

Local Materials in Geopolymer Mortar: A Case Study on Metakaolin and Blast-Furnace Slag



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ABSTRACT

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blast-furnace slag, durability, geopolymer, metakaolin, mechanical behaviour, alkaline activation

The ubiquitous use of Portland cement in construction is accompanied by significant energy consumption and environmental impact. Geopolymeric cement has emerged as a sustainable alternative, boasting mechanical properties that are potentially favorable and a notably lower environmental footprint. This study evaluates the mechanical, physical, microstructural, and durability characteristics of geopolymer mortars synthesized from local aluminosilicate precursors—namely metakaolin (MK) and granulated blast-furnace slag (GBFS)—activated with sodium silicate solutions of varying molar ratios (1.2 to 2). Mechanical parameters assessed include compressive and flexural strengths and dynamic modulus, while physical properties encompass workability and porosity. Microstructural analysis was conducted, and durability was gauged through compressive strength reduction and alkalinity loss following sulfuric acid exposure. The performances of these geopolymer mortars were juxtaposed with those of conventional Portland cement mortar. It was revealed that an optimal geopolymer formulation incorporates 75% aluminosilicate material and 25% alkaline solution, with a liquid-to-solid ratio of 0.5 and a sodium silicate solution molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) of 1.8. This specific formulation yielded a compressive strength that surpassed that of the Portland cement mortar and displayed comparable porosity and resistance to compressive strength reduction post-acid exposure.

1. INTRODUCTION

Geopolymeric binders made from industrial by-products (waste) can be considered a very interesting alternative to conventional Portland cement-based binders in the construction sector [1-3]. These new binders have the advantage of reducing CO₂ emissions and limiting the energy consumption required to produce cement [1-4]. The inorganic polymer formed during the curing process has excellent mechanical properties (good resistance to fire and chemical attack) and high durability [2, 3, 5]. It is generally produced by the activation of aluminosilicate raw materials such as calcined clays (CC), granulated blast-furnace slag (GBFS), fly ash (FA), waste glass (WG), metakaolin (MK), etc., by an alkaline solution of silicates and/or sodium hydroxides; the resulting mixture hardens at room temperature [3]. The process of forming this geopolymeric binder is called “geopolymerisation”. Researchers have varying ideas about how to describe this chemical reaction [6]. In general, the main stages of this reaction can be summarised as the dissolution of the aluminosilicate powder present in the raw materials by the alkaline solution, which allows the formation of aluminate and silicate species in monomeric form; then the formation of the large networks of oligomers in the aqueous phase by

condensation, which allows the formation of a geopolymeric gel and the release of the water consumed by the aluminosilicate raw materials in the dissolution stage. As the connectivity of the gel network increases, the result is a geopolymeric matrix [6, 7].

Geopolymeric materials have a wide range of applications, in view of their physical, chemical and mechanical properties [6]. They can be used in structural elements like as the Queensland’s University GCI building in Australia with three suspended floors (2013) and the first residential building in Liepensk, Russian Federation with 20 floors (1989), and in marine structures [8, 9], in the restoration of historic buildings and in works in aggressive environments [5]. They can also be used as an absorbent material, repair material, thermal insulation material, 3D printing material and as an ecological binder for road construction like as the Brisbane West Wellcamp public Airport - Toowoomba, Queensland in Australia (operational since 2014) [6].

According to the pre-existing literature, fly ash, granulated blast-furnace slag and metakaolin are materials rich in aluminosilicates. They are widely used in the production of geopolymers. Most research has focused on fly ash-based geopolymers [10, 11]. Fly ash geopolymer exhibits low mechanical strength and slow curing when cured at room

temperature. On the other hand, it provides good mechanical strength when cured at high temperatures [12]. Slag-based geopolymer has good mechanical strength, durability and resistance to chemical attack, but has a very fast setting time [13-16]. In addition, metakaolin-based geopolymer has better mechanical properties. However, it requires a large amount of water, which significantly affects its rheological behaviour (poor workability) due to its very high specific surface area [17, 18].

In order to minimise these limitations, some researchers have worked on the combination of slag and metakaolin. Borges et al. [19] studied the mechanical, physical and durability properties of geopolymer mortars composed of metakaolin and blast-furnace slag. The mixes were prepared with a combination of 60% metakaolin and 40% slag with different molar ratios (MR) of the activator, which is sodium silicate solution ($SS=Na_2O/SiO_2$). These mixes were compared with a reference mortar based on metakaolin alone. The results of that study showed that the addition of slag to geopolymer mortars (GM) improved their mechanical strength and reduced their porosity.

Hasnaoui et al. [20] studied the effect of the proportion of slag, metakaolin, activator and the molar ratio ($MR=SiO_2/Na_2O$) of the sodium silicate solution on the performance of geopolymer mortars, such as workability, mechanical and physical properties and efflorescence stability. The best performances were obtained with the geopolymer matrix 50% slag and 50% metakaolin, with a ratio (slag + metakaolin/activator) equal to 3 and a molar ratio varying between 1.6 and 1.8. The geopolymeric mortars obtained had good properties compared to Portland cement mortars (PM).

Khalil et al. [21] also studied the fresh and hardened properties of geopolymer mortars composed of metakaolin and blast-furnace slag. Mixtures were prepared with two combinations (50% metakaolin / 50% slag) and (100% slag) with different activator molar ratios ($MR = 1.1, 1.3, 1.5$ and 1.7) and water/binder ratios (0% and 15%). The results showed that the optimum mix for the highest compressive strength and acceptable workability was the 100% slag mix with a molar ratio of 1.7.

From the literature review, it is clear that the properties of geopolymers were different from one study to another. These properties depend on the chemical and physical characteristics of the aluminosilicate raw materials (Si/Al and Na_2O/Al_2O_3 ratios [22]), the activators (optimum concentration which provides the best geopolymer performance [23, 24]) and the curing conditions (optimum temperature which increases the reaction speed of the raw materials [23]) [5]. The metakaolin and blast-furnace slag have different origins and contain a different percentages of aluminosilicates minerals (%Si and %Al). Consequently, it is difficult to predict the optimum mix and the future behaviour of geopolymers materials because the availability and the source of raw materials change from place to place which constitute a real challenge in development and use of geopolymers. In this context, the present study investigates the properties of geopolymeric mortars based on local materials – namely metakaolin from Djebel Debagh in the Guelma region and blast-furnace slag from Elhadjar in the Annaba region. The effect of the percentage of aluminosilicate raw materials, the alkaline activating solution and the molar ratio on the workability, setting time, porosity, mechanical properties and efflorescence stability were studied in order to identify the optimum matrix mixture. Finally, the optimum mixture

obtained was tested for resistance to sulphuric acid attack (durability properties).

2. MATERIALS AND METHODS

2.1 Materials

Portland cement of type CEM II/A, strength class 42.5, manufactured by GICA (Skikda – Algeria) was used to prepare the reference mortar. Its specific surface is $3371\text{ cm}^2/\text{g}$ and its chemical composition is given in Table 1.

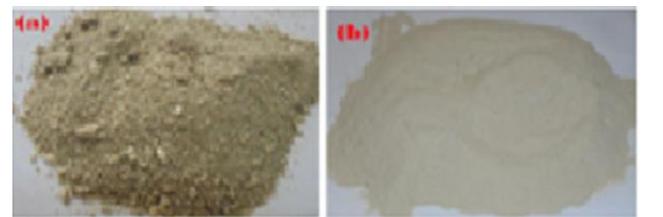
The granulated blast-furnace slag (GBFS) was collected from the El Hadjar metallurgical plant in Annaba. The slag was first dried in an oven at 105°C for 24 hours. It was then crushed using the Micro-Deval machine for 12 hours (Figure 1) [25] to obtain a fineness of about $5388\text{ cm}^2/\text{g}$ (Figure 1). Its chemical characteristics, shown in Table 1, were determined by X-ray fluorescence spectroscopy (XRF). The ground slag particles are irregularly shaped and angular, as shown in the scanning electron microscope (SEM) image (Figure 2).

Metakaolin (MK) was obtained by calcining Djebel Debagh grade-3 (DD3) kaolin from the Guelma region. The DD3 kaolin was first dried in an oven at 105°C for 24 hours and then finely ground in the Micro-Deval machine. The clay was then sieved to $80\text{ }\mu\text{m}$ and calcined in a kiln at 750°C for 5 hours [26]. Images of the transformation of DD3 kaolin to metakaolin are shown in Figure 1. The fineness of MK is about $5521\text{ cm}^2/\text{g}$ and its chemical composition, found by XRF, is given in Table 1. The MK particles have a flattened leaflet shape as shown in the SEM image (Figure 2).

Natural quartz sand, obtained from the sand pit in the Oum Ali region (Tebessa), was used as an aggregate in the production of all mortars. This sand is graded according to the standard sand (0/2 mm).

A solution consisting of 45% sodium silicate (SS) (Na_2O/SiO_2) and 55% water with a molar ratio (MR) SiO_2/Na_2O of 2.06 and $H_2O/Na_2O = 13.58$ is used as an activator. Sodium hydroxide (NaOH) was added to the sodium silicate solution to vary the molar ratios for the different mixtures.

A reagent-grade (95-97%) H_2SO_4 sulphuric acid solution was used to prepare the acid solutions used in the durability study.



The processing stages of GBFS: (a) before grinding, (b) after grinding



Conversion stages from DD3 kaolin to metakaolin: (a) before grinding, (b) after grinding, (c) after calcination

Figure 1. Preparation stages for GBFS and MK

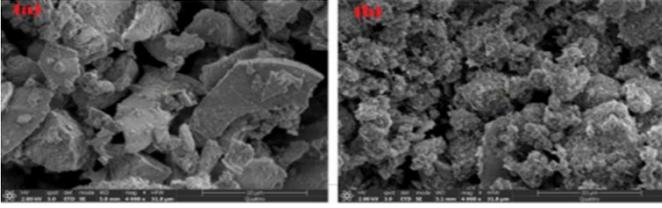


Figure 2. SEM images of GBFS (a) and MK (b)

Table 1. Chemical composition of cement, GBFS and MK

Components	MK	GBFS	CEM II/A 42.5
SiO ₂	40.81	37.4	24.92
Al ₂ O ₃	49.619	9.2	6.58
CaO	0.462	40.6	58.6
MgO	7.037	3.93	1.21
Fe ₂ O ₃	0.584	0.45	3.65
MnO	0.409	2.32	-
TiO ₂	0.170	0.306	-
SO ₃	0.554	1.3	2.17
K ₂ O	0.133	0.968	0.85
Na ₂ O	0.132	0.290	0.08
SrO	0.015	0.350	-
BaO	-	2.69	-
PAF	-	-	1.7

2.2 Composition of mixtures

Portland cement mortar (PM) and geopolymer mortar (GM) were prepared according to standard NF EN 196-1 [27] with 450 g of binder, 1350 g of standard sand and 225 g of water (W) (W/C = 0.5). In the geopolymer mixes, Portland cement (C) was replaced by a binder composed of GBFS, MK, sodium silicate solution (SS) and sodium hydroxide (NaOH). Three specimens for each mixture were prepared and tested to ensure reproducibility and reliability of measurements. These specimens were cured and stored in closed boxes at room temperature before testing.

Each geopolymer mortar was composed of a mixture of 50% GBFS and 50% MK (constant), a liquid/solid ratio of 0.5 (constant), three different proportions between the aluminosilicate raw materials (AM) and the alkaline solution (AS) (70%-30%, 75%-25% and 80%-20%) and five molar ratios (MR) of the activator (1.2, 1.4, 1.6, 1.8 and 2). The

choice of these percentages was based on the work of Davidovits [28, 29], who showed that the geopolymeric binder has good mechanical and physical properties when prepared with 55 to 70% aluminosilicate materials, 25 to 35% activator and a molar ratio (MR) varying between 1.45 and 1.95. The different compositions of the mortars studied are given in Table 2.

2.3 Test protocols

The different geopolymeric mortars were studied in two phases. The aim of the first phase was to determine the optimum geopolymer formulation – i.e. the percentages of GBFS and MK, molar ratio and solid/liquid ratio (aluminosilicate/alkaline solution materials) which provides the better results in terms of efflorescence stability, compressive strength, workability, setting time and porosity. The second was to study the durability of the optimum formulation against sulphuric acid attack. The loss of mass, compressive strength and reduction in alkalinity of the geopolymer mortar after exposure to acid were compared to Portland cement mortar in order to better understanding its durability.

First phase: Optimum formulation

In order to determine the optimum geopolymer formulation, various tests were carried out on geopolymer (GM) and reference (PM) mortars in the fresh and hardened states. Initially, the characterisation of the two mortars (GM and PM) was based on workability tests in accordance with standard NF P18-452 [30], setting time tests in accordance with standard NF EN 480-2 [31], and open porosity tests in accordance with standard NF EN 18-459 [32]. Mechanical performance (compressive and flexural strength, dynamic modulus) was then determined in accordance with standards NF EN 196-1 [27] and NF EN 12504-4 [33] respectively. Compressive strength, flexural strength and dynamic modulus were measured on three 40×40×160 mm prismatic specimens after 28 days of curing. These specimens were cured and stored in closed boxes at room temperature. The dynamic modulus (Ed) was determined using the following formula:

$$E_d = V^2 \rho \frac{(1+\nu)(1-2\nu)}{(1-\nu)}$$

Table 2. Composition of Portland and geopolymer mortar mixes

Mixes	AM%+AS%	MR	AM (g)	SS (g)	NaOH (g)	W (g)	C (g)
GM1		1.2		246.3	31.92	89.5	
GM2		1.4		267.9	22.9	77.7	
GM3	70% AM	1.6	315	286.8	15	67.3	
GM4	+30% AS	1.8		303.4	8.00	58.1	
GM5		2		318.2	1.83	50	0
GM6		1.2		205.3	26.6	112.1	
GM7		1.4		223.3	19.1	102.2	
GM8	75% AM	1.6	337.5	239	12.5	93.55	
GM9	+25% AS	1.8		252.9	6.7	85.9	
GM10		2		265.2	1.5	79.2	0
GM11		1.2		164.2	21.3	134.7	0
GM12		1.4		178.6	15.25	126.8	
GM13	80% AM	1.6	360	191.2	9.98	119.84	
GM14	+20% AS	1.8		202.3	5.33	113.74	
GM15		2		212.2	1.2	108.3	
PM	-	0	0	0	0	225	450

AS= SS+NaOH
Sand (g)=1350

With:

$$V = \frac{L}{T}$$

V: the speed of the ultrasonic pulse (m/s).

L: the length of the specimen (160 mm).

T: the transit time in μsec .

ρ : the apparent density of the specimens (kg/m^3).

ν : the Poisson's ratio of 0.2 was estimated as a mean value between 0.15 and 0.25, in line with the literature [34].

The efflorescence of the GM mortars was then assessed quantitatively by visual comparison. The test consisted of partially immersing cubic mortar samples measuring $50 \times 50 \times 50$ mm in 40 g of distilled water at room temperature to induce efflorescence. Efflorescence is the reaction of calcium hydroxide with water and CO_2 to form carbonate deposits [35, 36], which appear as a powdery, whitish deposit on the surface of the samples. Efflorescence can cause a slight deterioration in the mechanical properties of geopolymers [37].

Finally, the SEM was used to analyse the microstructure of the geopolymer mortar.

Second phase: Sustainability study

Specimens of the optimum formulation of the geopolymer mortar (GM) and the reference mortar (PM), measuring $50 \times 50 \times 50$ mm, were prepared and cured in the same way as above. After 28 days of curing, the specimens were immersed for 28 days in three sulphuric acid solutions with three different concentrations: 1%, 3% and 5%. These tests were carried out in accordance with ASTM C267 [38]. For each of the different mortar mixes, at least three test specimens were exposed to sulphuric acid to account for measurement uncertainties. These mortars were compared with control mortars not exposed to acid. Every 14 days, the external surfaces of specimens were cleaned from the solution and their new masses measured in order to calculate the loss of mass. The acid solutions were then renewed and the samples immersed in the acid solution again.

At the end of the acid exposure (28 days), the compressive strength of all the specimens was measured. The loss of alkalinity of the mortars was also determined on the geopolymer and reference mortars exposed to the 5% solution. The test was carried out using the phenolphthalein method [39]. The test consisted of dividing the specimens into two parts and then applying a 1% phenolphthalein solution to the internal surfaces to determine the depth of acid penetration. The phenolphthalein solution causes a purple colour contrast between healthy areas ($\text{pH} \geq 9$) and degraded surface areas ($\text{pH} < 9$) [39, 40]. Next, the thickness of the area of mortar degraded by the effect of sulphuric acid was measured in both directions. Finally, the ratio of the degraded thickness to the total thickness of the sample was determined.

3. RESULTS AND DISCUSSION

3.1 Phase 1

3.1.1 Workability

Figure 3 shows the evolution of the flow time of PM and GM mortars as a function of the MR and the percentages AM and AS. It can be seen that all the GM have lower workability than PM. In addition, as the MR increase, the flow time progressively increases, due to the decrease in the amount of water added for each formulation and also due to the increase

in the viscosity of the alkaline solution when MR increases. It can therefore be concluded that increasing the MR reduces the workability of the geopolymeric mortars. This trend also applies to increases in the percentage of aluminosilicate materials (AM). Here, a gradual increase in the flow time can be observed, which reduces the workability of geopolymeric mortars. This decrease is due to the high water demand of the aluminosilicate materials (MK and GBFS) [17-20]. Mixes formulated with 80% aluminosilicate materials have very low workability compared to other mixes (70% AM and 75% AM).

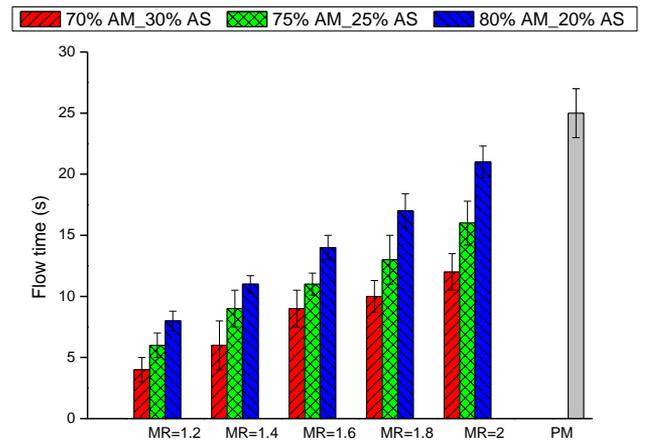


Figure 3. Flow times for Portland cement mortar and geopolymer mortars

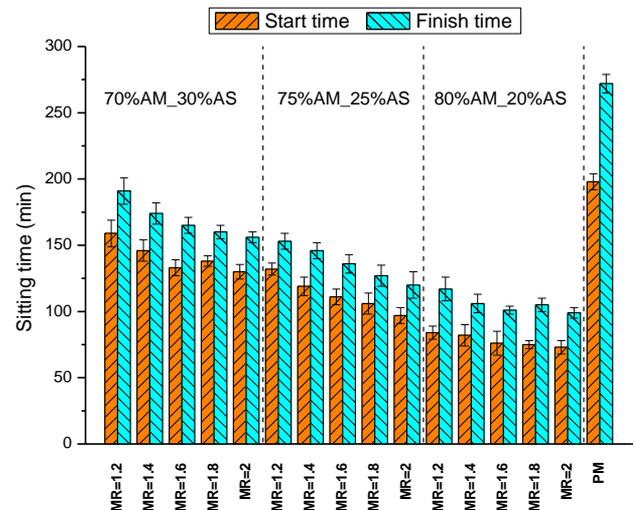


Figure 4. Setting times (start and finish) for Portland cement mortar and geopolymer mortars

3.1.2 Setting time

Figure 4 shows the setting start and finish times of PM and GM as a function of the MR and the percentages of AM and AS. It was found that the geopolymer mortars set faster than the Portland cement mortars. The setting (start and finish) times of the different geopolymer mortars varied between 73 and 159 min for the setting start and between 99 and 191 min for the setting finish. Furthermore, increasing the AM percentage from 70% to 80% and the MR molar ratio from 1.2 to 2 progressively decreased the setting time of the geopolymer mortars. This was due to the increase in the amount of SiO_2 and Al_2O_3 , which accelerated the geopolymerisation process and rapidly develops the

geopolymer binding matrix. These results are in agreement with those reported in the literature [41, 42]. The setting start times of the first, second and third groups of GM (70%AM_30%AS; 75%AM_25%AS; 80%AM_20%AS) were, on average, 1.4, 1.8 and 2.1 times faster than the Portland cement mortar, respectively. The setting finish times of the three GM groups were, on average, 1.6, 2.1 and 2.6 times shorter than those of the Portland cement mortar. In addition, the average time between start and finish of setting for all the GM was approximately 25 minutes, whereas for the Portland cement mortar, it was 74 minutes (approximately 3 times longer).

3.1.3 Porosity

Figure 5 shows the porosity of PM and GM mortars as a function of MR and AM and AS percentages. It can be seen that the PM has the highest porosity (19.19%), while the porosities of geopolymer mortars (from GM1 to GM15) varied between 16.96% and 18.63%. These results are in agreement with previous research [20-43]. It should also be noted that the porosity increases when the percentage of AS increases. This behaviour was observed for all MR. The lowest porosity was obtained for the combination of 70%AM_30%AS, regardless of MR, while the highest porosity was obtained for the combination of 80%AM_20%AS. This was probably due to the decrease in alkalinity of the medium when the amount of AS increases.

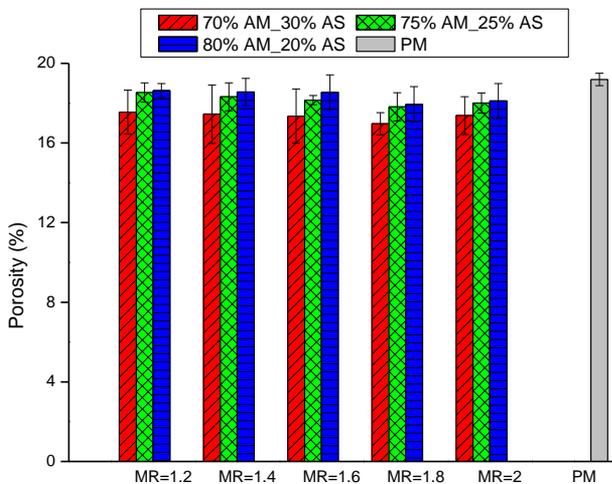


Figure 5. Porosity of Portland cement mortar and geopolymer mortars

3.1.4 Mechanical strengths

Figures 6 and 7 show the compressive strength (CS) and flexural strength (FS) at 28 days of PM and GM mortars as function of MR and the percentages of AM and AS. The results show that all the geopolymers formulated with 70% and 75% AM have higher mechanical strengths than PM (CS = 27.32 MPa and FS = 5.5 MPa). On the other hand, the geopolymers formulated with 80% AM have lower mechanical strengths (CS and FS) than the PM, regardless of the MR.

The maximum compressive and flexural strengths were 45.80 MPa and 6.65 MPa respectively. They were obtained for the GM5 mix (70%AM_30%AS and MR = 2). The minimum values of CS and FS were obtained for mortars formulated with 80%AM_20%AS. It should also be noted that increasing the proportion of AM (GBFS+MK) from 70% to 75% and then

to 80% leads to reduce the mechanical strengths. On the other hand, the mechanical strengths (CS and FS) increase when the MR increases from 1.2 to 2. This was a priori due to the effect of dissolving large quantities of aluminosilicate raw materials, which catalyses the geopolymerisation process and consequently improves the mechanical properties of the mortars [44-47]. These results are similar to those obtained in previous studies [20].

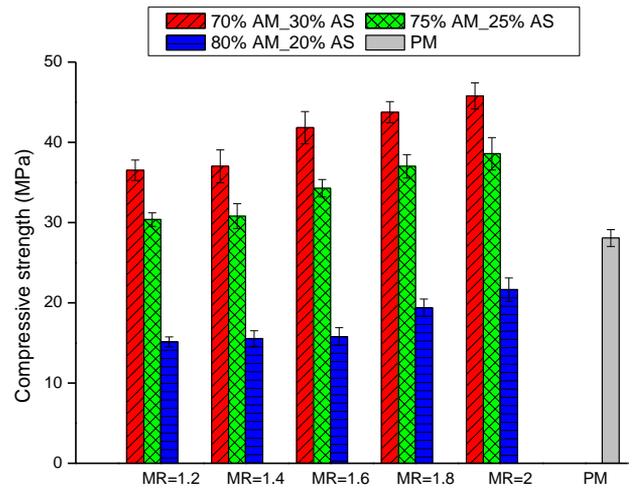


Figure 6. Compressive strength of Portland cement mortar and geopolymer mortars at 28 days

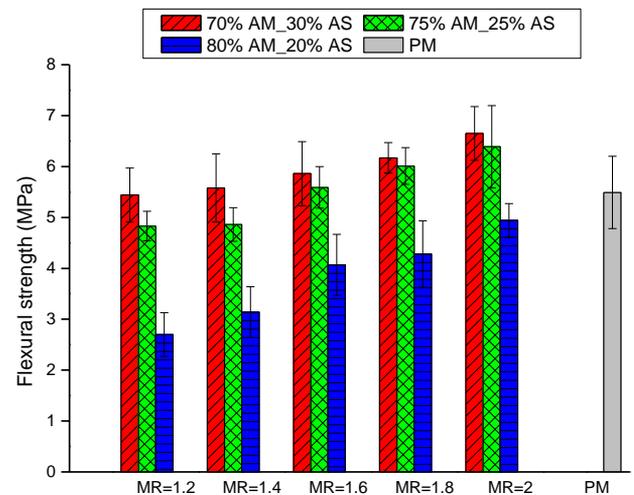


Figure 7. Flexural strength of Portland cement mortar and geopolymer mortars at 28 days

3.1.5 The dynamic modulus

Figure 8 shows the evolution of the dynamic modulus of elasticity of GM and PM as function of the MR and the percentages of AM and AS after 28 days. The results show that the Portland cement mortar has a higher dynamic modulus of elasticity than the geopolymer mortars. These results were in agreement with the mechanical strength results, as the dynamic modulus is related to the compressive strength [48]. Therefore, the geopolymer mortars show lower stiffness compared to the Portland cement mortar. These results are in agreement with the literature [49-52]. It should also be noted that the dynamic modulus of geopolymers is only slightly affected by the percentages of AM_AS and MR.

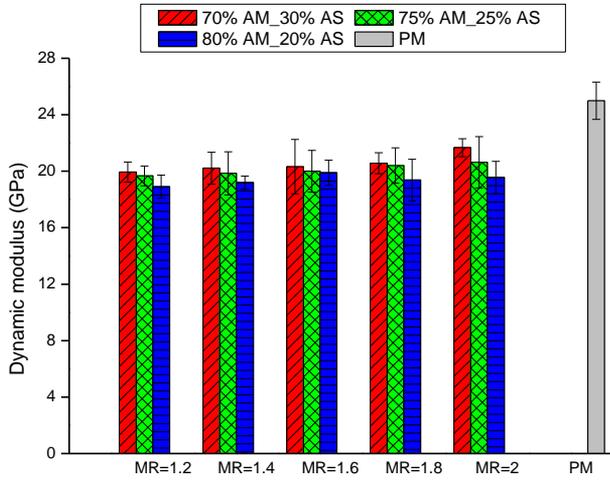


Figure 8. Dynamic modulus of elasticity of Portland cement mortar and geopolymer mortars at 28 days

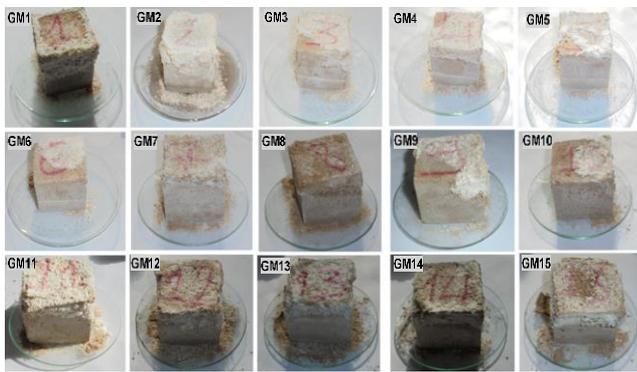


Figure 9. Visible efflorescence formation on the surfaces of geopolymer mortar specimens

3.1.6 Efflorescence

Figure 9 shows photos of the formation of efflorescence for different geopolymer mortars. The visual analysis shows visible efflorescence on the outer surfaces of the geopolymer mortar specimens. The formation of efflorescence depends on the porosity, water absorption and degree of alkalinity in the composition of the geopolymer materials [52]. Globally, it can be seen that efflorescence was greater for combination of 80% AM (GM1, GM12, GM13, GM14, GM15) compared to the

other combinations. This is due to the higher porosity of this combination. It can also be stated that efflorescence decreases as the molar ratio increases. This is probably due to the high amount of silica in the geopolymer cement matrix gel. Silica reduces porosity and permeability, thus delaying the leaching process [52]. In addition, combinations with 75% AM (GM6, GM7, GM8, GM9, GM10) show low efflorescence.

3.1.7 Microstructural characterisation

Figure 10 shows a scanning electron microscope of GM9 geopolymer mortar containing 75% AM and 25% AS with a MR of 1.8 after 28 days. This image shows the presence of microspores in the microstructure. This is probably due to the compaction of the mixture and the high MR [19]. It is also possible to see the presence of a few MK and GBFS particles that have not completely reacted with the activator. This is probably due to the high molar ratio, which accelerated the reaction of MK and GBFS, but at the same time limited the completion of the reaction of the particles [19]. In general, the GM9 mixture showed good homogeneity and microstructural bonding.

Optimum formulation

From the results obtained in the first phase, it can be concluded that the mixes (GM8, GM9, GM10) formulated with a combination of 75% aluminosilicate materials (50% GBFS+50% MK) and 25% alkaline solution and a molar ratio varying between 1.6 and 2 show better efflorescence stability, with good mechanical strengths and workability, acceptable setting time and low porosity. The GM9 mixture of 75% AM and 25% AS with MR = 1.8 was deemed the optimum formulation, which has been tested in the second phase (durability against sulphuric acid attack).

3.2 Phase 2: Chemical durability

3.2.1 Visual appearance

Figure 11 shows the visual appearance of optimum Geopolymer Mortar (GM9) and PM before and after 28 days to exposure to sulphuric acid solutions for different concentrations (1%, 3% and 5%). It shows that the physical degradation of the mortars increases as the acid concentration increases from 1% to 5%. Furthermore, GM and PM mortars exposed to 1% acid show slightly physical degradation. Moreover, mortars exposed to 3% and 5% acid showed visible physical degradation, with the formation of a non-cohesive paste in both PM and GM.

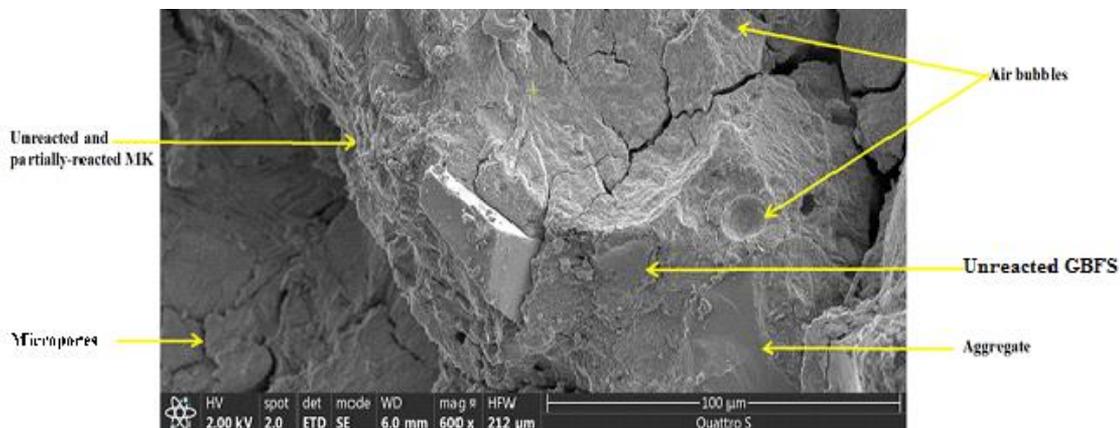


Figure 10. Scanning electron micrograph of GM9 geopolymer mortar



Figure 11. Visual appearance of GM and PM before and after 28 days to exposure to 1%, 3% and 5% sulphuric acid solution

3.2.2 Change of mass

Figure 12 shows the percentage change in mass of the optimum geopolymer mortar (GM9) and PM specimens as function of time (14 and 28 days) and acid solution concentration (1%, 3% and 5%). The results show mass gain (positive “+” values) at 1%, followed by mass loss (negative “-” values) at 3% and 5% for all GM and PM specimens. The mass losses increased progressively as the acid concentration increased from 3% to 5%. The mass gains were due to the infiltration of the sulphuric acid solution into the internal porosity of the specimens which firstly increases the masses of the test specimens. These results were in agreement with those of the literature [53]. The mass change (gain or loss) of GM and PM was greater after 28 days for all three acid concentrations. The mass gain was lower for GM than for PM. This behavior was the same for the mass loss at 3%.

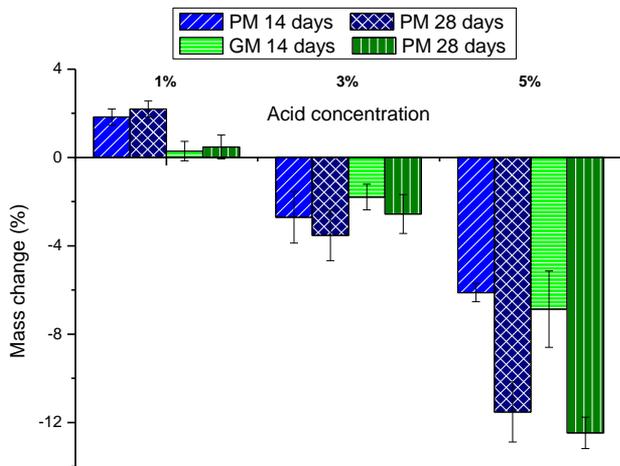


Figure 12. Percentage change in mass of GM and PM after 14 and 28 days exposure to 1%, 3% and 5% sulphuric acid solution

3.2.3 Compressive strength

Figure 13 shows the evolution of compressive strength of optimum GM9 and PM after 28 days to exposure to sulphuric acid for the three concentrations (1%, 3% and 5%). It can be seen that the exposure of GM and PM to sulphuric acid causes a progressive decrease in compressive strength when the acid concentration increases.

Figure 14 shows that at low and medium levels of acid attack (1% and 3%), the geopolymer and Portland cement mortars have almost the same degradation of compressive strength after exposure to sulphuric acid. The percentages of strength reduction were around 7% and 22% respectively compared to the initial strength. At high levels of chemical

attack (5%), the difference between the strengths before and after acid attack is much greater (around 39% for GM and 48% for PM), and the geopolymer mortar has the advantage of being more resistant compared to the Portland cement mortar. This performance of GM seems due to the low porosity of GM compared to PM which makes the microstructure of GM more dense than PM. GM offered an improved level of resistance against penetration of sulphuric acid and consequently better corrosion resistance of the matrix binder compared to conventional mortar (PM). These results were in agreement with those reported in the literature [54].

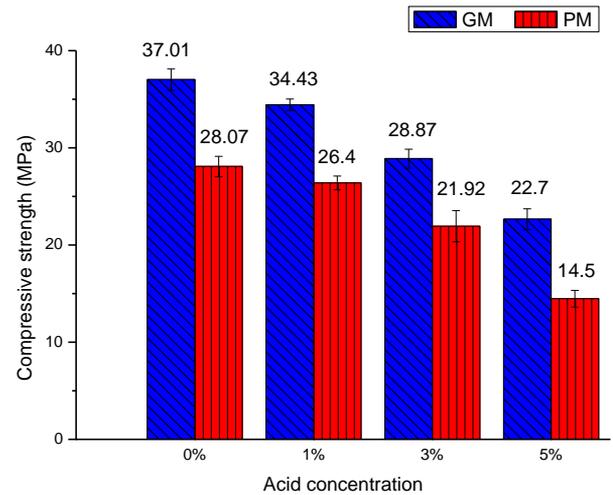


Figure 13. Evolution of compressive strength of GM and PM as a function of acid concentration after 28 days of exposure

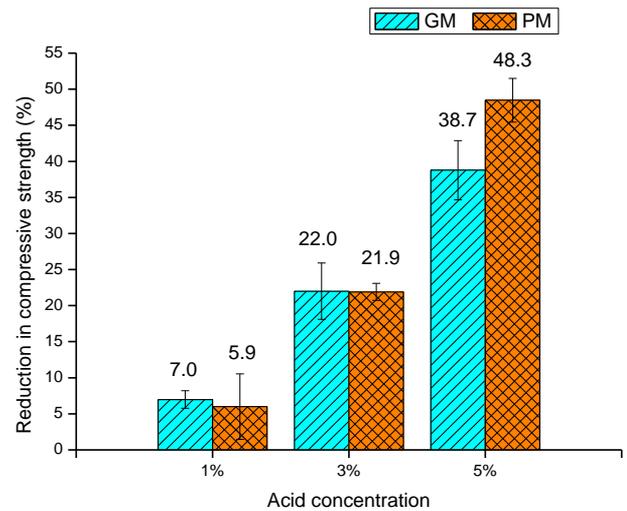


Figure 14. Percentage reduction in compressive strength after exposure to acid

3.2.4 Loss of alkalinity

Figures 15 and 16 shows the results of alkalinity tests of unexposed and exposed GM and PM after 28 days at 5% sulphuric acid solution. The results show that the GM has greater alkalinity loss (64%) than the PM (16%). This loss of alkalinity in GM confirms the previous results of reduced compressive strength. The majority of the acid-penetrated outer surface of the GM specimen – i.e. that which has lost its alkalinity – is bonded to the undamaged cementitious matrix of the material. This leads to the conclusion that GM is more

resistant to sulphuric acid penetration than PM. These results were in agreement with those reported in the literature [36].

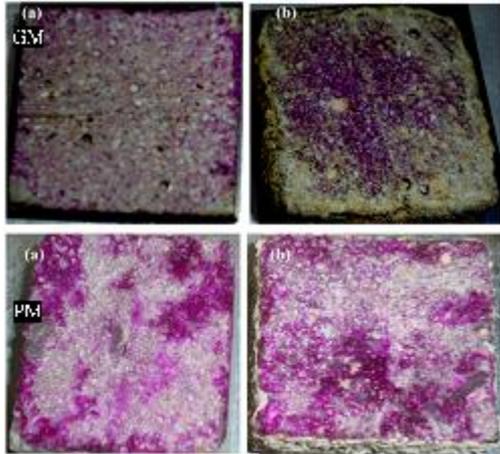


Figure 15. Loss of alkalinity in GM and PM, (a) unexposed and (b) after 28 days' exposure to 5% sulphuric acid

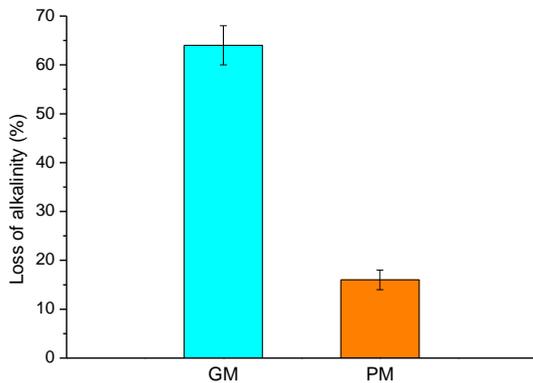


Figure 16. Percentage loss of alkalinity in GM and PM after 28 days' exposure to sulphuric acid at 5% concentration

4. CONCLUSION

This work studied the physical, mechanical and durability properties of geopolymers mortars based on the use of local materials (metakaolin MK and Granulated Blast Furnace Slag GBFS). From the test results, it can be concluded that:

- The workability and setting time of the geopolymers mortars decrease when the molar ratio (MR) and percentage of aluminosilicate materials (AM) increase. Moreover, increasing the percentage of aluminosilicate materials (AM) leads to increase the porosity.
- The high percentage of GBFS and MK (80% of AM) reduces the mechanical strengths (CS and FS). The mechanical strengths increase when the MR increases from 1.2 to 2. Furthermore, geopolymers mortars have a lower stiffness (dynamic modulus) than Portland cement mortars.
- Increasing the molar ratio ($\text{SiO}_2/\text{Na}_2\text{O}$) of the alkaline solution reduces the formation of visible efflorescence on the geopolymers mortars surfaces.
- The geopolymeric mortar formulation based on local materials with a matrix of 50% of GBFS and 50% of MK, a combination of 75% aluminosilicate materials and 25% alkaline solution, a liquid/solid ratio of 0.5 and an

alkaline solution molar ratio $\text{MR} = 1.8$ is the optimum formulation. This formulation shows acceptable workability and setting time (start =106 and finish =127 min), better mechanical strengths (CS=37 MPa et FS=6 MPa), lowest porosity (17.82%) and the best efflorescence stability. SEM analysis shows good microstructural bonding in the geopolymer matrix.

- The geopolymer mortar of the optimum formulation exposed to sulphuric acid at 1%, 3% (low and medium acid attack concentrations) showed a reduction in compressive strength similar to that of a Portland cement mortar (around 7 and 22% respectively). At high acid attack concentration (5%), GM showed lower reduction of compressive strength than PM so a better durability (38% and 48% respectively). In addition, the same optimum formulation showed better durability than Portland cement mortar in terms of alkalinity loss.

For future massive and common use of local geopolymers in Algeria, this research contributes to the body of knowledge by providing useful data for the development of a suitable code of conduct. This code must be based on the results of data research carried out in the laboratory and in situ on real structures.

For the rest of this work, it is recommended to conduct field studies to evaluate geopolymers performance in real conditions. It is recommended also to assess the life-cycle environmental impacts and economic viability of this local geopolymers binders compared to conventional binders.

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REFERENCES

- [1] Davidovits, J. (1994). Properties of geopolymer cements. In First International Conference on Alkaline Cements and Concretes, 1: 131-149. <http://www.geopolymer.org/wp-content/uploads/KIEV.pdf>.
- [2] Hassan, A., Arif, M., Shariq, M. (2019). Use of geopolymer concrete for a cleaner and sustainable environment—A review of mechanical properties and microstructure. *Journal of cleaner production*, 223: 704-728. <https://doi.org/10.1016/j.jclepro.2019.03.051>
- [3] Amran, Y.M., Alyousef, R., Alabduljabbar, H., El-Zeadani, M. (2020). Clean production and properties of geopolymer concrete: A review. *Journal of Cleaner Production*, 251: 119679. <https://doi.org/10.1016/j.jclepro.2019.119679>
- [4] Naik, T.R. (2008). Sustainability of concrete construction. *Practice periodical on structural design and construction*, 13(2): 98-103. [https://doi.org/10.1061/\(ASCE\)1084-0680\(2008\)13:2\(98\)](https://doi.org/10.1061/(ASCE)1084-0680(2008)13:2(98))
- [5] Singh, N.B., Middendorf, B. (2020). Geopolymers as an alternative to Portland cement: An overview. *Construction and Building Materials*, 237: 117455. <https://doi.org/10.1016/j.conbuildmat.2019.117455>
- [6] Cong, P., Cheng, Y. (2021). *Advances in geopolymer*

- materials: A comprehensive review. *Journal of Traffic and Transportation Engineering (English Edition)*, 8(3): 283-314. <https://doi.org/10.1016/j.jtte.2021.03.004>
- [7] Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G.C., Palomo, A., van Deventer, J.S. (2007). Geopolymer technology: The current state of the art. *Journal of materials science*, 42: 2917-2933. <https://doi.org/10.1007/s10853-006-0637-z>
- [8] Almutairi, A.L., Tayeh, B.A., Adesina, A., Isleem, H.F., Zeyad, A.M. (2021). Potential applications of geopolymer concrete in construction: A review. *Case Studies in Construction Materials*, 15: e00733. <https://doi.org/10.1016/j.cscm.2021.e00733>
- [9] Dawczynski, S., Krzywon, R., Gorski, M., Dubinska, W., Samoszuk, M. (2017). Geopolymer Concrete - Applications in Civil Engineering.
- [10] Ma, C.K., Awang, A.Z., Omar, W. (2018). Structural and material performance of geopolymer concrete: A review. *Construction and Building Materials*, 186: 90-102. <https://doi.org/10.1016/j.conbuildmat.2018.07.111>
- [11] Ng, C., Alengaram, U.J., Wong, L.S., Mo, K.H., Jumaat, M.Z., Ramesh, S. (2018). A review on microstructural study and compressive strength of geopolymer mortar, paste and concrete. *Construction and Building Materials*, 186: 550-576. <https://doi.org/10.1016/j.conbuildmat.2018.07.075>
- [12] Adam, A.A., Horiato, X.X.X. (2014). The effect of temperature and duration of curing on the strength of fly ash based geopolymer mortar. *Procedia engineering*, 95: 410-414. <https://doi.org/10.1016/j.proeng.2014.12.199>
- [13] Wang, S.D., Pu, X.C., Scrivener, K.L., Pratt, P.L. (1995). Alkali-activated slag cement and concrete: A review of properties and problems. *Advances in cement research*, 7(27): 93-102. <https://doi.org/10.1680/adcr.1995.7.27.93>
- [14] Tennakoon, C., San Nicolas, R., Sanjayan, J.G., Shayan, A. (2016). Thermal effects of activators on the setting time and rate of workability loss of geopolymers. *Ceramics International*, 42(16): 19257-19268. <https://doi.org/10.1016/j.ceramint.2016.09.092>
- [15] Perná, I., Hanzlíček, T. (2016). The setting time of a clay-slag geopolymer matrix: The influence of blast-furnace-slag addition and the mixing method. *Journal of Cleaner Production*, 112: 1150-1155. <https://doi.org/10.1016/j.jclepro.2015.05.069>
- [16] Kumar, S., Kumar, R., Mehrotra, S.P. (2010). Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. *Journal of materials science*, 45: 607-615. <https://doi.org/10.1007/s10853-009-3934-5>
- [17] Duxson, P., Fernández-Jiménez, A., Provis, J.L., Lukey, G.C., Palomo, A., van Deventer, J.S. (2007). Geopolymer technology: The current state of the art. *Journal of materials science*, 42: 2917-2933. <https://doi.org/10.1007/s10853-006-0637-z>
- [18] Provis, J.L., Duxson, P., van Deventer, J.S. (2010). The role of particle technology in developing sustainable construction materials. *Advanced Powder Technology*, 21(1): 2-7. <https://doi.org/10.1016/j.apt.2009.10.006>
- [19] Borges, P.H., Banthia, N., Alcamand, H.A., Vasconcelos, W.L., Nunes, E.H. (2016). Performance of blended metakaolin/blastfurnace slag alkali-activated mortars. *Cement and Concrete Composites*, 71: 42-52. <https://doi.org/10.1016/j.cemconcomp.2016.04.008>
- [20] Hasnaoui, A., Ghorbel, E., Wardeh, G. (2019). Optimization approach of granulated blast furnace slag and metakaolin based geopolymer mortars. *Construction and Building Materials*, 198: 10-26. <https://doi.org/10.1016/j.conbuildmat.2018.11.251>
- [21] Khalil, M.G., Elgabbas, F., El-Feky, M.S., El-Shafie, H. (2020). Performance of geopolymer mortar cured under ambient temperature. *Construction and Building Materials*, 242: 118090. <https://doi.org/10.1016/j.conbuildmat.2020.118090>
- [22] Rowles, M., O'connor, B. (2003). Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite. *Journal of materials chemistry*, 13(5): 1161-1165. <https://doi.org/10.1039/B212629J>
- [23] Yao, X., Zhang, Z., Zhu, H., Chen, Y. (2009). Geopolymerization process of alkali-metakaolinite characterized by isothermal calorimetry. *Thermochimica Acta*, 493(1-2): 49-54. <https://doi.org/10.1016/j.tca.2009.04.002>
- [24] Alonso, S., Palomo, A. (2001). Alkaline activation of metakaolin and calcium hydroxide mixtures: Influence of temperature, activator concentration and solids ratio. *Materials Letters*, 47(1-2): 55-62. [https://doi.org/10.1016/S0167-577X\(00\)00212-3](https://doi.org/10.1016/S0167-577X(00)00212-3)
- [25] Bensaifi, E., Bouteldja, F., Nouaouria, M.S., Breul, P. (2019). Influence of crushed granulated blast furnace slag and calcined eggshell waste on mechanical properties of a compacted marl. *Transportation Geotechnics*, 20: 100244. <https://doi.org/10.1016/j.trgeo.2019.100244>
- [26] Rabehi, B., Boumchedda, K., Ghernouti, Y. (2012). Study of calcined halloysite clay as pozzolanic material and its potential use in mortars. *International Journal of the Physical Sciences*, 7(31): 5179-5192. <https://doi.org/10.5897/IJPS11.184>
- [27] EN, N. (2016). 196-1. Méthodes D'essais des Ciments—Partie 1: Détermination des Résistances. AFNOR: Paris, France.
- [28] Davidovits, J. (2008). Geopolymer chemistry and applications, 2011: Institute Geopolymer. Saint Quentin, France.
- [29] Davidovits, J. (2013). Geopolymer cement. A review. *Geopolymer Institute, Technical papers*, 21: 1-11.
- [30] AFNOR, N. (2017). P 18-452, Concretes-Measuring the flow time of concretes and mortars using a workability meter. AFNOR, Paris.
- [31] EN, B. (2006). 480-2 Admixtures for concrete, mortar and grout. Test Methods. Determination of Setting Time.
- [32] NF EN. (2010). 18-459. Concrete - Test for hardened concrete: porosity and density test.
- [33] NF EN. (2005). 12504-4. Tests for concrete in structures-Part 4: Determination of the speed of sound propagation.
- [34] Lamond, J.F., Pielert, J.H. (2006). Significance of tests and properties of concrete and concrete-making materials. ASTM international.
- [35] Cong, P., Cheng, Y. (2021). Advances in geopolymer materials: A comprehensive review. *Journal of Traffic and Transportation Engineering (English Edition)*, 8(3): 283-314. <https://doi.org/10.1016/j.jtte.2021.03.004>
- [36] Zhang, Z., Provis, J.L., Ma, X., Reid, A., Wang, H. (2018). Efflorescence and subflorescence induced microstructural and mechanical evolution in fly ash-based geopolymers. *Cement and Concrete Composites*, 92: 165-177.

- <https://doi.org/10.1016/j.cemconcomp.2018.06.010>
- [37] Zhang, Z. H., Yang, T., Wang, H. (2014). The effect of efflorescence on the mechanical properties of fly ash-based geopolymer binders. In 23rd Australasian Conference on the Mechanics of Structures and Materials (ACMSM23), 1: 107-112.
- [38] ASTM C267 - 01(2012) Standard Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacing and Polymer Concretes.
- [39] Aiken, T.A., Kwasny, J., Sha, W., Soutsos, M.N. (2018). Effect of slag content and activator dosage on the resistance of fly ash geopolymer binders to sulfuric acid attack. *Cement and Concrete Research*, 111: 23-40. <https://doi.org/10.1016/j.cemconres.2018.06.011>
- [40] Parrott, L.J., Killoh, D.C. (1989). Carbonation in a 36 year old, in-situ concrete. *Cement and Concrete Research*, 19(4): 649-656. [https://doi.org/10.1016/0008-8846\(89\)90017-3](https://doi.org/10.1016/0008-8846(89)90017-3)
- [41] Jumrat, S., Chatveera, B., Rattanadecho, P. (2011). Dielectric properties and temperature profile of fly ash-based geopolymer mortar. *International Communications in Heat and Mass Transfer*, 38(2): 242-248. <https://doi.org/10.1016/j.icheatmasstransfer.2010.11.020>
- [42] Gado, R.A., Hebda, M., Lach, M., Mikula, J. (2020). Alkali activation of waste clay bricks: Influence of the silica modulus, SiO₂/Na₂O, H₂O/Na₂O molar ratio, and liquid/solid ratio. *Materials*, 13(2): 383. <https://doi.org/10.3390/ma13020383>
- [43] Borges, P.H., Banthia, N., Alcamand, H.A., Vasconcelos, W.L., Nunes, E.H. (2016). Performance of blended metakaolin/blastfurnace slag alkali-activated mortars. *Cement and Concrete Composites*, 71: 42-52. <https://doi.org/10.1016/j.cemconcomp.2016.04.008>
- [44] Muraleedharan, M., Nadir, Y. (2021). Factors affecting the mechanical properties and microstructure of geopolymers from red mud and granite waste powder: A review. *Ceramics International*, 47(10): 13257-13279. <https://doi.org/10.1016/j.ceramint.2021.02.009>
- [45] Xu, H., Van Deventer, J.S.J. (2000). The geopolymerisation of aluminosilicate minerals. *International journal of mineral processing*, 59(3): 247-266. [https://doi.org/10.1016/S0301-7516\(99\)00074-5](https://doi.org/10.1016/S0301-7516(99)00074-5)
- [46] Cheng, H., Lin, K.L., Cui, R., Hwang, C.L., Chang, Y.M., Cheng, T.W. (2015). The effects of SiO₂/Na₂O molar ratio on the characteristics of alkali-activated waste catalyst-metakaolin based geopolymers. *Construction and Building Materials*, 95: 710-720. <https://doi.org/10.1016/j.conbuildmat.2015.07.028>
- [47] Gao, K., Lin, K.L., Wang, D., Hwang, C.L., Tuan, B.L.A., Shiu, H.S., Cheng, T.W. (2013). Effect of nano-SiO₂ on the alkali-activated characteristics of metakaolin-based geopolymers. *Construction and Building Materials*, 48: 441-447. <https://doi.org/10.1016/j.conbuildmat.2013.07.027>
- [48] Zhang, P., Zheng, Y., Wang, K., Zhang, J. (2018). A review on properties of fresh and hardened geopolymer mortar. *Composites Part B: Engineering*, 152: 79-95. <https://doi.org/10.1016/j.compositesb.2018.06.031>
- [49] Mobili, A., Giosuè, C., Bitetti, M., Tittarelli, F. (2016). Cement mortars and geopolymers with the same strength class. *Proceedings of the Institution of Civil Engineers*, 169(1): 3-12. <https://doi.org/10.1680/coma.14.00063>
- [50] Bondar, D., Lynsdale, C.J., Milestone, N. B., Hassani, N., Ramezani-pour, A.A. (2011). Engineering properties of alkali-activated natural pozzolan concrete. *ACI Materials Journal*, 108(1): 64-72.
- [51] Mobili, A., Belli, A., Giosuè, C., Telesca, A., Marroccoli, M., Tittarelli, F. (2017). Calcium sulfoaluminate, geopolymeric, and cementitious mortars for structural applications. *Environments*, 4(3): 64. <https://doi.org/10.3390/environments4030064>
- [52] Longhi, M.A., Rodriguez, E.D., Walkley, B., Zhang, Z., Kirchheim, A.P. (2020). Metakaolin-based geopolymers: Relation between formulation, physicochemical properties and efflorescence formation. *Composites Part B: Engineering*, 182: 107671. <https://doi.org/10.1016/j.compositesb.2019.107671>
- [53] Chen, K., Wu, D., Yi, M., Cai, Q., Zhang, Z. (2021). Mechanical and durability properties of metakaolin blended with slag geopolymer mortars used for pavement repair. *Construction and Building Materials*, 281: 122566. <https://doi.org/10.1016/j.conbuildmat.2021.122566>
- [54] Khawaji, M. (2023). Hydration, microstructure, and properties of fly ash-based geopolymer: A Review. *Materials Science-Poland*, 41(2): 263-287. <https://doi.org/10.2478/msp-2023-0006>

NOMENCLATURE

MK	Metakaolin
GBFS	Granulated Blast-Furnace Slag
SS	Sodium Silicate Solution
MR	Molar Ratios
W	Water
AM	Aluminosilicate raw Materials
AS	Alkaline Solution
C	Cement
GM	Geopolymer Mortars
PM	Portland mortars
CC	Calcined Clays
FA	Fly Ash
WG	Waste Glass
XRF	X-Ray Fluorescence spectroscopy
SEM	Scanning Electron Microscope
NaOH	Sodium hydroxide
Ed	Dynamic modulus
CS	Compressive Strength
FS	Flexural Strength