

Review

Natural pozzolan based geopolymers: A review on mechanical, microstructural and durability characteristics



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HIGHLIGHTS

- Use of natural pozzolans in development of geopolymers.
- Properties of natural pozzolan based geopolymers.
- Factors influencing the geopolymerization of natural pozzolan.
- Durability & microstructural characteristics of natural pozzolan based geopolymers.
- Applications of natural pozzolan based geopolymers.

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ABSTRACT

Natural pozzolans are tremendous source of reactive silica and alumina required for geopolymer synthesis as an alternative binder for ordinary Portland cement. They are available at a comparatively low cost and generate a low ecological footprint through their simple extraction. Following review paper summarizes the mechanical and durability characteristics as well as the microstructural properties of natural pozzolan based geopolymers and their potential as binding material. The microstructural characteristics are based on the advanced analytical techniques used so far to understand geopolymerization, the phase composition, mechanical and durability properties evolution. From this review is obvious that significant analytical techniques have been successfully carried out on fresh and hardened natural pozzolan based geopolymer obtained in alkaline medium, which helped to understand underlying chemical reaction and external factors affecting final properties. These analyses have shown that natural pozzolan based geopolymer has potential to be used as sustainable building materials. But, for its large scale utilisation there is need to upscale the manufacturing process at a pilot-plant in order to address the macroscopic challenges that may arise at that level.

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1. Introduction

Natural pozzolan is a type of aluminosilicate generally from volcanic origin, that can react with lime at ambient temperature to form a solid rock [1]. The term pozzolan refers to the city of Pozzuoli in Italy where it has been first discovered by Romans. The latter observed that those natural pozzolan have cementing properties and started using them for making building blocks [2]. The cementitious characteristics are known as pozzolanic properties which depends on the amount of reactive SiO₂ and Al₂O₃ available in the aluminosilicate [2,3]. Because of the pozzolanic properties natural pozzolan have been widely used as supplementary cementitious material (SCM) in Portland cement industry [1].

The use of natural pozzolan for making various types of cement have been reviewed in recent time. The first one was made by Siddique et al. in 2011 who summarized the effects of using volcanic ash as SCM in cement paste and mortar [4]. The microstructure, physical, mechanical and durability properties of cement paste and mortar were thus reviewed. The authors reported that the addition of volcanic ash had beneficial effect on long term physical and mechanical properties, electrical resistivity of resulting cement paste and mortar. The second review authored by Cai et al. in 2016 reported the fresh properties, microstructural, mechanical, and durability properties of concretes using volcano-related materials as SCM and lightweight aggregate [5]. That review highlighted that volcano-related materials can be used to develop the concretes with moderate properties. Their use as SCM significantly improved the durability properties of cement paste and mortar. More recently another comprehensive review dealing this time with the use of volcanic ash for developing alternative cement-based materials named alkali activated materials and geopolymer was successfully reported [6]. The main contribution of that paper was the summary of the existing literature addressing the relationship between the inherent properties of volcanic ash and the synthesis parameters as well as their potential use as raw material for geopolymer synthesis.

The present paper reviews and discusses mechanical, microstructural and durability characteristics of natural pozzolan based geopolymer obtained with alkaline solution as hardener or activator. Since, the mechanical and durability characteristics of geopolymer cement and concretes depend on their properties at nano-structural level this review also aims at giving better understanding of the microstructural analysis results used so far to elu-

cidate the nanometric characteristics of geopolymer materials from natural pozzolan.

1.1. Overview on geopolymers

Geopolymers are inorganic aluminosilicate binders that have polymeric silicon-oxygen-aluminium framework structures. Geopolymers binders result from reaction of solid aluminosilicate from source material (natural pozzolans, industrial and agricultural waste products) with highly concentrated aqueous alkali hydroxide or alkali silicate solution. The alkaline source supplies alkali metal cations thus raising the pH of solution it accelerates the dissolution of solid precursors [7]. The available calcium content of reacting components should be low to enable the formation of three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds [7,8]. As studied by Davidovits, the network of the silico-aluminate based geopolymers consists of SiO₄ and AlO₄ tetrahedra linked alternately by sharing all the oxygens. The positive ions present in framework of cavities balances the negative charge of Al³⁺ in IV-fold coordination [8,9]. The basic empirical formula for geopolymer chain is as given in Eq. (1).



where M is the monovalent alkali metal or cation such as K⁺, Na⁺, Ca²⁺, Li⁺; the symbol ‘-’ indicates the presence of bond, n is the degree of polycondensation or polymerisation; z is 1, 2, 3, or higher.

Geopolymers are considered as environmental friendly binder, since they harden at ambient temperatures and therefore, their synthesis demands less energy, and depending on the activator up to 80 % less CO₂ is emitted in comparison to ordinary Portland cement [10–12]. In 1908 for the first time, a German scientist Hans Kühl investigated the setting properties of ground granulated blast furnace slag (GGBFS) with caustic potash (KOH) solution [1,7,13,14]. In 1937, Chassevent observed the reactivity of slags using caustic potash and caustic soda solution [1,13,15]. However, in 1940 the first extensive experimental study on clinker less cements was done by Purdon [16,17]. His work focused on the reaction of GGBFS with caustic soda or caustic alkalis. In 1957, Glukhovskiy discovered the possibilities of producing the binder using low basic calcium or calcium free aluminosilicate and solutions of alkali metal known as soil cements and corresponding concretes as soil silicates [18,19]. Later in 1981, Davidovits produced binders by

mixing alkalis with a burnt mixture of kaolinite, lime stone and dolomite named as geopolymer since they have a polymeric structure. These types of materials belong to the alkaline binding system as discovered by Glukhovskiy [1,13].

1.1.1. Mechanism of geopolymerization

The general mechanism of geopolymerization consists in a three-stage reaction: Dissolution – Coagulation, Coagulation – Condensation, Condensation – Polymerization [20]. The reaction starts with the breakage of siloxane (Si–O–Si) ions with OH[−] ions from alkali activating solution yielding silanol (–Si–OH) and silate (–Si–O[−]) species. The presence of alkali cations normalizes the negative charge while the formation of Si–O[−]–Na⁺ bond hinders the reversion to siloxane [13]. The OH[−] ions also impacts the Si–O–Al bond in the same way and forms complex species, majorly Al(OH)₄[−] anions [8]. The dissolution step depends on the temperature, pH of mixture and possible treatments of the source materials. Higher fineness and higher pH favours the dissolution step and monomeric aluminate and silicate units are formed [21]. In the 2nd stage, the assemblage of ionic species helps to generate contact between the disaggregated products and polycondensation starts causing an increase in the coagulated structure. The silica monomers inter-react to form dimers and then polymers. In the last stage, the further reaction products precipitate because the particles present in the initial solid phase are forming three-dimensional polymeric chain and ring structures consisting of Si–O–Al–O bonds. However, these three steps can overlap with each other and occur almost simultaneously, thus making it difficult to isolate and examine each of them separately [7,8,13,21–23].

1.2. Raw materials for geopolymer synthesis

The raw materials for geopolymer synthesis could be natural pozzolanic materials like volcanic ash (tuff), diatomaceous earth, opaline cherts, shales and pumicites etc. or naturally tempered pozzolanic materials like zeolite, kaolinite, phonolite etc. Artificial raw materials for geopolymers include pozzolanic materials from industrial or agricultural waste such as low calcium fly ash, silica fume, brick powder, granulated blast furnace slag, sugarcane bagasse ash, rice husk ash etc. [3,24–28]. Since recent decades, geopolymers are being used as an alternative to conventional binders with a lot of work carried out on metakaolin or fly ash based

geopolymers, however, only little has been done on the use of natural pozzolans for geopolymer synthesis. Since industrial by-products such as fly ash and slag are available only to the extent that they arise in the production of the main product, their use is limited. In addition, decarbonisation will continue to reduce the burning of coal, which is already leading to a shortage of fly ash for concrete production in some countries. This makes the use of alternative binders with a low ecological footprint increasingly important.

1.2.1. Production of natural pozzolans

Pyroclastic rocks resulting from the explosive volcanic eruptions are considered as wide category of natural pozzolans. The explosive volcanic eruption projects minute particles of melted magma into the atmosphere while the rapid pressure decrease results in formation of microporous structure by release of gases dissolved in particles of the magma. Simultaneously, quenching process results for their glassy state. On contrary, non-explosive eruption results in crystallisation of molten magma (little or no pozzolanic activity) due to insufficient quenching [2].

The deposits of volcanic pozzolans exposed to weathering and cementation of loose particles through diagenetic or other natural processes form compact layers (tuffs). Weathering can cause either zeolitisation or argillification resulting in zeolitic minerals or clay minerals respectively, therefore, zeolitisation enhances the pozzolanic properties [2,29]. Fragments of rocks, minerals and volcanic glass produced during the volcanic eruption having sizes less than 2 mm are characterized as volcanic ashes [5,6,29]. The size of the volcanic ashes reduces with the distance from the volcano and can be as small as 0.034 μm for 621 km distance from the volcano [5]. Based on the chemical composition and degree of vesicularity, extrusive volcanic eruptions can form four different types of volcanic ashes named as: felsic, intermediate, mafic and ultramafic. Felsic rocks are acidic and result from explosive eruptions while mafic are basaltic and are result of non-explosive eruption [6,30].

1.2.2. Reactivity of natural pozzolans

The capacity of aluminosilicate material to dissolve in alkaline medium defines its reactivity [31]. The latter depends on fineness / specific surface area of particles, chemical and mineralogical composition of materials [32,33]. Table 1 presents the chemical composition of various natural pozzolans used by researchers for

Table 1
Chemical composition of various volcanic ashes.

Source	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	TiO ₂	MnO	P ₂ O ₅	LOI	Total
Mt. Shinmoe, Southern, Japan [38]	54.9	16.4	8.8	10.9	1.7	2.8	3.3	0.8	0.2			99.9
South East, Iran [39–40]	61.7	15.9	8.0	4.3	2.1	3.2	2.0	0.4			1.9	97.7
North West, Iran [39–40]	70.1	11.1	2.5	1.3	2.3	1.0	0.9	0.1			10.3	89.4
North West, Iran [41]	64.7	11.9	6.8	3.0	4.3	2.3	1.1	0.5			5.2	94.5
South East, Iran [41]	68.5	11.8	2.9	3.7	3.2	1.6	1.4	0.4			6.1	93.6
South East, Iran [41]	68.3	12.6	3.9	2.7	3.3	2.4	1.4	0.3			4.4	94.8
Chihuahua, Mexico [11]	59.5	9.4	8.0	2.3							14.3	79.3
Foumbot West Region, Cameroon* [42]	44.2	14.1	10.4	13.2	1.5	3.7	9.7	2.7	0.2	0.6	−0.6	100.3
Foumbot West Region, Cameroon [43]	43.4	15.3	11.1	12.5	1.7	4.5	6.8	2.9	0.2	0.9		99.3
Djoungo, Littoral Region, Cameroon [44]	46.3	15.4	9.1	13.3	–	3.9	6.7	2.8	0.2	0.6	−0.4	98.4
Djoungo, Littoral Region, Cameroon [45]	44.0	15.3	9.3	12.8	1.4	5.6	7.0	2.9	0.2	0.5	1.1	98.9
Loum, Littoral Region, Cameroon [32]	47.7	15.4	8.3	12.9	1.1	3.6	6.5	2.8	0.2	0.5	0.7	98.9
Galim, West Region, Cameroon [45–48]	41.4	15.4	7.9	12.9	1.0	2.2	6.5	3.0	0.2	0.5	9.3	90.9
Jordan cement factories Lafarge, Jordan [49]	40.2	13.9	9.7	15.2	1.5	3.7	9.6				4.8	93.7
Bayburt Stone waste, Turkey [50]	68.9	12.0	3.9	0.3	2.4	0.2	1.3				10.1	89.2
Rhine Land, Germany [51]	58.6	17.7	4.7	6.2	5.1	3.4	2.4					98.0
Yellow Tuff, Italy [2]	54.7	17.7	3.7	3.8	6.4	3.4	0.9				9.1	99.7
Bacoli, Italy [2]	53.1	17.9	9.0	4.3	7.6	3.1	1.2	0.3			3.0	99.5
Barile, Italy [2]	44.1	19.2	9.0	4.3	7.6	3.1	1.2	0.3			3.0	91.8
Coastal Region, Ecuador [52]	68.2	11.5	3.7	4.1			1.0					88.5
Coastal Region, Ecuador [52]	66.0	11.0	4.7	3.9			1.5					87.1

* The negative value of loss on ignition presents that there was a gain in mass after heating the sample till 1000 °C which could be possibly because of the oxidization [44].

Table 2
Mineralogical composition of volcanic ashes [25,32–33,35–37,41–48,50–51,53–64].

Group	Common Minerals	Probability of Occurrence
Feldspar Group	Alkali feldspar including Albite ((Na,Ca)[(Si,Al) ₄ O ₈]) (now as Plagioclase classified), Anorthoclase ((Na,K)[AlSi ₃ O ₈]), Sanidine ((K,Na)[(Si,Al) ₄ O ₈]), Microcline (K[AlSi ₃ O ₈]) Plagioclase feldspars including Anorthite ((Ca,Na)[(Si,Al) ₄ O ₈]), Oligoclase ((Na,Ca)[(Si,Al) ₄ O ₈])	High Average
Olivine Group	Forsterite (Mg ₂ [SiO ₄]) Fayalite (Fe ₂ [SiO ₄])	Average Low
Foids	Nepheline ((Na,K)[AlSi ₃ O ₄]) Leucite (K[AlSi ₂ O ₆])	Average Low
Pyroxene Group	Augite (Ca,Fe)(Mg,Fe)[Si ₂ O ₆], Diopside (CaMg[Si ₂ O ₆])	Low
Mica Group	Muscovite (KAl ₂ [(OH) ₂ AlSi ₃ O ₁₀]), Biotite (K(Mg,Fe ²⁺) ₃ [(OH,F) ₂](Si,Al) ₄ O ₁₀)	Low
Oxide minerals	Quartz (SiO ₂), Hematite (Fe ₂ O ₃), Anatase (TiO ₂) Maghemite (γ-Fe ₂ O ₃)	Average Low
<i>Minerals formed by alteration</i>		
Zeolite Group	Heulandite ((Ca,Na,K) ₉ [(Si,Al) ₃₆ O ₇₂]-26H ₂ O), Analcime (Na[AlSi ₂ O ₆]-H ₂ O), Phillipsite ((K,Na,Ca) ₄ [(Si,Al) ₁₆ O ₃₂]-12H ₂ O), Chabazite ((Ca,Na) ₄ [(Si,Al) ₁₂ O ₂₄]-13H ₂ O), Mordenite ((Na,Ca,K) ₆ [AlSi ₅ O ₁₂] ₈ -28H ₂ O)	Low
Sulphates	Anhydrite (CaSO ₄)	Low
Carbonates	Calcite (CaCO ₃), Manganocalcite (MnCO ₃)	Low
Amphibole Group	Ferrohornblende (Na _{0.5} Ca ₂ (Fe ²⁺ ,Mg) ₄ (Al,Fe ³⁺ ,Fe ²⁺)[(OH)(Si,Al) ₄ O ₁₁] ₂), Magnesianhornblende (Na _{0.5} Ca ₂ (Mg,Fe ²⁺) ₄ (Al,Fe ³⁺ ,Fe ²⁺)[(OH)(Si,Al) ₄ O ₁₁] ₂)	Low
Clay Minerals	Montmorillonite ((Al _{1.67} Mg _{0.33})(OH) ₂ Si ₄ O ₁₀]-Na _{0.33} (H ₂ O) ₄), Illite ((K,H ₃ O)Al ₂ [(H ₂ O,OH) ₂](Si,Al) ₄ O ₁₀)	Low
Chlorite Group	Chlorite ((Mg,Fe ²⁺ ,Al) ₃ [(OH) ₂ AlSi ₃ O ₁₀]-Mg,Fe ²⁺ ,Al) ₃ (OH) ₆)	Low

geopolymer synthesis. This indicates the presence of a fair amount of silica and alumina indicating the suitability of these raw materials for geopolymer synthesis. Higher amount of loss on ignition in some of the materials indicate the presence of dissolved gasses such as CO₂ and water in glassy form, showing the presence of carbonates and clay minerals respectively [6]. The difference in the chemical composition observed in that table depends upon factors like composition of magma, temperature and humidity conditions, nature of eruption, crystal content and dissolved gasses of erupting magma [4,34]. Mineralogical compositions of various volcanic ashes determined by X-ray diffraction (XRD) analysis in various studies are presented in Table 2. Weathering of volcanic glass with time due to climatic condition can produce minerals as mica and clay [6]. It must recall that it is not easy to distinguish between highly and lowly reactive natural pozzolan based only on the chemical and mineralogical composition of the whole sample. This is because only the chemical composition of the glassy phase can determine the degree of reactivity of natural pozzolan. The determination of the reactivity of natural pozzolan has been performed by using the chemical method [35–37]. This involves the dissolution of natural pozzolan in concentrated NaOH or KOH solution at different temperatures and the analysis of the leachate by ICP-OES. The tests showed that roughly, natural pozzolan has a lower reactivity compared to other aluminosilicates, and the glassy phase is mainly constituted of Si, Al, Fe, Ca and Mg with Si as the major component [35–37]. Finally, a total amount of at least 20 wt-% reactive phases are require in natural pozzolan to be suitable for geopolymer synthesis [37].

2. Characteristics of geopolymer pastes

2.1. Calorimetry

Various calorimetry techniques were used to assess the reactivity and geopolymerization of natural pozzolan by measuring heat released during reaction. The two techniques used were Differential Scanning Calorimetry (Isothermal and non-Isothermal DSC) which measures the heat released when temperature rises and Isothermal Conduction Calorimetry (ICC) which measures the heat

flow at a constant temperature. The non-Isothermal DSC of four volcanic ashes carried out by Lemouagna et al. highlight that when temperature rises the maximum heats released were reached between 131 and 166 °C; whereas, the Isothermal DSC at 90 °C showed that the maximum heats released were very low compared to the one of metakaolin for example [56]. The authors thus, concluded that volcanic ash is less reactive than calcined clay. This was later on confirmed by the investigation of Djobo et al. who studied the heat released during geopolymerization of Cameroonian volcanic ash at 27 °C by ICC [35]. The latter stressed that the calorimetric curve of geopolymerization of volcanic ash is characterized by a single exothermic peak whose maximum is reached in less than 1 h. This peak which is associated with sorption of alkaline activator solution on the surface of ash particles and dissolution of the ash particles. This demonstrates that the maximum dissolution rate and the maximum amount of dissolved species is achieved within 1 h. Fig. 1 shows the ICC curve depicting the stages of geopolymerization reaction and the effect of fineness on the rate of heat evolution. The fast retardation after the first peak attributes to the wetting process and later stage dissolution and polymerization reaction continues in apparently thermally steady state with lower rate of heat evolution [65].

According to a research study of Kani et al., during geopolymerization of natural pozzolan the reaction time (time at which no further heat is released, and the rate of heat evolution fell to zero) ranges from 21 to 29 h, and the apparent activation energy varies between 49.6 and 64.8 kJ/mol. These data allowed to understand that depending on the temperature at which the reaction takes place and the synthesis conditions, the geopolymerization of natural pozzolan ends within 21–29 h [65]. It is worth pointing out that the activation energy translates the minimum energy that should be applied to the system to undergo a chemical reaction. So, the higher activation energy observed means that higher temperature is required for the geopolymerization and indicates the low reactivity of natural pozzolan compared to fly ash or metakaolin.

2.2. Setting time

Setting time of geopolymer mixtures depends upon the specific surface area and content of free CaO available in the mixture. The

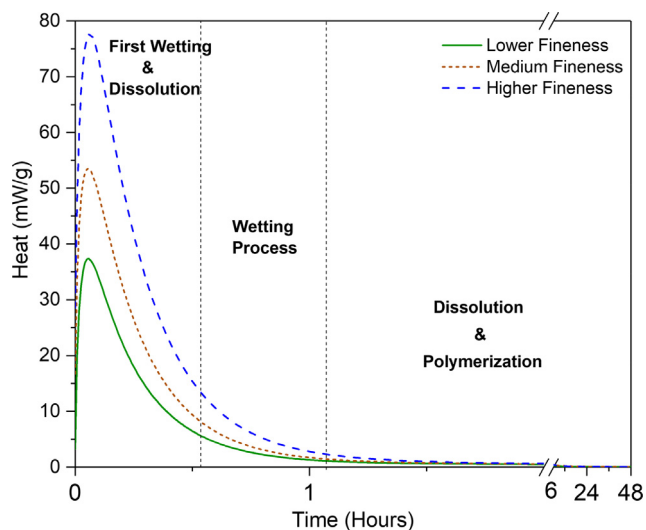


Fig. 1. Heat evolution on different stages of geopolymerization reaction and effect of fineness on heat evolution [32,65].

lower the specific surface area and lower the content of free CaO in the source material leads to higher setting time of geopolymer mixtures. Setting time of geopolymer mixtures can also be controlled with the amount and modulus of the activator sodium silicate; the higher the $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio the lower is the setting time [37]. Tchakoute et al. studied the compressive strength and setting time of two Cameroonian volcanic ashes originating from Djoungo and Galim named as Z_D and Z_G respectively [37]. Alkaline activating solutions with $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 0.7, 0.9, 1.1, 1.3 and 1.4 were prepared with NaOH (12 M) and Na_2SiO_3 (28.7 % SiO_2 , 8.9 % Na_2O). Liquid to solid mass ratio for Z_G was kept constant at 0.49 and for Z_D at 0.37. Low specific surface area ($2.3 \text{ m}^2/\text{g}$) and low free CaO (3.23 wt.-%) content of Z_D resulted in a setting time longer than 14 days and low compressive strength. Whereas, for Z_G (specific surface area of $15.7 \text{ m}^2/\text{g}$ and free CaO of 5.11 wt.-%) based geopolymers it was shown that the setting time was reduced with the increase of $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, from 490 min to 180 min, hence higher compressive strength was achieved, as shown in Fig. 2 [37,66,67]. Similar trend was also observed for volcanic ash based geopolymer partially replaced with metakaolin. With increase of $\text{SiO}_2/\text{Na}_2\text{O}$ content in alkaline solution and increased content of metakaolin in the mixture, the initial setting time decreased from 500 min to 160 min for Z_D -metakaolin mixtures,

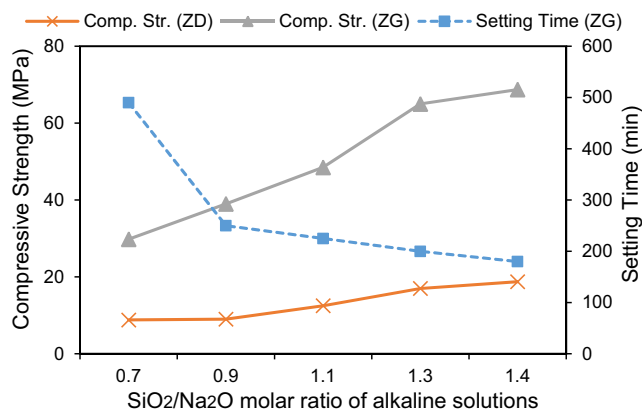


Fig. 2. Effect of $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of alkaline solution on setting time and 28 day compressive strength of Z_D and Z_G based geopolymer; after Tchakoute et al. [37].

while for Z_G -metakaolin geopolymer initial setting time decreased from 220 min to 125 min [45].

Tchakoute et al. studied the setting time of fused soda-volcanic ash based geopolymer. Fused soda-volcanic ash with varying overall $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ molar ratio was prepared by calcination of mixture at 550°C for 1 h [53]. Results of setting time indicated that with decrease of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ from 0.29 till 0.13, setting time decreased by 40 % (from 25 to 15 min), while with further decrease of $\text{Al}_2\text{O}_3/\text{Na}_2\text{O}$ from 0.10 till 0.06 the setting time increased from 16 min to 20 min. The authors reported that these results were found to be in correlation with amount of amorphous phase calculated for each sample and compressive strength, furthermore, it was reported that excess of fused soda hindered the geopolymer synthesis process [48,68].

Influence of the particle size of volcanic ashes on the setting time of geopolymer paste was studied for volcanic ash samples milled for 30, 60, 90 and 120 min and it was reported that with increase of milling duration the initial setting time of geopolymer paste samples firstly decreased from 600< minutes for 30 min milling time to 150 min for 60 min milling time. With further increase of milling time to 90 min the initial setting time decreased to 15 min. However, with further increase of milling time to 120 min the setting time increased slightly to 22 min. The increase of milling time increases the fineness of particles and thus the dissolution rate increases. However, with excessive milling causes agglomeration of particles and recrystallization or polycondensation of glassy phase forms quartz, thus reducing the reactivity of pozzolan sample [32].

3. Physical and mechanical properties

3.1. Water absorption, bulk density and apparent porosity

Water absorption, bulk density and apparent porosity are the primary physical characteristics of the geopolymers. Many influencing factors for these three parameters were investigated. Effect of particle size, $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio, curing temperature and age of sample on water absorption, bulk density and apparent porosity have been studied.

Djubo et al. varied the milling time for Cameroonian volcanic ash samples between 30 and 120 min and reported that in most cases minimum bulk density and maximum water absorption and apparent porosity for the paste sample prepared with volcanic ash milled for 90 min was found at 28 days of age. No direct relationship between particle size and physical properties was examined. However, it was seen that with increasing curing temperature (27°C , 45°C and 60°C) water absorption increased from 8.7 % to 11.4 %, apparent porosity increased from 17.5 % to 19.8 %, while bulk density decreased from $2105.6 \text{ kg}/\text{m}^3$ to $1798.5 \text{ kg}/\text{m}^3$ for Cameroonian volcanic ash based samples at 28 days of age [32]. However, the relation is not consistent with the results presented in [44], where with increase of curing temperature from 27°C to 80°C , decrease in water absorption and apparent porosity and increase in bulk density has been observed at 28 days of age. This apparent discrepancy could be due to different examined temperatures and different nature of tested samples. In later study, the temperature between 27°C and 80°C has not been studied. It can be assumed that with increase of curing temperature, initially water absorption and apparent porosity increases while bulk density decreases. However, with further increase of curing temperature the trend becomes opposite. It should also be noted that in [32] authors used paste samples while in [44] mortar samples were used. Nevertheless, detailed investigation is necessary to fill the gap of knowledge for paste and mortar samples.

Influence of curing period was examined between 7 days and 180 days for mortar samples [44]. With increase of curing period from 7 days to 28 days, a gain in water absorption and apparent porosity was found. However, from 28 to 180 days the values of these two properties changed slightly. However, reverse trend for bulk density had been recorded. With increasing age of sample, bulk density decreased for samples cured at 27 °C, while no uniform trend has been seen for samples cured at 80 °C [44]. No clear influence of water to binder ratio on water absorption of geopolymer samples has been observed [58].

Silica modulus of activator solution has been found to effect the physical properties of geopolymer paste samples. Lemougna et al. studied the effect of $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio on the water absorption and bulk density of geopolymer paste samples. It has been reported that with increase or decrease of $\text{Na}_2\text{O}/\text{SiO}_2$ beyond optimum, the water absorption increases, while bulk density doesn't change appreciably with change of $\text{Na}_2\text{O}/\text{SiO}_2$ ratio. For optimum $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratio of 0.25, minimum water absorption of 14.08 % and maximum bulk density of 1910 kg/m^3 was recorded [42].

Inclusion of aluminium and calcium by partial replacement of volcanic ash by bauxite or calcined oyster shell (both 0 to 30 %) respectively, led to a progressive increase of apparent porosity of the paste [47].

3.2. Compressive strength and indirect tensile strength

Factors affecting the degree of geopolymerization are particle size, type and concentration of alkali activator, pre-treatment of raw material and curing conditions [32,36,69]. Primary findings from different authors using volcanic ashes for geopolymerization are summarized in Table 3. It is seen that raw volcanic ash without any pre-treatment have poor reactivity due to low dissolution of volcanic ash in alkaline medium, therefore, pre-treatment of volcanic ashes like calcination, alkali fusion, mechanical activation and partial replacement with secondary cementitious materials is suggested [32,40,41,45,47,48,52–54,70]. Sodium hydroxide,

sodium silicate, potassium hydroxide and potassium silicate are the majorly used alkali activator solutions [41].

Higher concentration of the activator improves the dissolution of the aluminosilicate and therefore, improves the mechanical properties. However, depending upon the type of activator, curing conditions and mineral type after reaching a certain content of alkali no significant increase in strength can be observed as shown in Fig. 3 [36,38].

The optimum concentration of alkalis should be determined from properties and economic point of view. Bondar et al. studied the effect of using various concentration of NaOH and KOH for Tuffan pozzolan based geopolymer paste samples and found out that longer time or higher temperature is required for the sample with higher concentration of alkaline solution beyond 7.5 M concentration and unfavourable properties such as efflorescence and brittleness can enhance due to increased free alkali content in the binding system [36,71].

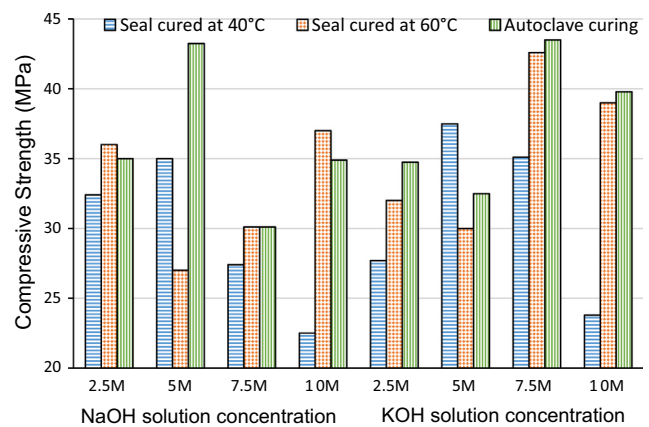


Fig. 3. Effect of type and concentration of activator on geopolymer compressive strength seal and cured at 40 °C, seal and cured at 60 °C and autoclave cured at 2 MPa pressure & 150 °C for 3 h; after Bondar et al. [36].

Table 3
Summary of primary findings and synthesis parameters studied on natural pozzolan based geopolymer.

Author	Raw material & Activation	Alkaline Solution Used	Curing Condition	Compressive Strength
Djobo et al. [32]	Mechanical activation of volcanic ash in ball mill	$\text{Na}_2\text{SiO}_3/\text{NaOH} = 2.4$, $\text{SiO}_2/\text{Na}_2\text{O} = 1.4$, Liquid/ash (mass) = 0.4	27, 45 and 60 °C for 24 h afterwards cured at room temperature in a plastic bag	0–37.4 MPa at 28 days 6.6–53.6 MPa at 90 days
Tchakoute et al. [37]	Volcanic ash of particle size 80 μm	$\text{SiO}_2/\text{Na}_2\text{O} = 0.7, 0.9, 1.1, 1.3$ and 1.4 liquid/solid = 0.49, 0.37, Na_2SiO_3 and NaOH	24 \pm 3 °C	23–50 MPa at
Tekin [50]	Marble, travertine and volcanic ash waste crushed and grinded	NaOH 1, 5 and 10 M	22 \pm 2 °C & 40 \pm 5% R.H. 45 °C for 24 h after demoulding 75 °C for 24 h	46 MPa at 90 days
Bondar et al. [41]	Heat treated dacite and andesite ashes at 700 and 800 °C and ground to <75 μm	NaOH, KOH, Na_2SiO_3	20, 40, 60, and 80 °C	0–81 MPa at 28 days
Takedan et al. [38]	Volcanic ash with particle size <200 μm	8.5–16.5 M NaOH, Na_2SiO_3	50 °C and 80% relative humidity for 72 h.	80.1 MPa at 3 days
Villa et al. [11]	Homogenized zeolite sample	$\text{Na}_2\text{SiO}_3/\text{NaOH} = 0.4, 1.5, 5, 10$ and 15 ratios using 7 M NaOH, activator/ligand = 0.6	40, 60, and 80 °C	8–35 MPa at 90 days
Lemougna et al. [42]	Volcanic ash ground and sieved through a 400 μm mesh	Volcanic ash mixed with NaOH with $\text{Na}_2\text{O}/\text{SiO}_2 = 0.15\text{--}0.35$, water/ash = 0.21	Seal cured at 40 °C for 24 h, then unsealed cured at 40 °C for 24 h. Afterwards, samples were cured for 5 days in water and open air at 40, 70 and 90 °C	55 MPa at 7 days
Haddad & Alshbuol [49]	Basaltic Tuff of fineness in excess of 700 m^2/kg	Na_2SiO_3 , NaOH (10, 12, 14 M)	40, 80 and 120 °C	30 MPa at 28 days
Vogt et al. [51]	Volcanic tuff of Blaine fineness = 6000 cm^2/g	Na_2SiO_3 and 50% NaOH.	80 °C	22.7 MPa at 7 days

The modulus of sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}$) is an important parameter influencing the properties. Keeping the alkali content constant, the higher modulus of water glass promotes development of higher strength within a specific range due to greater contribution of silica. In other way, if the solid sodium silicate content is kept constant in a mixture then the effect of alkali activation is higher than silica. Therefore, it is necessary that an optimum modulus of sodium silicate is selected depending upon the raw material and curing condition. In general, a higher modulus is preferred; a lower modulus should be used only if the alkali activation is insufficient [36,51].

Curing conditions have been found to affect the geopolymerization as well. Higher curing temperature improves the mechanical properties by increasing the rate of dissolution at early ages but does not have much effect on final strength [11,32,72]. However, higher temperature curing also causes fast evaporation of water and propagation of shrinkage cracks, therefore, extended curing should be avoided [38,49,50]. Wet curing causes efflorescence in the samples [50].

The addition of reactive Al_2O_3 helps to improve the mechanical properties of the material by increasing the geopolymeric phase of the material which imprisons the unreacted/partially reacted crystalline phase of the starting material and thereafter, helping to reduce the efflorescence [54,73,74].

At early ages, alkali activated natural pozzolan concrete have lower static modulus of elasticity (SME) compared to OPC concrete. However, long term results indicated 5–20% higher SME for alkali activated natural pozzolan concrete than OPC concrete. SME for geopolymers is also affected by the curing temperature; higher curing temperature at early ages improves SME to a limit depending upon water to binder ratio. The higher curing temperature can cause evaporation of water, therefore, causing loss of strength due to incomplete geopolymerization and hence, lower SME [59]. SME has been found to increase with increased concentration of alkaline activator and the results have been found to be comparable to results of compressive strength [75]. For natural pozzolan based geopolymer mortar synthesised with varying concentration of NaOH, modulus of rupture of have been recorded between 0.732 MPa and 8.490 MPa, ultimate strain between 200 μe and 795 μe and modulus of elasticity between 3481 MPa and 21554 MPa [75].

Indirect tensile strength of geopolymer specimens have been found directly proportional to their compressive strength [59]. In comparison to ordinary Portland cement (OPC) concrete specimens, natural pozzolan based geopolymer concrete exhibit higher indirect tensile strength at later ages. At 7 days, the indirect tensile strength of natural pozzolan based geopolymer was 16.25% less in comparison to 7 days old OPC samples, while at 28 days it increased by 33.7% in comparison to OPC sample of same age [59]. The indirect tensile strength of natural pozzolan based geopolymer is greatly influenced by the curing temperature, as the tensile strength majorly depends on the bond between aggregate and gel. The higher temperature curing improves the strength of geopolymeric gel itself while it may not necessarily increase the interface between aggregate and gel, as at higher temperature and in sealed curing condition, water cannot reabsorb to enhance the matrix bonding properties particularly at the interface of matrix and aggregate [59].

4. Microstructural characteristics of hardened products

4.1. X-ray diffractometry (XRD)

Roughly after geopolymerization or alkaline activation reaction there is the possibility of formation of new crystalline phases and the disappearance of some minerals initially present in the alumi-

nosilicate. It is worth recalling that during geopolymerization or alkaline activation reaction the amorphous phase reacts preferentially to the crystalline phase. The mineralogical changes observed depend upon the type and composition of the alkaline solution, the type and content of calcium source in the mix design. One of the main change is the shift of the 2 θ range characteristic of the glassy phase of natural pozzolan. In the case of natural pozzolan based geopolymer, which are obtained with high silica modulus (molar ratio $\text{SiO}_2/\text{Na}_2\text{O} > 1.4$) the changes observed are generally the decrease of peaks intensity and often the disappearance of minerals. For example, it was reported that nepheline and clay mineral-like muscovite, initially present in volcanic ash had taken part to the geopolymerization, while, for the other minerals only the peak intensity was affected [45]. The formation of new crystalline phases (generally hydrated minerals) occurs in the alkali-activated natural pozzolan system which are obtained with alkaline solution containing very low silica modulus (molar ratio $\text{SiO}_2/\text{Na}_2\text{O} < 1.4$) or by using only highly concentrated NaOH and KOH solution. The new crystalline phases formed include zeolite minerals type (hydroxysodalite, sodalite, sodium hydrogen silicate hydrate, potassium aluminium silicate hydrate, sodium aluminosilicate hydrate, sodium calcium aluminium silicate hydrate) and carbonate mineral like natrite (Na_2CO_3) [36,46,48,49,53,57,63]. The new minerals were reported to be formed due to the reaction between the glassy phase and the alkali from the alkaline solution [46]. Moreover, in the system with additional calcium source calcium based hydrated minerals such as calcium silicate hydrate ($\text{CaSiO}_4\text{H}_2\text{O}$) can also be formed [46].

4.2. Fourier transform infrared (FTIR) spectroscopy

Table 4 summarizes the infrared bands assigned to various wavenumbers for natural pozzolan based geopolymers. During alkali activation, every bridging oxygen atom (BO) on the surface of the original aluminosilicate is replaced by two negatively charged non-bridging oxygen atoms (NBO), which are charge compensated by alkalis. As a result, the infrared (IR) band attributable to the T-O-Si asymmetric stretching vibration of the TO_4 tetrahedral of an aluminosilicate in glass has been found to shift to lower energy with increasing alkali content [36,51,76].

4.3. Mössbauer spectroscopy

The chemical composition of natural pozzolan showed it is constituted of up to 16 wt-% of iron oxide, and it was reported that iron takes part to the reaction [42,79]. In order to understand the behaviour of iron during alkaline activation of natural pozzolan ^{57}Fe Mössbauer spectroscopy of natural pozzolan has been studied by Lemougna et al. [43] the findings of that work involved the followings:

- The reactivity of iron depends on the form in which it is available in the material.
- Iron exists in its two-ionic form Fe^{2+} and Fe^{3+} it is contained in ferroan forsterite and augite mineral in both octahedral and tetrahedral geometry.
- After geopolymerization there is the conversion of some octahedral Fe^{2+} into tetrahedral Fe^{3+} suggesting their participation in the reaction.
- Finally, iron plays role of network forming and is beneficial for the development of strength.

4.4. ^{27}Al and ^{29}Si nuclear magnetic resonance (NMR)

This test has been used to address the structural changes that happen during geopolymerization of volcanic ash with varying silica modulus and curing temperature. The test results showed that

Table 4
Infrared (IR) bands attributed to natural pozzolan based geopolymers [35,37,45,47,54,56–57,62,64,76–78].

Assignments	Wave number (cm ⁻¹)		Comments
	Natural pozzolan	Natural pozzolan based geopolymer	
O–H Stretching	2917–2856, 3420	2360, 3410–3455	Strong band of surface adsorbed and chemical bound water
O–H Bending	1540, 1645–1667	1540, 1645–1667	Strong band of surface adsorbed and chemically bound water
O–C–O stretching	Absent	1407–1484	Strong band due to carbonation of free Na + into Na ₂ CO ₃
Si–O–Si, Si–O–Al asymmetric stretching	1093–1000	968–1035 879–1027	Strong band. Bridging oxygen atom (BO) of the original aluminosilicate framework. After reaction the band shift to lower value indicating non-bridging oxygen atoms have replaced bridging oxygen atoms on the surface of aluminosilicate and is charge compensated by alkalis
Symmetric stretching Si–O–Si	798	798	Medium band
stretching Si–OH	Absent	882	Strong band appears in lesser polymerized product
Si–OH Bending	Absent	840–842	Strong band appears in lesser polymerized product
Stretching Al 6-coordinated geometry (Al _(VI) –OH & Al _(VI) –O)	736–916	Absent	Should disappear after polymerization
Si–O symmetric stretching	Absent	620–715	Should appear as shoulder only in polymerized product
Si–O–Si, Al–O–Si symmetric stretching	Absent	480–600	Should appear only in polymerized product

in ²⁷Al NMR spectra the characteristic peak (16 ppm) describing the Al in 6-fold coordination disappears after geopolymerization, indicating transformation to 4-fold coordination of Al atoms [35]. The main peak centred at 62 ppm in volcanic ash characteristic of Al in 4-fold coordination shifts to higher frequency after reaction indicating Al substituting Si atom in tetrahedral sites with 3 bridging oxygen [35,80]. For higher curing temperatures partial crystallization of amorphous phases is indicated by the increase of the peak widths [35].

²⁹Si have been found to provide better insight of the structural variation in the geopolymer matrix by change of silica modulus and curing temperature. The characteristic peak of Si in tetrahedral environment lies between –60 and –120 ppm frequency. The broad peaks indicate the Si(IV) in different environments [35,81]. The variation of silica modulus in geopolymer products shifts the main peak of Q⁴ from –89 to –86 ppm after reaction, which occurs because of de-shielding due to decrease of mean electronic cloud around SiO₄ tetrahedra, increase of the mean Si–O bond length and decrease of mean Si–O–T (T = Si or Al) bond angle [35,82].

4.5. Thermogravimetric analysis (TGA)

Mass loss during thermogravimetric analysis can be used to measure the extent of geopolymerization. Higher overall mass loss relates to higher extent of geopolymerization [51]. The TGA curve can be divided into three stages as shown in Fig. 4. The first stage corresponds to evaporation of physically adsorbed water in the geopolymer matrix and appears before 100–150 °C [35]. The second stage starting from 150 °C till 600 °C corresponds to chemically bound water, which comes from dissolution of aluminosilicate raw materials to form aluminate and silicate species. So, this stage gives useful information about the extent of geopolymerization reaction [35,61,83]. However, TGA is not representative of chemical and nano-structural evolution taking place during reaction as it considers only the final reaction product [35,84]. This is the case of a recent study where authors observed and increase of the extent of reaction by isothermal calorimetry with decreasing silica modulus, but the TGA result showed different behaviour as the recorded mass losses between 150 and 600 °C were 2.14, 2.91 and 2.67% respectively for silica modulus of 1.66, 1.50 and 1.40 [35]. Therefore, it should be used carefully and preferably in combination with other analytical tests (FTIR, Calorimetry etc.) to give final conclusion. The total mass losses and temperature range of stage I and II depend on the synthesis conditions and to the reactivity of the initial ash. The values

recorded so far vary between 3.5 and 14 wt-% [35,46,56,57]. The third stage represents the mass loss due to decomposition of carbonates, whose effect decreases with yield of the reaction [46,51,61,83]. The latter stage is generally observed in the alkali activated system with high amount of calcium and sodium oxide (Na₂O) content. It should be noted that in the alkali activated system the temperature range of the stage I and II overlaps due to the incorporation of calcium in the binder composition [85]. The latter being the mixture of N–A–S–H, K–A–S–H, C–A–S–H, N–(C)–A–S–H and/or C–S–H whose decomposition take place at very low temperature (below 250 °C) [42,46,57,86,87].

4.6. Scanning electron microscopy & energy dispersive X-ray spectroscopy (SEM/EDX)

The morphology and the composition of the resulting geopolymer matrix depends on the chemical composition of natural pozzolan, curing temperature and type of alkali activating solution and its SiO₂/Na₂O molar ratio. The different features generally observed in the micro-structure includes unreacted particles and reacted phases. The latter may be constituted of geopolymer phase, hydrated gel and new crystalline phases. The geopolymer phase is based on mixture of poly (ferro-sialate-siloxo), poly (ferro-sialate-disiloxo) and poly (ferro-sialate-multisiloxo) binder types with Ca²⁺, Mg²⁺, and Na⁺ as charge-balancing cations [32,35]. The

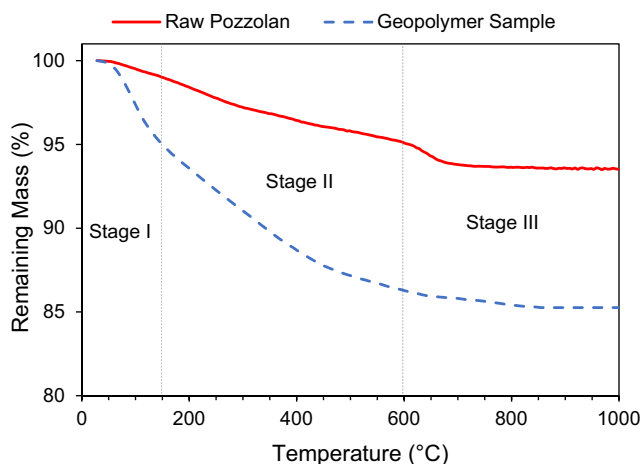


Fig. 4. Thermogravimetric curve representing 3 stages of mass loss [35,51].

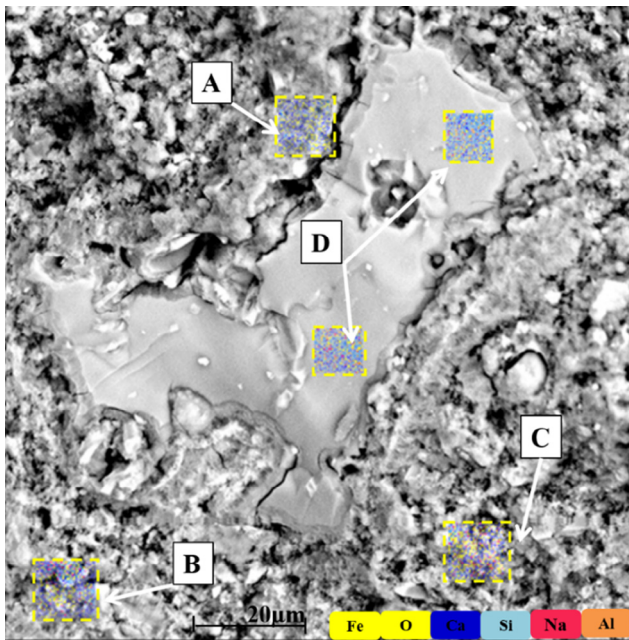


Fig. 5. High magnification combined SEM-EDS map of alkali-activated oyster shell-volcanic ash showing various phases: A) C–S–H gel; B) and C) various type of (N, C)–A–S–H gel; D) unreacted volcanic ash. adapted from [46]

hydrated phase is constituted of sodium or potassium aluminosilicate gel (N–A–S–H, K–A–S–H). Because of the presence of CaO in natural pozzolan and sometime when additional calcium source is added various types of hydrated phases sodium calcium aluminosilicate hydrate (N, C–A–S–H), calcium aluminosilicate hydrate (C–A–S–H) and calcium silicate hydrate (C–S–H) are formed. Higher curing temperatures result in micro-crystalline gel structure due to formation of zeolites while lower curing temperature results in more homogeneous gel [40]. Scanning electron microscope (SEM) images coupled with EDX results show distinguishable reacted phases and unreacted particles, as depicted in Fig. 5 [33,46]. With the increase in concentration of NaOH solution the gel structure becomes more dense with lesser amount of unreacted particles [46]. The undissolved particles in geopolymer matrix can cause formation of cracks, however, addition of optimum amount of Al_2O_3 helps to reduce the micro crack in geopolymer matrix [54]. Nevertheless, amount of Al_2O_3 beyond optimum exhibited much non-homogenous microstructure with cracks, this could be because of formation of octahedral Al at very high Al content which cannot incorporate into gel network [54].

5. Durability characteristics

Considering geopolymer binders as an alternative to OPC concrete, the durability characteristics of natural pozzolan based geopolymers should be studied in order to achieve dense, crack free micro-structure, low capillary porosity and fine pore structure [88]. As geopolymers are considered as environmental friendly binding materials, therefore, the durability characteristics of natural pozzolan based geopolymers are important to be studied.

5.1. Sulphate resistance

Bondar et al. studied the sulphate resistance of alkali activate natural pozzolan in 2.5% Na_2SO_4 and 2.5% MgSO_4 solution. Maximum loss of compressive strength recorded was 19.5% after 2 years of immersion in sulphate in solution. Maximum expansion

of 0.074% was recorded after 6 months of immersion. X-ray diffraction analysis of the samples immersed in sulphate solution was conducted by extruding the sample from surface and middle of the sample. Results indicate that mainly sodium aluminium sulphate ($\text{Na}_3\text{Al}(\text{SO}_4)_3$), langbeinite ($\text{K}_2\text{Mg}_2(\text{SO}_4)_3$), palygorskite ($(\text{MgAl})_5(\text{SiAl})_8\text{O}_{20}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$), leonite ($\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and picomerite ($\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) minerals were formed because of the reaction with sulphate present in solution [58].

5.2. Acid resistance

Acid resistance of geopolymers have found to be closely related to the porosity of specimens, pore size diameter, connectivity of pores and presence of Na-rich gel in geopolymer gel structure [44]. It must note that the literature about this subject is very few. Till now there is only two published papers dealing with acid resistance of volcanic ash based geopolymers. This show the lack of information and the necessity for scientists to focus on this topic. The effects of adding calcium rich material (calcined oyster shell) and Al-rich material (bauxite) on 3% sulphuric acid resistance of volcanic ash based geopolymers were studied [47]. The authors reported a decrease from –2.32 to –1.91% of mass loss with the bauxite content up to 30 wt-%, and from –2.32 to –1.72 with only 10 wt-% of calcined oyster shell added. This trend was due to the beneficial effect brought by these minerals additive on the extent of geopolymerization. Djobo et al. studied the influence of curing temperature on acid resistance of volcanic ash based geopolymers for 180 days in 5 wt-% H_2SO_4 solution [44]. For first 90 days, for samples cured at 27 °C and 80 °C the monthly mean rate of strength loss was recorded as 0 and 3.5% respectively, thereafter, the monthly mean rate of strength loss increased appreciably to 8 and 6% respectively. Maximum loss of strength for samples cured at 27 °C and 80 °C after 180 days of immersion in acidic solution was found to be 24% and 60% respectively, while ordinary Portland cement completely destroys under these conditions [44,89,90]. This result demonstrated that heat curing has detrimental effect on acid resistance of volcanic ash based geopolymer. Visually there was no surface degradation in samples till 180 days of immersion in acid, but the samples became only lighter in colour. The SEM combined with EDX analysis of samples immersed into sulfuric acid helped to identify gypsum as reaction product between sulphate from acid and calcium from volcanic ash. The formation of gypsum which was much prominent for heat cured samples was indicated as responsible of the higher strength losses compared to the sample cured at room temperature [44].

5.3. Corrosion of steel reinforcement

More alkalis present in geopolymers based on natural pozzolan makes the pH at the steel-concrete interface higher than normal OPC concrete. The pH value is normally higher than 10, which helps to improve the corrosion resistance [75,88]. However, further research is necessary to understand this parameter.

5.4. Permeability

The long term durability of concrete depends mainly on the pore network and their connectivity inside the concrete block. Thus the determination of the permeability has been found to be suitable test to assess the sustainability of concrete against aggressive agents (carbon dioxide, chloride etc.). It should be noticed that regarding geopolymer concrete from natural pozzolan there are only two research papers dealing with its transport properties capacity. The data available involve oxygen permeability and chloride penetration test.

Oxygen permeability of two Iranian natural pozzolan based geopolymers was determined by using 'cembureau permeameter' [88,91]. The results showed that oxygen permeability of natural pozzolan based geopolymers concrete varies with synthesis conditions and it ranges from $1.5 \times 10^{-17} \text{ m}^2$ to $5 \times 10^{-17} \text{ m}^2$ at 90 days. The authors concluded that natural pozzolan based geopolymers concrete exhibited 10–35% lower oxygen permeability compared to OPC concrete at 90 days. In the studied system, the oxygen permeability decreased with the curing temperature and extent of geopolymerization and decreased with the amount of water in the system. For the samples with lower water to binder ratio the rate of reduction of permeability was faster for 7 and 28 days of age and later was slowed down with age of sample. With increasing age of the sample permeability decreased at a higher rate of reduction at early ages. The lower water to binder ratio forms fewer capillary pores thus lower permeability. Permeability of the specimens also decreased with higher curing temperature, as higher curing temperature promotes the geopolymerization with higher dissolution and polymerization rate and water removal resulting in pore space blockage, hence a stronger structure with lower shrinkage is generated [88].

Pore structure and pore solution composition effects the rapid chloride permeability. Increase in temperature with high applied voltage, measurement before reaching steady state migration of current and passage of current by all ions in the pore solution makes the experimental implementation of rapid chloride permeability test (RCPT) difficult for the lower quality concretes as with higher passage of current at assigned voltage more heat is produced [75,88,92]. Therefore, Bondar et al. measured the rapid chloride permeability of natural pozzolan based geopolymer concrete samples according to ASTM C1202, [93], however, to reach the similar conditions as OPC mixtures the applied voltage was reduced to 20 V DC (up to 500 mA and 90 °C) instead of 60 V DC for OPC specimens for 6 h. While, Ghafoori et al. measured the RCPT of natural pozzolan based geopolymer mortar by reducing the voltage to 10 V. It was reported that with reduction of water to binder ratio the chloride permeability decreased for natural pozzolan based geopolymers by approximately 11% to 14% for 0.04% reduction in solution to binder ratio [75,88]. With increasing age of the samples, chloride permeability reduced with a higher rate of reduction at early ages [88]. Samples cured in sealed conditions showed 20% lower chloride permeability in comparison to samples cured in moist conditions [88]. With increasing concentration of alkaline activator the rapid chloride permeability has been found to decrease from 6308 C to 1054 C [75].

Long term chloride penetrability of natural pozzolan based geopolymer concrete was determined in accordance with ASTM C1556 [94], for saturated samples sealed from three sides. The only exposed surface was introduced to 2.8 M (16.25 wt-%) NaCl solution for 90 days. It should be noted that the average salinity of sea water is 3.5 wt-% [88]. The ground concrete samples were collected at every 5 mm depth by using lathe machine equipped with diamond-tipped bit. The total chloride content of the powdered samples was determined according to AASHTO T260 [88,95]. Results indicated that the total integral chloride ion penetrability of geopolymer concrete at 41 mm depth after 90 days is 0.63 to 1.13, which is in range of AASHTO T259 moderate to high (0.8–1.3) chloride ion penetrability [88,96]. The chloride penetrability was found to be lower in samples with lower water to binder ratio and is found to be 20% lower in samples cured at 40 °C with 20% lower water to binder ratio [88].

5.5. Shrinkage properties

Natural pozzolan based geopolymers have significantly lower drying shrinkage in comparison to the OPC concrete with same

water to binder and cement to aggregate ratio [59,97,98]. The drying shrinkage of natural pozzolan based geopolymers depends on curing temperature, humidity and water to binder ratio. In sealed curing conditions, the higher water to binder ratio reduces the drying shrinkage [59]. For natural pozzolan based geopolymer concrete samples sealed cured at ambient temperature, with increase of water to binder ratio from 0.45 to 0.55 the drying shrinkage reduced from 1185×10^{-6} to 514×10^{-6} at 180 days [59]. Higher curing temperature also reduces the drying shrinkage which could be because of removal of water at higher temperature and further cross-linking of hydration product. The lowest amount of drying shrinkage reported was 239×10^{-6} and 161×10^{-6} for natural pozzolan based geopolymer with water to binder ratio of 0.45 and 0.55 respectively, seal cured at 60 °C [59]. Fog cured samples show higher amount of drying shrinkage because of retention of water in geopolymer matrix giving rise to more porous microstructure [59].

Kani and Allahverdi studied the effect of $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of natural pozzolan based geopolymer on the total shrinkage and found out that at constant $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio the total shrinkage at 90 days ranges between 0.29% and 0.83 % for $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio less than 0.6 and with further increase of $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio to 0.6 and beyond total shrinkage increases significantly from 1.52% to 4.81%. The acceptable value of total shrinkage for industrial application is less than 1% [62]. The total shrinkage also increased with increase of $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio, and the changes occurred were more prominent compared to those happened because of varying $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio [62]. For $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio between 3.44 and 7.69 the linear shrinkage has been found to decrease, while with further increase of $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio the linear shrinkage increased which is associated with the gel characteristics of the geopolymer binder as linear shrinkage originates from the capillary tension with the gel framework [48,53]. Shrinkage control measurement was studied by curing the 1 and 7 days pre-cured samples hydrothermally at 85 °C for 20 h, and it was found that for all hydrothermally cured samples total shrinkage increased till 7 days and thereafter, became constant with age of sample. The most suitable results were obtained for hydrothermally cured samples after 1 day procuring, and the total shrinkage ranged between 0.26 and 0.46 % [62].

Thermal shrinkage of volcanic ash based geopolymers have been found to be approximately 2% after two cycles of heating up to 1000 °C and cooling, which is approximately 4 times lesser than metakaolin based geopolymers, indicating the suitability of these binders [42,57]. During first heating cycle, significant shrinkage has been observed for heating temperature up to 110 °C because of evaporation of less tightly bound water, after this for further heating of up to 600 °C, the sample behaves more or less stable [42,57]. During first cooling cycle, the already heated samples shrinks almost linearly at coefficient of thermal expansion of $8 \times 10^{-6} \text{ K}^{-1}$ to $16 \times 10^{-6} \text{ K}^{-1}$. In second heating and cooling cycle, the thermal expansion coefficient has been recorded to be same as that in first cycle [42,57].

5.6. Wetting and drying cycles

Lemougna et al. investigated the compressive strength of alkali activated natural pozzolan in wet and dry condition [42,56,57]. The work showed that after 24 h immersion of samples into water (wet condition) there is a decrease of the compressive strength of up to 89%. But the compressive strength was partially or totally recovered when samples were dried overnight at 90 °C. This was attributed to the partial dissolution of Si–O–Na bond and hydrolysis of some silica bond –Si–O–Si– from hydrated minerals (zeolitic minerals) or silicate gel which are generally soluble into water. These were due to the presence of excess of alkali (Na^+) during the

synthesis. These observations were later confirmed by the work of Djobo et al. where alkali-activated volcanic ash with a calcium source (oyster shell) was tested [46]. The latter investigation reported a decrease of up to 50% of the compressive strength in wet condition for samples aged of 180 days. All these previous works reported only the 24 h immersion into water on strength evolution. Recently a more comprehensive studied on the performance of 28 days aged volcanic ash based geopolymer mortars specimens in 25 wetting and drying cycles was reported. Considering one cycle of drying and wetting as drying specimens at 65 °C for 24 h followed by soaking in water at room temperature for 24 h. Results indicate that samples cured at 27 °C had 24% reduction in compressive strength after 25 cycles while samples cured at 80 °C had 14% reduction in compressive strength, with no visual deterioration up to 25 cycles of wetting and drying [44]. These works showed that volcanic ash based geopolymers mortars performed well in dry and wet condition and are suitable for severe hot and dry climate.

6. Applications

Geopolymer mortar samples lie within the ASTM recommendation of building materials. While heating up to 900 °C geopolymer samples lost 40% of their initial compressive strength and shrank slowly, which indicates the suitability of these materials for low grade refractories and potential building material [35,42]. Geopolymers formed by mixture of volcanic tuff and NaOH (14 M) had an Zn²⁺ uptake efficiency of 97.78% against 78.51% volcanic tuff and uptake capacity of 8.15 and 6.54 mg/g respectively, at pH of 7 dosage of 0.7 g and therefore, have been found feasible for removal of heavy metals [99]. In a more recent study on the natural zeolite based foamed geopolymer concrete, it is recommended that zeolite based geopolymers are suitable for household masonry wall construction according to NTE 638 and NTE 643 Ecuadorian construction technical standards [78].

7. Conclusions

Natural pozzolans can be used as potential raw material for geopolymer synthesis because of their huge availability in nature, lower cost associated with extraction and comparatively lower environmental footprint. The extend of geopolymerization increases with the increase of curing temperature giving higher compressive strength at early ages with no significant impact on later age strength, however, addition of other cementitious materials helps to improve the mechanical and durability properties of these geopolymers. The work presented here describes the suitability of natural pozzolan based geopolymer as alternative binder, however, for practical application of these binder additional research studies should be conducted such as rheological characteristics, freeze thaw resistance, carbonation, alkali silica reaction, light weight geopolymer concrete, fibre reinforced geopolymer concrete and geopolymer concrete for special applications. Greater number of efforts are needed to establish standard testing procedures for geopolymer cement and concrete. Life cycle analysis (LCA) of natural pozzolan based geopolymers should be carried out to investigate the sustainability and role in reduction of greenhouse gases.

Conflict of interest

The authors declare that they have no conflict of interest.

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