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Research Article

Volcanic tuff as a raw material for alkali-activated materials

Abderrachid Boumaza*, Mohamed Lyes Kamel Khouadjia*, Hamdi Oualid [2] and Hichem Alioui [3]

[1] *Department of Civil Engineering/ laboratory of Materials and durability of constructions (LMDC), University of Mentouri Constantine 1, Algeria.*
[2] *Department of Civil Engineering / Laboratory LEEGO, University of Sciences and Technology Houari Boumediene (USTHB), Algeria.*
[3] *Department of Civil and Hydraulic Engineering / Laboratory of Civil Engineering and Environment, University of Mohamed Seddik Benyahia Jijel, Algeria.*

(Abderrachid.boumaza@doc.umc.edu.dz) Email of the corresponding author

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Abstract – Currently, the use of geopolymers as cementitious materials is constantly evolving due to their excellent properties and efficiency, such as low CO2 emissions, high compressive strength, and low permeability. On the other hand, volcanic tuff can be used as a potential raw material for synthetic geopolymers due to its reactivity, wide availability in nature, low extraction cost, and relatively low environmental impact. This paper presents a review of recent studies on the use of volcanic tuff as a main binder in the manufacture of geopolymers. The results reported by the researchers concern durability and mechanical performance, as well as the factors affecting these properties, such as the effect of activator types, sodium hydroxide (NaOH) concentration, curing temperature, and the addition of other cementitious materials. The results clearly showed that increasing the activator concentration and curing temperature had a significant effect on mechanical properties, as well as that the activator (Na2SiO3 + NaOH) reduced water absorption values by creating a more compact structure in all samples than activation by NaOH alone. Recent results suggest that volcanic tuff-based geopolymers have mechanical, physical, and durability properties similar to or better than those of ordinary Portland cement concrete, but further research is needed to make them an economically and technically efficient building material.

Keywords – Geopolymers, Compressive Strength, Low Permeability, Volcanic Tuff, Reactivity, Ordinary Portland Cement

I. INTRODUCTION

Ordinary Portland Cement (OPC) substitutes have been researched for many years due to emissions of CO2 of cement manufacture. Alkali-Activated Materials (AAM) stand out as viable alternatives to OPC binders. When silica and aluminum-rich raw materials are added to a highly alkaline solution, they activate it to create semi-crystalline, three-dimensional polymers known as geopolymer[1]. These binders have the benefit of being made from a wide variety of aluminosilicate minerals, including metakaolin, fly ash, and slag. In addition, clay minerals are widely used around the world due to their distinctive physicochemical characteristics [2].

On the other hand, Volcanic tuff can be used in the synthesis of geopolymers, although these binders are still in the research and development stage and need more work to be useful and affordable building materials.

The main objective of this research concerns the review of several study which carried out on the mechanical and durability properties of volcanic tuff-based geopolymers produced with an alkaline solution as activator, and highlights the state of the art in the creation of volcanic tuff-based geopolymer blends. The mechanical properties and durability of geopolymeric materials depend on raw material reactivity and synthesis parameters, so this study also aims to provide a better understanding of the effect of curing temperature and activator concentration on mechanical properties and durability, and to address factors affecting the degree of raw material reactivity.

II. VOLCANIC TUFF AND REACTIVITY

The oldest and most abundant source of natural stone is considered to be volcanic tuffs, distinguished by their considerable silica and zeolitic mineral content[3]. Volcanic tuffs are igneous rocks formed by the hardening of material ejected during a volcanic eruption, and constitute a formidable source of reactive silica and alumina required for the synthesis of geopolymers as an alternative binder to ordinary Portland cement [4]. Depending on their degree of crystallinity and mineralogical composition, volcanic tuffs display a wide range of reactivity, depending on the nature of the magma's gyration and hardening mode. For example, an intrusive eruption leads to magma crystallization because hardening occurs over a long period of time (with little or no pozzolanic activity), whereas an extrusive eruption leads to the formation of the glassy phase due to the sudden abscission of temperature (highly reactive) ([5],[4]).

III. TUFF-BASED GEOPOLYMER AND ITS ADVANTAGES

The use of natural pozzolans for the synthesis of geopolymers is becoming increasingly important due to the limited use of industrial by-products such as fly ash and slag associated with the production of the main product [4]. In addition, the current worldwide interest in reducing greenhouse gas emissions is already leading to a future shortage of fly ash for concrete production in some countries.

On the other hand, the first stone constructions used reactive volcanic tuffs in combination with lime to make strong, durable mortars that withstood weather conditions and seismic shocks for centuries [5].

The use of volcanic tuff in geopolymer synthesis has been investigated ([1],[3],[5],[6],[7],[8],[9],[10]). Indeed, Volcanic tuffs (VT) are an excellent source of the reactive silica and alumina required for geopolymer synthesis. As an alternative binder to ordinary Portland cement, VT offers economic and environmental advantages due to its reasonable price and ease of extraction. Several factors influence the degree of geopolymerization, including particle size, alkaline activator type and concentration, raw material pretreatment, and curing conditions [4].

IV. COMPRESSIVE STRENGTH

Geopolymers must meet two essential requirements to be considered as potential alternatives to ordinary Portland cement (OPC) materials. They must have compressive strength and durability comparable or superior to those of ordinary cement. Compressive strength is influenced by the type and concentration of alkaline activators, the pretreatment of raw materials, and curing conditions ([1],[3] ,[9]-[8]). Table 1 summarizes the main findings of various authors on the geopolymerization of volcanic tuff. Ilker Tekin. [3] examined how curing temperatures and the alkaline activator NaOH affected the compressive strengths of samples obtained from geopolymer composite pastes (GCMs) of marble, travertine, and volcanic tuff and obtained a compressive strength of cast-in-place geopolymer composites reaching 46.5 MPa with 10 M 0.8 TV:0.2 travertine wastes, without heat treatment ,which is close to the results reported by Dongping et al. [7] who aimed to investigate the alkaline activation potential of volcanic tuff at ordinary temperatures with calcium-based materials, fly ash, and their mixtures as additives and obtained a compressive strength of 37.13 MPa at 28 days. In contrast to the parametric study carried out by Kantarci Fatih et al. [1] to examine the impact of activator (type and concentration) and curing temperature on the mechanical and

microstructural properties of volcanic tuff-based geopolymer mortar and concrete, which achieved a maximum compressive strength of around 37.9 MPa in samples at 90 days and a curing temperature of 120 °C, which are relatively compatible with the results of the experimental study conducted by Rami Haddad et al. [9], to investigate the mechanical properties of geopolymer concrete (GPC) made from Jordanian basaltic tuff. The most effective mixes achieve compressive strengths in excess of 30 MPa after curing at 80 °C. Sevgi Özen. [8] confirms these results, however, at a slightly lower curing temperature, where he finds better mechanical performance of Bayburt Tuff-based geopolymer at 30 MPa after thermal curing for 90 days at a curing temperature of 40 °C. Another study quite different from the one mentioned above, by Areej Almalkawi et al. [5] aimed to create one-part geopolymers based on volcanic tuff by calcining volcanic tuff at a moderate temperature followed by mechanochemical treatment of aluminosilicates. Results show that at 28 days under dry curing conditions, compressive strengths were satisfactory up to 22 MPa. The concentration of NaOH.
activator is the most important factor, and here is a kind of consensus on its effect: it has been found in several studies that compressive strength increases with increasing activator concentration ([1],[3],[9]-[8]).

Table 1. Summary of the main results and synthesis parameters studied for volcanic tuff-based geopolymers

Author	Raw material	Alkaline Solution Used	Curing Condition	Compressive Strength
Tekin [3]	Marble, travertine and volcanic tuff wastes	NaOH (1, 5 and 10 M)	22 ± 2 %, 40 and 75 C after demolding	46 MPa in dry state (20 °C)
Faith et al [1]	volcanic tuff	Na2SiO3 + NaOH and NaOH	90, 105 and 120 °C	37.9 MPa in120 °C
Haddad et al [9]	basaltic tuff	Na_2SiO_3 + NaOH	40, 80 and 120 C	30 MPa in 80 °C
Sevgi Özen [8]	volcanic tuff	Na_2SiO_3 + NaOH (12 M)	40°C and 90°C	30 MPa in 40 °C
Areej et al [5]	volcanic tuff	lime, sodium sulfate and soda ash (Na_2CO_3)	/	22 MPa
Dongping et al [7]	Volcanic tuff, Fly ash, CaO and $CaSO_4$	Na_2SiO_3 + NaOH	/	37,13 MPa

V. Durability

Volcanic tuff-based geopolymers are in the early stages of development, with little research into their durability characteristics. Water absorption and wetting and drying cycle are two of the main physical properties of geopolymers. Among the important variables affecting water absorption and wetting and drying cycle are those relating to activator concentration and type.

A. *Water absorption and Apparent porosity*

Enes Ekinci et al [10] studied the effect of different additives, nano silica, micro silica, and styrene-butadiene latex, on the performance of volcanic tuff-based GPCs with two different activation techniques (Na2SiO3 + NaOH or NaOH alone), and found that activation with Na2SiO3 + NaOH reduced water absorption values by creating a more compact structure in all samples than with NaOH activation alone, regardless of additive type, and that MS additions had a more effective effect on water absorption properties than NS additions. However, the relation is not consistent with the results of the study by Ilker Tekin et al.[11] showing that specimens prepared with a higher activator concentration (NaOH) absorb less water than those prepared with a lower activator concentration (5 M NaOH), which is due to the greater compactness and lower porosity of the microstructure of specimens prepared with a higher activator concentration, the relation is consistent with the results of Ilker Tekin's previous study [3], where he showed that specimens prepared with lower NaOH concentrations between 1 M and 5 M gradually collapsed due to efflorescence. Other 10 M pastes did not fail, but there was a slight efflorescence.

B. *Wetting and drying cycle*

Dongping et al. [7] examined the evolution of residual compressive strengths of solidified blocks over 300 freeze-thaw cycles and found that at the end of the cycle, compressive strength decreased by around 28%. This is close to the results reported by Enes Ekinci et al. [10] where they found a decrease in compressive strengths of pure sampled samples (without additions) of around 32.84% (activated with NaOH) and 19% (activated with Na2SiO3 + NaOH). Furthermore, this study also showed that NaOH-activated samples are less resistant to FT effects than Na2 SiO3 + NaOH-activated samples, and pure samples (K) experienced a maximum reduction in compressive strength, as shown in Fig. 1. This finding demonstrates that all additives have a positive effect on the FT resistance of GPC samples.

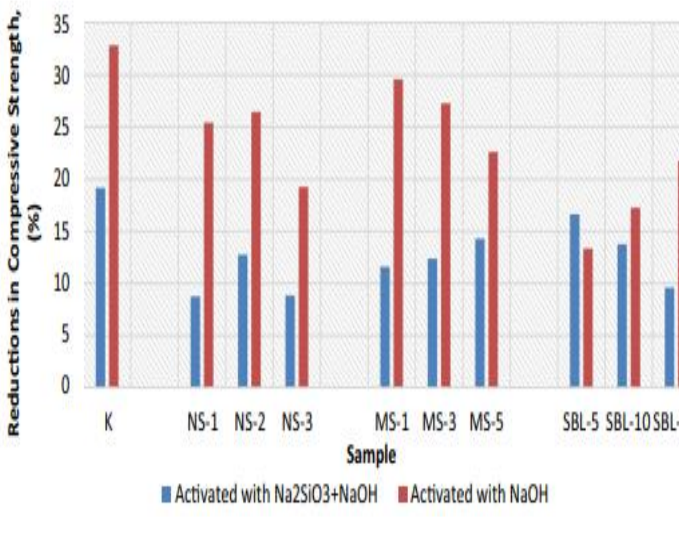

Fig. 1 Reductions in compressive strength values of all GPC samples after 300 FT cycles.[10]

VI. CONCLUSION

Due to their wide availability in nature, low extraction costs and low environmental impact, volcanic tuffs can be used as potential raw materials for geopolymer synthesis. Indeed, the increasing activator concentration and curing temperature increases the extent of geopolymerization, as well as the type of activator had a significant effect on water absorption values. However, the addition of other cementitious materials improves the mechanical properties and durability of these geopolymers. Volcanic tuff-based geopolymers are suitable as alternative binders, according to the work presented here. These binders are still in the development phase and require further research, notably on rheological and durability characteristics, to validate blends with wider world sources of volcanic tuff, and to become economically and technically efficient construction materials.

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