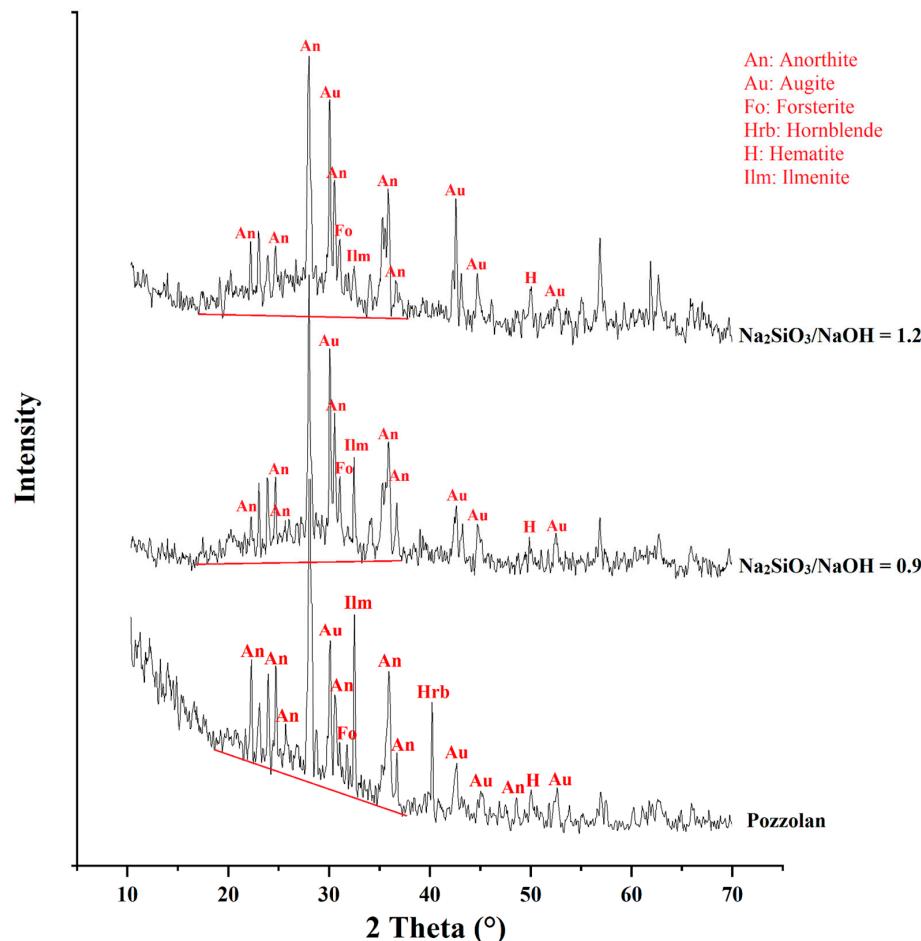


Figure 11. Diffractograms of geopolymers synthesized with low (0.9) and high (1.2) ratio of $\text{Na}_2\text{SiO}_3/\text{NaOH}$ compared with that of pozzolan.

SEM Analysis

Two geopolymers, synthesized with a low Na_2SiO_3 -to- NaOH ratio (Figure 12A) and a high Na_2SiO_3 -to- NaOH ratio (Figure 12B), were chosen to study the effect of the ratio on the microstructure of geopolymers and to confirm the results of the XRD and FTIR. Figure 12 shows the micrographs of the two geopolymers. From this figure, it can be observed that both geopolymers contain efflorescence in the form of needles. Comparing the two microstructures of the two geopolymers in Figure 12, the geopolymer synthesized with a $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 0.9 (Figure 12A) shows a heterogeneous structure punctuated by vacuoles compared to that synthesized with a ratio of 1.2 (Figure 12B). These results confirm the findings of density, porosity, and compression strength, showing that increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio decreases porosity (Figure 9) and increases the density (Figure 9) and the compression strength of geopolymers (Figure 8).

Furthermore, as can be seen in Figure 12, the amount of N-A-S-H gel, shown in the form of geopolymeric plates, in the micrograph of Figure 12A is greater than that of

Figure 12B. These also support the results of the microstructural characterization by XRD; increasing the intensity of the amorphous phase halo (Figure 11) and FTIR by shifting the vibration band of Si-O-Si and Si-O-Al towards the lowest wavenumbers (Figure 10), confirms that increasing the $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio from 0.9 to 1.2 favors the dissolution reaction of the volcanic pozzolan and the formation of more N-A-S-H gel, and consequently, the increase in the mechanical properties of geopolymers based on volcanic pozzolan.

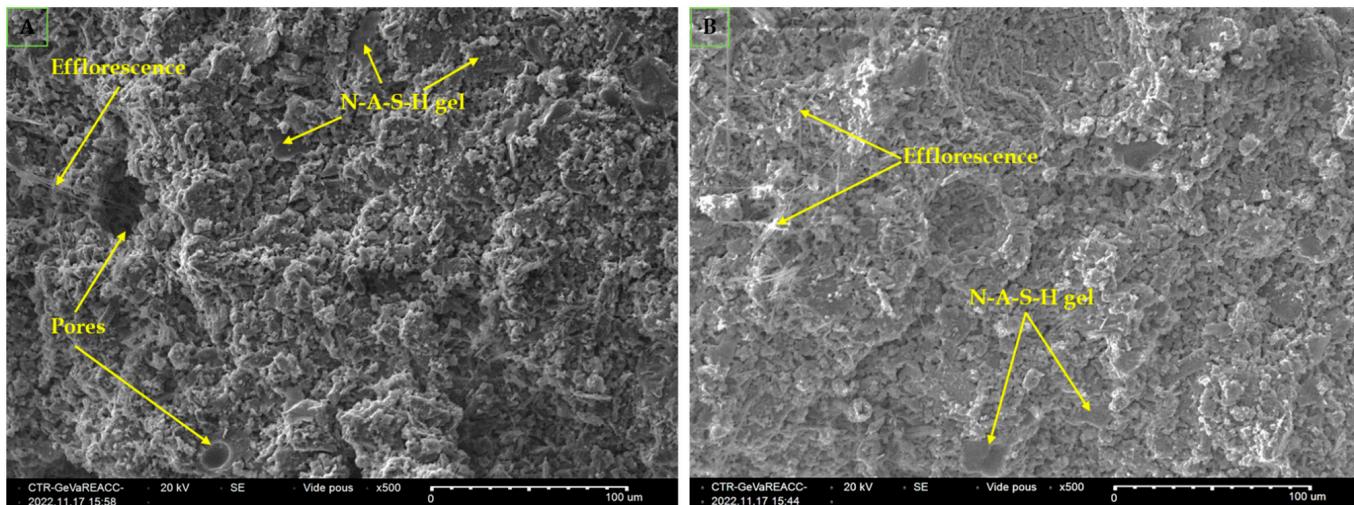


Figure 12. Comparison of the microstructure of geopolymers synthesized by the Na_2SiO_3 -to- NaOH ratios of 0.9 (A) and 1.2 (B).

4. Conclusions and Future Research Direction

This study demonstrates that the use of natural volcanic pozzolan as a precursor material for geopolymer synthesis is a promising alternative to Portland cement. The optimal parameters for activation, as determined in this study, are a NaOH molarity of $8 \text{ mol}\cdot\text{L}^{-1}$ and $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio of 1.2. These parameters promote the dissolution reaction of the volcanic pozzolan and the formation of a dense matrix composed of N-A-S-H gel, resulting in a less porous material with a relatively high compressive strength. This study highlights the importance of understanding the impact of various parameters on the properties of geopolymers. The optimization of these parameters is crucial in the development of efficient and sustainable geopolymer materials for practical applications.

Future research directions could include further investigations into the effects of other parameters, such as curing conditions and particle size, on the properties of geopolymers. Additionally, studies on the long-term durability and environmental impact of pozzolan-based geopolymer could be conducted to evaluate their potential as a sustainable alternative to traditional construction materials. The development of new activators, particularly those that are derived from industrial byproducts or waste materials, could also be explored to further reduce the environmental impact of pozzolan-based geopolymer production.

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