



Article Strength Development and Durability of Metakaolin Geopolymer Mortars Containing Pozzolans under Different Curing Conditions

Burak Işıkdağ^{1,*} and Mohammad Rahim Yalghuz²

- ¹ Department of Construction, Porsuk Vocational School, Eskişehir Technical University, Eskişehir 26140, Turkey
- ² Department of Civil Engineering, Eskişehir Technical University, Eskişehir 26555, Turkey; mryalghuz@gmail.com
- * Correspondence: bisikdag@eskisehir.edu.tr; Tel.: +90-222-2137577

Abstract: This study presents the strength development and durability of heat and non-heat-cured geopolymer mortars (GMs) produced using metakaolin (MK), ground granulated blast-furnace slag (GGBFS), silica fume (SF), ground calcined perlite (GCP), raw perlite (RP), potassium hydroxide (KOH), sodium metasilicate (Na₂SiO₃), standard sand, and tap water. An optimal combination of MK with various pozzolans and constant solid/liquid and alkaline activator ratios were determined. It was found that the GMs, including MK and GGBFS with a 1.45 solid/liquid ratio and 2.0 alkaline activator ratio, resulted in compressive strength at 88 MPa. Analysis of GMs was performed using scanning electron microscopy (SEM), EDX (Energy Scattered X-ray Spectrophotometer), and X-ray diffraction (XRD). According to the results obtained, mainly alumino-silicate-based formation, potassium from KOH solution, and calcium from GGBFS were determined. The SEM images showed that the grains with high silica content, approximately $6-7 \mu m$ in size, are quartz crystals and embedded in the gel structure. The heat-cured GMs were exposed to MgSO₄, Na₂SO₄, and HCl solutions for the durability tests. The strength of the heat-cured GMs was found as sufficient. The use of pozzolans in GMs resulted in improvements in terms of strength and durability.

Keywords: pozzolans; geopolymers; strength; durability; microstructure

1. Introduction

Geopolymer is an alternative to ordinary Portland cement, which contributes to carbon dioxide emissions and global warming [1]. Compared to Portland cement, a lower temperature is required for its production and approximately 80% less CO₂ emissions occur [2,3]. Waste and industrial byproducts can be used as raw materials or inert fillers in geopolymers [4]. In this case, production prices decrease and geopolymers become sustainable construction materials. In the last decades, geopolymers have attracted increasing attention as they have performances comparable to Portland cement [4]. Geopolymer is produced by combining mineral materials with strong alkali solutions to form a three-dimensional amorphous alumino-silicate network [5]. As a result of the dissolution and rearrangement of alumino-silicate, oligomers are formed that bind large polymers together [6]. Such geopolymers produced from calcined materials such as metakaolin (MK) give high strength [4,7]. The crystal and chemical structures of natural minerals vary depending on the reaction of silica and alumino with alkaline solutions [8]. Amorphous geopolymers are produced at condensation temperatures between 20-90 °C while crystalline geopolymers are obtained in an oven between the temperatures of 150 and 200 °C [9,10]. Generally, geopolymers are produced through heat-curing for about 2–72 h [11,12]. While geopolymers do not



Citation: Işıkdağ, B.; Yalghuz, M.R. Strength Development and Durability of Metakaolin Geopolymer Mortars Containing Pozzolans under Different Curing Conditions. *Minerals* **2023**, *13*, 857. https://doi.org/10.3390/ min13070857

Academic Editors: Fernando Pelisser and Dachamir Hotza

Received: 2 May 2023 Revised: 21 June 2023 Accepted: 21 June 2023 Published: 24 June 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). form a calcium-silicate-hydrate gel, they use the polycondensation of silica and alumino precursors to achieve sufficient strength [13].

MK is unique in that it is an all-natural material that is not a byproduct of an industrial process [4]. It is obtained by the calcination of kaolin, a hydrated aluminosilicate mineral clay [4]. Furthermore, MK is a high-performance material used in geopolymer production due to its high SiO₂ and Al₂O₃ content. It is a white and amorphous alumino-silicate obtained by sintering kaolin clay at 600–900 °C temperatures. The Si:Al ratio of geopolymers produced from MK varies between 0.5 and 3.0. However, the high Si:Al ratio of a geopolymer requires high Na content which can be achieved by the addition of sodium hydroxide [14]. MK and slag-based geopolymers provide the highest performance in terms of strength and durability in geopolymer production. High compressive strength was achieved at the early stages with the geopolymers produced from calcined materials such as MK [15,16].

Granulated blast-furnace slag (GGBFS) is a byproduct obtained as a waste material in crude iron production [17]. About 95% of GGBFS consists of silica, calcium, magnesium, aluminum, and oxygen. The amorphous Si/Al ratio of GGBFS-blended geopolymers is between 2.3 and 3.1 [18]. Approximately 300 kg of slag is obtained from one ton of iron production [19]. Therefore, GGBFS is used in cement and geopolymer to provide environmental and economic benefits [20]. The most distinctive feature of the use of GGBFS in geopolymers is that it shortens the setting time [21]. GGBFS can be activated using a mild alkaline solution, while metakaolin and fly ash can be activated using a medium or high alkaline solution [22]. The increased GGBFS content in geopolymers leads to more calcium dissolution, thus producing more C-S-H gels [21,22]. Comparatively, the inclusion of GGBFS or high calcium material in the geopolymer system seems suitable for strength development [21,22].

Raw perlite (RP) is an acidic and glassy volcanic rock containing 2–6% water. It generally contains more than 70% silica and can be used in plaster, concrete, mortar, and ceiling flooring [23,24]. When heated up to 800–1150 °C, its volume increases by 10–30% and turns into low-density, high-heat-resistant, and white-colored expanded perlite (EP) [25,26]. EP is used as a heat and sound insulation material in the construction industry [26,27]. It is a lightweight insulation product with porous and hygroscopic features having a specific weight of 2.2–2.4 g/cm³, coarse density of $30-190 \text{ kg/m}^3$, and a thermal conductivity constant of 0.050–0.070 W/mK [26,27]. Recent studies have shown that ground calcined perlite (GCP) can be used in the production of geopolymers [26,27]. Increasing perlite fineness improves the compressive strength of geopolymer and chemical resistance to aggressive environments [1,25]. In general, fine perlite reduces pores in geopolymer, creates a more compact structure, and provides more strength [27]. The mechanical properties of geopolymers can be enhanced by increasing the curing temperature and duration as well as the activator molarity [23–27]. The addition of kaolin or metakaolin improves mechanical properties [25]. However, compressive strength decreases as a result of the increase in the amount of perlite used during the synthesis of geopolymers containing fly ash or GGBF [23]. Furthermore, partial replacement of the pozzolans with perlite leads to the formation of amorph N-A-S-H gel [1,23,27].

Silica fume (SF) is a byproduct of the silica and ferrosilica industry [5,13,28]. Therefore, the SiO₂ content of SF is related to the type of alloy produced [28]. SF is an excellent pozzolanic material thanks to having a very fine grain structure and containing a high ratio of SiO₂ [5,28]. The particle size of SF is usually 1 micron, and the surface area is between 13,000 and 30,000 m²/kg [13,28]. When SF is used with Portland cement, it causes excessive water consumption due to its fineness [5,13,28]. It is known that while the use of SF in geopolymers negatively affects workability, it positively affects the compressive and flexural strengths [13,28]. This is explained by the denser and void-free microstructure of the SF-modified geopolymer [13,28].

The aim of this study is to produce geopolymer mortars (GMs) by using MK, SF, GGBFS, RP, GCP, and alkaline solutions to reduce the amount of waste accumulated

in landfills. In this way, both the reduction of the damage to the environment and the costs of transportation and disposal of wastes can be saved. The study evaluated the strength development and durability of GMs containing multiple pozzolans under ambient and thermal curing. Furthermore, as is known, the sulfate attack is one of the most aggressive environmental degradations that affect the long-term durability of cementbased materials [29,30]. If MK is to find future use in a wide variety of cementitious applications, it is necessary to find out its effect on the sulfate resistance of concrete and mortar [29,30]. Therefore, the behavior of heat-cured GMs under the influence of sulfate and acid was also investigated. The use of GCP in GMs and the comparison with other geopolymers in terms of strength and durability is a novelty in this study. Scanning electron microscopy (SEM), EDX (Energy Scattered X-ray Spectrophotometer), and X-ray powder diffraction (XRD) analyses were performed to reveal the mechanism and formation of gel products that enhance the strength development of GMs. The results for emerging GMs can serve as the basis for the development of a high-strength building material for structural application. In addition, performance research on geopolymer binders containing GCP is not sufficient in the literature. To this end, we considered investigating the effect of GCP content on the mechanical performance, durability, and microstructure of GMs exposed to different curing conditions.

2. Materials and Methods

2.1. Materials

GMs were produced using MK, GGBFS, RP, GCP, SF, standard sand, potassium hydroxide (KOH), and sodium metasilicate (Na₂SiO₃) as shown in Figure 1. In addition, magnesium and sodium sulfate solutions were used for the durability tests. MK, GGBFS, SF, GCP, and RP were obtained from AVS Kaolin Industrial Minerals (İstanbul Turkey), Bolu Cement Factory (Bolu, Turkey), ETİ Electrometallurgy (Antalya, Turkey), and GENPER Companies (İstanbul, Turkey), respectively. The chemical and physical properties of mineral materials used in the study are given in Table 1. CEN standard sand was obtained from Limak Cement Factory (Kırklareli, Turkey). The grain size distribution of the sand used in the study is given in Table 2. Na₂SiO₃ (36% purity Na₂SiO₃) and KOH were obtained from Detsan Chemical Company (Eskişehir, Turkey) and were used at 0.65 M and 8 M in an alkaline solution, respectively. The chemical properties of Na₂SiO₃ and KOH are given in Tables 3 and 4.



Figure 1. Materials used in the study: (a) MK; (b) GGBFS; (c) SF; (d) GCP; (e) RP; (f) Na₂SiO₃; (g) standard sand; (h) KOH.

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	LOI	Specific Weight g/cm ³	Specific Surface cm ² /g
MK	50.00	45.00	0.50	1.00	0.50	0.40	0.51	0.24	1.10	2.6	17,100
GGBFS	40.55	12.83	1.10	0.75	35.58	5.87	0.68	0.78	0.80	2.9	4150
SF	91.57	0.45	0.20	0.00	0.70	0.33	2.58	0.55	1.80	2.2	195,000
GCP	74.00	14.33	0.97	0.00	0.50	0.28	4.95	3.00	0.10	2.8	3470
RP	71.00	13.50	1.00	0.00	1.20	0.15	5.50	3.30	3.30	2.1	4530

Table 1. Chemical and physical properties of mineral materials used in the study.

Table 2. Grain size distribution of standard sand.

Properties						
Sieve opening (mm)	0.08	0.16	0.50	1.00	1.60	2.00
Remaining %	99	87	72	34	6	0
Limit	99 ± 1	87 ± 5	67 ± 5	33 ± 5	6 ± 5	0

Table 3. Chemical properties of Na₂SiO₃.

Na ₂ O (%)	SiO ₂ (%)	Density (20 $^\circ$ C, g/mL)	Fe (%)	Heavy Metal (%)
8.75	27.43	1.371	0.005	0.005

Table 4. Chemical properties of KOH.

KOH (%)	K ₂ CO ₃ (%)	Cl (%)	SO ₄ (%)	NaOH (%)	Fe (%)
90–92	0.2–0.5	0.0031	0.0017-0.005	1.0	0.0001-0.0003

2.2. Method

GMs were produced as heat-cured and non-heat-cured within the study. Sixty specimens were produced for each group including twenty different mortar mixtures. Thus, three hundred specimens were produced in total. The mixture ratios were determined at the end of the trial mortar mixture productions. GGBFS was used at high rates in mixtures because it contributes sufficiently to the development of strength, is an industrial waste material, is economical, environmentally friendly, and reduces carbon dioxide emissions [17–22]. The ratios of standard sand, water, KOH, and Na₂SiO₃ were kept constant, and the ratios of MK, GGBFS, SF, GCP, and RP were mixed with different proportions, as shown in Table 5.

The mixtures were mixed in a mortar mixer and tested according to the TS EN 196-1 standard [31]. KOH was mixed with tap water for 24 h before the production and the solution was prepared by mixing it with Na₂SiO₃ the next day. During the production, the alkali solution consisting of KOH and Na₂SiO₃ was mixed with MK, SF, GGBFS, GCP, and RP in different proportions in the mortar mixer. GCP was used in the 50% water-saturated condition by weight. It was aimed to examine the change in geopolymers with the change of the weight ratios of the materials by keeping the water ratio constant. Volumetric stability of the mixtures was not aimed in the study because, since many mixture components were interacting, volumetric expansion or shrinkage may occur in both fresh and hardened mixtures.

The mixtures were then poured into $40 \times 40 \times 160 \text{ mm}^3$ molds and compacted in the shaking table. The group of specimens in the molds was kept for 24 h in a laboratory environment at room temperature and then subjected to oven curing at 100 °C for 24 h, and the other group of specimens in the molds was cured directly in a laboratory environment at room temperature for seven days. This task was conducted without any covering or coating process. Blistering or cracking was not observed on the GMs which were taken out of the oven.

Mix Code	Mix No	МК	GGBFS	GCP	RP	SF	Water	кон	Na ₂ SiO ₃	Sand	CaO/SiO ₂	Al ₂ O ₃ /SiO ₂	CaO/Al ₂ O ₃
	1	9.12	13.68	0.00	0.00	0.00	9.58	4.56	1.48	61.57	0.48	0.55	0.88
MK-	2	6.84	15.96	0.00	0.00	0.00	9.58	4.56	1.48	61.57	0.57	0.48	1.20
GGBFS	3	4.56	18.24	0.00	0.00	0.00	9.58	4.56	1.48	61.57	0.67	0.40	1.65
	4	2.28	20.52	0.00	0.00	0.00	9.58	4.56	1.48	61.57	0.77	0.33	2.33
MIZ	1	5.70	15.96	0.00	0.00	1.14	9.58	4.56	1.48	61.57	0.54	0.41	1.34
MK-	2	4.56	15.96	0.00	0.00	2.28	9.58	4.56	1.48	61.57	0.52	0.34	1.53
GGBF5-	3	3.42	15.96	0.00	0.00	3.42	9.58	4.56	1.48	61.57	0.50	0.28	1.78
SF	4	2.28	15.96	0.00	0.00	4.56	9.58	4.56	1.48	61.57	0.48	0.23	2.13
MK-	1	5.70	13.68	3.42	0.00	0.00	9.58	4.56	1.48	61.57	0.44	0.41	1.08
GGBFS-	2	4.56	14.82	2.28	0.00	1.14	9.58	4.56	1.48	61.57	0.47	0.35	1.34
GCP-	3	3.42	15.96	1.14	0.00	2.28	9.58	4.56	1.48	61.57	0.51	0.30	1.69
SF	4	2.28	17.10	0.00	0.00	3.42	9.58	4.56	1.48	61.57	0.54	0.25	2.19
	1	4.56	17.10	1.14	0.00	0.00	9.58	4.56	1.48	61.57	0.60	0.39	1.52
MK-	2	4.56	15.96	2.28	0.00	0.00	9.58	4.56	1.48	61.57	0.54	0.38	1.40
GGBFS-	3	4.56	14.82	3.42	0.00	0.00	9.58	4.56	1.48	61.57	0.48	0.38	1.28
GCP	4	4.56	13.68	4.56	0.00	0.00	9.58	4.56	1.48	61.57	0.43	0.37	1.17
	1	18.24	0.00	0.00	4.56	0.00	9.58	4.56	1.48	61.57	0.00	0.72	0.00
MK-	2	15.96	0.00	0.00	6.84	0.00	9.58	4.56	1.48	61.57	0.00	0.64	0.00
RP	3	13.68	0.00	0.00	9.12	0.00	9.58	4.56	1.48	61.57	0.00	0.57	0.00
	4	11.40	0.00	0.00	11.40	0.00	9.58	4.56	1.48	61.57	0.00	0.50	0.00

Table 5. Mixing ratios of GMs by weight (%), and compound ratios.

The flexural and compressive strength tests were performed on the specimens according to standards after the curing process, as shown in Figure 2 [31]. Durability and unit weights were examined on heat-cured GMs because of their higher performance compared to non-heat-cured GMs. In addition, SEM, EDX, and XRD analyses were performed on the heat-cured GMs which had the highest strength from each mixture.



Figure 2. Specimens and test method: (**a**) curing specimens; (**b**) compressive strength test; (**c**) flexural strength test.

The heat-cured GMs produced for durability tests were kept in MgSO₄, Na₂SO₄, and HCl solutions for fourteen weeks. A solution with a pH value of 2 was prepared by mixing HCl at 30% purity and tap water. The pH meter was used to measure the pH values of the solutions, as given in Table 6. By mixing MgSO₄ and Na₂SO₄ separately with tap

water, two different solutions with 5% concentration were prepared. All the solutions were then renewed within four-week periods during the experiment by adding water or material and checking the pH when necessary. At the end of this period, the specimens were removed from the solutions and washed with tap water and their surfaces were dried. The mass loss and visual changes of the specimens were determined according to the ASTM C267-01 standard [32]. The flexural and compressive strength tests were performed on the specimens, and the results were interpreted by comparing them with control specimens at the same age.

Table 6. pH values of solutions.

Solution	рН
5% HCl	2.00
$5\% \text{ Na}_2 \text{SO}_4$	7.75
5% MgSO4	8.15

3. Results and Discussion

3.1. Influence of Multi Pozzolans on the Unit Weight of Heat-Cured GMs

Unit weights were determined for the heat-cured GMs. As seen in Figure 3, unit weights varied between 1.65 and 2.25 g/cm³. The lowest and highest unit weights were obtained in the 4MK-GGBFS-GCP and 4MK-GGBFS, respectively. Due to the use of multiple pozzolans and the complex geopolymerization reactions, irregular decreases and increases in the unit weight of the mixtures were observed. In addition, the unit weights of the GMs with GCP were lower than the others. This is because the unit weight of GCP is lower than the other pozzolans used in the study. Since RP had a slightly lower unit weight, GMs with RP also had lower unit weights.





3.2. Influence of Multi Pozzolans on the Strength of Heat and Non-Heat Cured GMs

As seen in Figure 4, the flexural strength of the heat-cured GMs varied between 2.5 and 10.0 MPa, while the flexural strength of the non-heat-cured GMs varied between 0.7 and 4.5 MPa. Furthermore, as seen in Figure 5, the compressive strength of the heat-cured GMs varied between 10 and 88 MPa, while the compressive strength of non-heat-cured mortars varied between 2 and 32 MPa. In both curing effects, the strengths showed a similar

tendency to decrease and increase. In the MK-GGBFS, decreasing MK and increasing GGBFS ratios caused a decrease in strength. Partial displacement of MK by GBFS slightly increased porosity due to C-A-S-H gel formation in the presence of calcium from GBFS. The rapid curing of geopolymers and unreacted water caused the formation of gaps and cracks in the internal structure and loss of strength [20,23,33]. The ratio of MK used in the MK-GGBFS-SF was lower, and a small decrease in strength was observed with the increase in the amount of SF and the decrease in the MK ratio. In the MK-GGBFS-GCP, the GCP ratio increased and the GGBFS ratio decreased by keeping the MK ratio constant. Thus, compared with mortar mixes containing SF, GCP, and RP, the higher availability of GGBFS led to higher mechanical and durability properties due to additional C-A-S-H gel formation [33,34]. As a result of the incomplete dispersion of SF, replacing MK with SF resulted in a mortar with a higher porosity and lower strength [33,35]. In the MK-GGBFS-GCP-SF, increases and decreases in strength were both observed with a decreasing GCP ratio and an increasing SF ratio. The reason for this irregularity was explained by the simultaneous decrease and increase in the ratio of four different pozzolans and the change in the chemical composition required for alkali activation. However, replacing N-A-S-H (Sodium aluminosilicate hydrate) with C-A-S-H gel led to a decrease in strength [33–36]. Furthermore, while the MK ratio decreased and the RP ratio increased in the MK-RP, no significant change was observed in the strengths of the mixtures. Rocha et al. have found similar strengths for GMs and proved that they can be used for applications where high early strength is required [36].



Figure 4. Flexural strength of heat-cured, and non-heat-cured GMs.

According to the results, sufficient strength showed that the production of GMs could be realized without heat curing. The increase in the content of Al₂O₃ and SiO₂ improved the geopolymerization and produced N-A-S-H and C-A-S-H gel, thus enhancing the strength properties of geopolymers [34,35]. When Figures 4 and 5 were examined, it was observed that the flexural and compressive strengths of heat-cured mortars were much higher. The increased curing temperature allowed rapid dissolution of the amorphous structures in MK at about 100 °C [2,37]. In general, the heat-curing effect was mainly observed in MK-GGBFS and MK-RP compared to the mixtures. In these two mixtures, flexural strengths increased 2–2.5 times under heat curing while compressive strengths increased approximately 3–3.5 times. Thus, raising the curing temperature was advantageous for removing water from the reaction system, which accelerated the growth of the gel phase. The flexural and compressive strengths of the heat-cured MK-GGBFS-SF, MK-GGBFS-GCP-SF, and MK-GGBFS-GCP increased approximately 1.3–1.5 and 2–2.5 times, respectively, compared to the non-heat-cured GMs. For this reason, the strength of the heat-cured GMs was considerably higher than that of the non-heat-cured GMs [2,37].



Figure 5. Compressive strength of heat-cured, and non-heat-cured GMs.

3.3. Durability of Heat-Cured GMs

Alkaline-activated mortars or geopolymers with low or no calcium may be more resistant to sulfate attack due to the high chemical stability of the N-A-S-H gel and the absence of calcium, which inhibits the formation of expansion-related crystalline phases [33]. Accordingly, due to the interaction on the surface of the GMs kept in acid and sulfate solutions, crack formation, whitening, and foaming were not observed, as seen in Figure 6. A slight reduction in overall weight and strength was observed compared to the control GMs.

3.3.1. Mass Loss in Heat-Cured GMs under the Influence of Acid and Sulphate

When the GMs kept in the solution and the GMs not kept in the solution were compared, there was a loss of mass at different rates depending on the ratios of the mixture components. The mass losses of the mixtures containing GCP and RP were higher than those in the other mixtures. Smaller mass losses were observed in GMs containing GGBFS, SF, and high MK content. However, denser and low-permeability mortars did not allow ion exchange between solution and matrix [33]. Thus, heat-cured GMs showed insignificant mass losses while under the effect of acid and sulfate as seen in Table 7.

3.3.2. Strength of Heat-Cured GMs under the Influence of Acid and Sulfate

When the GMs kept in the solution and the GMs not kept in the solution were compared, the compressive and flexural strengths decreased at different rates depending on the ratios of the mixture components. The strength of mixtures containing EP and RP decreased at a higher rate than those of other mixtures. Smaller mass losses were observed in GMs containing GGBFS, SF, and high MK content. While strength loss was observed in all mixtures under the influence of acid and sulfate, higher reductions in acid and sulfate effects were observed especially in MK-GGBFS-GCP and MK-RP. The increase in RP and GCP ratios in the mixtures was generally caused by a decrease in the strength under the influence of acid and sulfate, as seen in Figures 7 and 8. When the compressive and flexural strengths were examined, the HCl, Na₂SO₄, and MgSO₄ solutions had similar effects on all mixtures. For this reason, the strength losses brought the values close to each other. Furthermore, the crystallization of Na₂SiO₃ and SiO₂ on the surface of the GMs indicates that the matrix decomposes, leading to a loss of strength [33]. However, this type of formation was not observed in the study.



Figure 6. Heat-cured GMs kept in: (a) HCl solution; (b) Na₂SO₄ solution; (c) MgSO₄ solution.

M. C. L	N			
Mix Code	INO	MgSO ₄	Na_2SO_4	HC1
	1	1.21	0.34	1.04
MIC CODEC	2	0.86	0.53	0.52
MK-GGBFS	3	0.85	0.51	1.55
	4	0.16	0.68	0.17
	1	0.71	0.52	0.17
MIC CODEC CE	2	1.03	0.69	0.52
MK-GGDF5-5F	3	1.05	0.71	0.69
	$ \begin{array}{c} 1\\ 2\\ 3\\ 4\\ 1\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\ 2\\$	1.57	0.17	1.76
	1	1.32	0.56	0.95
MK-GGBFS-	2	1.51	0.37	0.19
GCP-SF	3	1.62	0.35	0.17
	4	1.61	0.72	1.15
	1	1.74	0.39	0.39
MK-GGBFS-	2	1.31	0.56	0.93
GCP	3	1.64	0.37	0.36
	4	1.03	0.84	0.42
	1	1.66	3.93	4.42
MIZ DD	2	2.59	2.87	4.38
WIN-KP	3	1.84	3.05	4.23
	4	2.33	3.47	4.13

Table 7. Mass loss of heat-cured GMs under the influence of acid and sulfate.



Figure 7. Flexural strength of heat-cured GMs kept in Na₂SO₄, MgSO₄, and HCl solutions.



Figure 8. Compressive strength of heat-cured GMs kept in Na₂SO₄, MgSO₄, and HCl solutions.

3.4. Influence of Multi Pozzolans on the Microstructure and Mineralogic Properties of Heat-Cured Geopolymers

The samples with the highest strength from each mixture were used to carry out SEM and XRD analyses. The differences in the morphologies of the five GMs were evaluated in terms of their porosity, homogeneity, and microcracks. Homogeneous, dense, and continuous matrices consisting of alumino-silicate gel were observed in SEM images along with the agglomeration of grains and there were some gaps between grains.

Figure 9a,b shows that the microstructures of the samples are quite dense, and layered structures are observed in different regions. These layered formations reveal the geopolymerization of multi pozzolans. This shows that the strengths are compatible with each other, and the aggregate binder–paste interface is sufficient. From the dense microstructure of the samples, it can be concluded that fine materials such as MK and GGBFS create high geopolymerization. In general, the higher amount of MK in the mixture reveals a denser microstructure. The increase in the variety of materials used in the mixtures indicates that the homogeneity in the microstructure decreases. The fact that the grain sizes of the materials entering the mixture are different is also another factor for this decrease. The excessively microcracked morphology indicates delayed geopolymerization and the pores presented microcracks, which is a characteristic of fast drying [36]. Since the highest strength is obtained in 1MK-GGBFS and 1MK-GGBFS-SF samples, it is concluded that the densities in the microstructure of the samples supported this situation.



Figure 9. SEM 250× image of heat-cured GMs: (**a**) 1MK-GGBFS; (**b**) 1MK-GGBFS-SF; (**c**) 2MK-GGBFS-GCP-SF; (**d**) 1MK-GGBFS-GCP; (**e**) 1MK-RP.

When Figure 9c–e are examined, it is seen that the pores are high in 1MK-GGBFS-GCP and 1MK-RP samples, which causes a decrease in strength. In general, better gel formation

is observed in mixtures containing GGBFS and SF compared to mixtures containing RP and GCP. This is due to the relatively larger particle size and porous nature of RP and GCP. In addition, it is concluded that the morphology of the samples is denser and the porosity decreases with the increase of MK ratio. The constant molarity and constant curing temperature of KOH and Na₂SiO₃ used in the production of the mixtures are supported by the reticulated structure formed in the geopolymerization mechanism. When the crack formations in the samples are compared, it is noteworthy that the 1MK-GGBFS sample is in better condition than the other samples; however, the strength of 1MK-GGBFS-SF is close to 1MK-GGBFS despite its relatively cracked structure. The unreacted raw MK particles may act as structural defects reducing the compressive strength of the mortar [36,38].

EDX analysis was performed to determine the elements contained in the grains and the gel structure and the ratios of the elements were determined. Local EDX analyses for grains in the sample matrix and binding interface are shown in Figure 10. This shows a predominantly alumino-silicate-based formation, potassium from the KOH solution used, and calcium from the GGBFS. The images reveal that the geopolymerisation reactions of GGBFS activated with an alkaline solution produce a denser microstructure [23]. SEM images show that the grains with high silica content, approximately 6–7 μ m in size, are quartz crystals and embedded in the gel structure. Furthermore, the ratio of Si/Na or K atoms in the alkali silicate solution affects the degree of polymerization of the dissolved species [39,40]. In addition, silica content is higher both as oxides and compounds in all regions selected in EDX analysis. The fact that the potassium and aluminum oxide ratios are not very variable indicates a reaction around the silica particles. Thus, the high potassium content gives information about the geopolymerization mechanism that occurs mostly on the surface.

As seen in Figure 11, the phases in the samples were determined by examining the crystal structures of the solids by XRD analysis. X-ray scattering techniques were applied without changing the properties of the examined sample. The rough samples were ground to a depth of ~63 μ m and the samples were kept in an oven at ~105 \pm 5 °C for 4 h to be dried and then they were measured in the standard scanning range ($2\theta = 5^{\circ}-70^{\circ}$). According to XRD patterns, MK is mainly amorphous while the crystals identified in MK are kaolinite, mullite, and quartz. Some peaks disappear after alkali activation, indicating that some crystals are partly dissolved during the reaction [16,41]. Quartz, albite, leucite, lycetite, calcian, and alumino-silicate minerals are identified in the GMs according to XRD diffractograms. The highest peaks are observed in quartz and albite is found in all mixtures. Large peaks displayed at $20^{\circ}-25^{\circ}$ 20 in the MK are characteristic of aluminosilicate glasses [16,42]. This peak becomes much less in the patterns of MK pastes, indicating the rapid dissolution of the raw material during the first hours of activation [16]. The XRD patterns of MK-based geopolymer pastes generally appear at peaks at about 29° 20 in association with N-A-S-H type gel formation [16,43,44]. XRD plots show the X-ray pattern of MK and show peaks of crystalline phases corresponding to illite, quartz, hematite, and anatase [45,46]. The peaks around 30.27°, 32.1°, 34.2°, 37.9°, 40.2°, 41.3°, and 46.6° 2θ in the patterns generally indicate sodium carbonates [16].



Figure 10. EDX analysis of heat-cured GMs: (**a**) 1MK-GGBFS; (**b**) 1MK-GGBFS-SF; (**c**) 2MK-GGBFS-GCP-SF; (**d**) 1MK-GGBFS-GCP; (**e**) 1MK-RP.



Figure 11. Cont.



Figure 11. XRD analysis of heat-cured GMs: (**a**) 1MK-GGBFS; (**b**) 1MK-GGBFS-SF; (**c**) 2MK-GGBFS-GCP-SF; (**d**) 1MK-GGBFS-GCP; (**e**) 1MK-RP.

The reactive soluble aluminosilicate, when combined with calcium sources, increased the silicon, aluminum, and calcium species in the aqueous phase, resulting in higher polycondensation [22,47]. Thus, the dense structure was defined by the dissolution of alkali-activated Al^{3+} , Si^{4+} , and Ca^{2+} [22,47]. Excess Na^+ ions disrupted the charge balance in the internal structure, and the liquid content of Na_2SiO_3 promoted intergranular bonding [22,48]. A high Si component promoted oligomer silicate formation by forming abundant silicate component, while Al species caused high $Al(OH)_4$ formation, resulting in oligomers silicate [22,49]. Ca, Si, and Al were dispersed to form the Si-O-Si/Al/Ca link of geopolymers and the tobermorite phase [22]. The Si-linkage of geopolymers was combined with the ionic bond of Ca-O to form a stronger chemical bond. While Ca^{2+} formed a strong ionic bond with Si⁴⁺ through oxygen atoms, excess Ca^{2+} combined with OH to form $Ca(OH)_2$. Ca^{2+} dissolved from GGBFS and reacted with OH in an alkaline solution to form calcium hydroxide (Ca(OH)₂), which then reacted with carbon dioxide (CO₂) to form calcite [22]. Thus, Ca^{2+} from GGBFS contributes to strength development.

4. Conclusions

- The lower unit weight of GCP and RP led to lower unit weight in GMs;
- As the rate of using pozzolan instead of MK increased, the strength of all mixtures decreased;
- The incomplete dispersion of SF caused the GMs to have higher porosity and lower durability;
- Partial displacement of MK by GBFS increased porosity due to the formation of C-A-S-H gel in the presence of calcium from GBFS;
- Due to RP's low contribution to strength, replacing MK with 4.5% RP reduced strength significantly. However, GMs containing GCP were found to be higher than GMs containing RP. This indicated that GCP contributed more to geopolymerization in the GMs compared to RP;
- Compared with mortar mixes containing SF, GCP, and RP, the higher availability of GGBFS led to higher strength and durability due to additional C-A-S-H gel formation;
- The increase in Al₂O₃ and SiO₂ content improved the geopolymerization and increased the strength by producing N-A-S-H and C-A-S-H gels;
- Heat curing allowed rapid dissolution of the amorphous structures in MK, which accelerated the growth of the gel phase;
- Color change, crack formation, and mass loss were not observed in the GMs under the influence of acid and sulfate;
- The strength decreased as the amount of pozzolan substituted for MK increased under the influence of acid and sulfate;
- Considering the waiting times of the GMs in acid and sulfate solutions, strength losses were found acceptable;
- SEM images showed aluminosilicate gel and grains combined with homogeneous, dense, and continuous matrices. With the determination of the binder liquid phases in the interface region, it was observed that the particles with a size of 6–7 μm with high silica content were seen as quartz crystals in gel structure. The dense structure was defined by the dissolution of alkali-activated Al³⁺, Si⁴⁺, and Ca²⁺;
- EDX analysis mainly included alumino-silicate, potassium from KOH solution, and calcium from GGBFS. The soluble aluminosilicate, when combined with calcium sources, increased the silicon, aluminum, and calcium species, resulting in higher polycondensation;
- XRD diffractograms showed the presence of quartz, albite, leucite, lycetite, calcyan, and alumino-silicate minerals in the GMs. The highest peaks were observed in quartz and albite in all mixtures. A high Si component promoted oligomer silicate formation by forming abundant silicate component;
- The 32 MPa strength of non-heat-cured GMs showed that the production of GMs could be carried out without heat curing. Ca²⁺ from GGBFS contributes to strength development.

In summary, the combined use of metakaolin and GGBFS in alkali-activated materials gives sufficient results in improving sulfate resistance and microstructures, which are of great importance for the practical application of geopolymers and the diversified use of GGBFS.

Author Contributions: Conceptualization, B.I. and M.R.Y.; methodology, B.I.; software, B.I. and M.R.Y.; validation, B.I. and M.R.Y.; formal analysis, B.I.; investigation, B.I. and M.R.Y.; resources, B.I.; data curation, B.I.; writing—original draft preparation, B.I.; writing—review and editing, B.I.; visualization, M.R.Y.; supervision, B.I.; project administration, B.I.; funding acquisition, B.I. and M.R.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: This work takes part of the master's thesis titled "Investigation of geopolymer mortar production and durability using different type of materials" written by Yalghuz M.R., supervisory by IŞIKDAĞ B. and conducted in Eskişehir Technical University, Institute of Graduate.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Kurek, I.; Florek, E.; Gozdur, W.; Ziejewska, C.; Marczyk, J.; Łach, M.; Korniejenko, K.; Duzy, P.; Choinska, M.; Szechynska-Hebda, M.; et al. Foamed eco-geopolymer modified by perlite and cellulose as a construction material for energy-efficient buildings. *Energies* 2022, 15, 4297. [CrossRef]
- Rovnaník, P. Effect of curing temperature on the development of hard structure of metakaolin-based geopolymer. *Constr. Build. Mater.* 2010, 24, 1176–1183. [CrossRef]
- 3. Habert, G.; d'Espinose de Lacaillerie, J.B.; Roussel, N. An environmental evaluation of geopolymer based concrete production: Reviewing current research trends. *J. Clean. Prod.* **2011**, *19*, 1229–1238. [CrossRef]
- 4. Catauro, M.; Tranquillo, E.; Barrino, F.; Poggetto, G.D.; Blanco, I.; Cicala, G.; Ognibene, G.; Recca, G. Mechanical and thermal properties of fly ash-filled geopolymers. *J. Therm. Anal. Calorim.* **2019**, *138*, 3267–3276. [CrossRef]
- Duan, P.; Yan, C.; Zhou, W. Compressive strength and microstructure of fly ash based geopolymer blended with silica fume under thermal cycle. *Cem. Concr. Compos.* 2017, 78, 108–119. [CrossRef]
- 6. Erfanimanesh, A.; Sharbatdar, M.K. Mechanical and microstructural characteristics of geopolymer paste, mortar, and concrete containing local zeolite and slag activated by sodium carbonate. *J. Build. Eng.* **2020**, *32*, 101781. [CrossRef]
- 7. Herwani; Pane, I.; Imran, I.; Budiono, B. Compressive strength of fly ash-based geopolymer concrete with a variable of sodium hydroxide (NaOH) solution molarity. *MATEC Web Conf.* **2018**, *147*, 01004. [CrossRef]
- 8. Topçu, İ.B.; Toprak, M.U.; Uygunoğlu, T. Durability and microstructure characteristics of alkali activated coal bottom ash geopolymer cement. *J. Clean. Prod.* **2014**, *81*, 211–217. [CrossRef]
- 9. Davidovits, J. Geopolymers: Inorganic polymeric new materials. J. Ther. Anal. 1991, 37, 1633–1656. [CrossRef]
- Yang, K.H.; Song, J.K.; Song, K.I. Assessment of CO₂ reduction of alkali-activated concrete. J. Clean. Prod. 2013, 39, 265–272. [CrossRef]
- 11. Poggetto, G.D.; D'Angelo, A.; Blanco, I.; Piccolella, S.; Leonelli, C.; Catauro, M. FT-IR study, thermal analysis, and evaluation of the antibacterial activity of a MK-geopolymer mortar using glass waste as fine aggregate. *Polymers* **2021**, *13*, 2970. [CrossRef]
- 12. Lee, W.; Lin, K.; Chang, T.; Ding, Y.; Cheng, T. Sustainable development and performance evaluation of marble-waste-based geopolymer concrete. *Polymers* **2020**, *12*, 1924. [CrossRef]
- 13. Okoye, F.N.; Durgaprasad, J.; Singh, N.B. Effect of silica fume on the mechanical properties of fly ash based-geopolymer concrete. *Ceram. Int.* **2016**, *42*, 3000–3006. [CrossRef]
- 14. Temuujin, J.; Minjigmaa, A.; Rickard, W.; Lee, M.; Williams, L.; Van Riessen, A. Preparation of metakaolin based geopolymer coatings on metal substrates as thermal barriers. *Appl. Clay Sci.* **2009**, *46*, 265–270. [CrossRef]
- 15. Görhan, G.; Aslaner, R.; Şinik, O. The effect of curing on the properties of metakaolin and fly ash-based geopolymer paste. *Compos. B Eng.* **2016**, *97*, 329–335. [CrossRef]
- 16. Li, Z.; Zhang, S.; Zuo, Y.; Chen, W.; Ye, G. Chemical deformation of metakaolin based geopolymer. *Cem. Concr. Res.* 2019, 120, 108–118. [CrossRef]
- 17. Pal, S.; Mukherjee, A.; Pathak, S. Investigation of hydraulic activity of ground granulated blast furnace slag in concrete. *Cem. Concr. Res.* 2003, *33*, 1481–1486. [CrossRef]
- 18. Lau, C.K.; Rowles, M.R.; Parnham, G.N.; Htut, T.; Ng, T.S. Investigation of geopolymers containing fly ash and ground-granulated blast-furnace slag blended by amorphous ratios. *Constr. Build. Mater.* **2019**, 222, 731–737. [CrossRef]
- 19. Escalante, J.; Gómez, L.; Johal, K.; Mendoza, G.; Mancha, H.; Méndez, J. Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions. *Cem. Concr. Res.* 2001, *31*, 1403–1409. [CrossRef]
- Perná, I.; Hanzlíček, T. The setting time of a clay-slag geopolymer matrix: The influence of blast-furnace-slag addition and the mixing method. J. Clean. Prod. 2016, 112, 1150–1155. [CrossRef]
- 21. Cheng, T.W.; Chiu, J.P. Fire-resistant geopolymer produced by granulated blast furnace slag. *Miner. Eng.* **2003**, *16*, 205–210. [CrossRef]
- 22. Aziz, I.H.; Abdullah, M.M.A.B.; Salleh, M.A.A.M.; Azimi, E.A.; Chaiprapa, J.; Sandu, A.V. Strength development of solely ground granulated blast furnace slag geopolymers. *Constr. Build. Mater.* **2020**, 250, 118720. [CrossRef]
- Sarı, A.; Tuzen, M.; Cıtak, D.; Soylak, M. Adsorption characteristics of Cu(II) and Pb(II) onto expanded perlite from aqueous solution. *J. Hazard. Mater.* 2007, 148, 387–394. [CrossRef] [PubMed]
- Aziz, A.; Bellil, A.; Hassani, I.E.A.E.; Fekhaoui, M.; Achab, M.; Dahrouch, A.; Benzaouak, A. Geopolymers based on natural perlite and kaolinic clay from Morocco: Synthesis, characterization, properties, and applications. *Ceram. Int.* 2021, 47, 24683–24692. [CrossRef]
- 25. Mohabbi, M. Investigation of sulfates effects in perlite-based geopolymer. Struct. Concr. 2019, 20, 1402–1410. [CrossRef]
- Çelikten, S.; Işıkdağ, B. Properties of geopolymer mortars derived from ground calcined perlite and NaOH solution. *Eur. J. Environ. Civ. Eng.* 2021, 26, 1879939. [CrossRef]

- 27. Çelikten, S.; Işıkdağ, B. Strength development of ground perlite-based geopolymer mortars. *Adv. Concr. Constr.* **2020**, *9*, 227–234. [CrossRef]
- Siddique, R. Utilization of silica fume in concrete: Review of hardened properties. *Resour. Conserv. Recycl.* 2011, 55, 923–932.
 [CrossRef]
- 29. Al-Akhras, N.M. Durability of metakaolin concrete to sulfate attack. Cem. Concr. Res. 2006, 36, 1727–1734. [CrossRef]
- 30. Khatib, J.M.; Wild, S. Sulfate resistance of metakaolin concrete. Cem. Concr. Res. 1998, 28, 83–92. [CrossRef]
- 31. *TS EN 196-1:2016*; Methods of Testing Cement-Part 1: 'Determination of Strength'. Turkish Standards Institution: Ankara, Turkey, 2016.
- ASTM C 267-01:2020; Standard Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes. ASTM International: West Conshohocken, PA, USA, 2020.
- Alcamand, H.A.; Borges, P.H.R.; Silva, F.A.; Trindade, A.C.C. The effect of matrix composition and calcium content on the sulfate durability of metakaolin and metakaolin/slag alkali-activated mortars. *Ceram. Int.* 2018, 44, 5037–5044. [CrossRef]
- 34. Huseien, G.F.; Mirza, J.; Ismail, M.; Ghoshal, S.K.; Ariffin, M.A.M. Effect of metakaolin replaced granulated blast furnace slag on fresh and early strength properties of geopolymer mortar. *Ain Shams Eng. J.* **2018**, *9*, 1557–1566. [CrossRef]
- Dombrowski, K.; Buchwald, A.; Weil, M. The influence of calcium content on the structure and thermal performance of fly ash based geopolymers. J. Mater. Sci. 2007, 42, 3033–3043. [CrossRef]
- 36. Rocha, T.S.; Dias, D.P.; França, F.C.C.; de Salles Guerra, R.R.; de Oliveira Marques, L.R.C. Metakaolin-based geopolymer mortars with different alkaline activators (Na⁺ and K⁺). *Constr. Build. Mater.* **2018**, *178*, 453–461. [CrossRef]
- 37. Chen, L.; Wang, Z.; Wang, Y.; Feng, J. Preparation and properties of alkali activated metakaolin-based geopolymer. *Materials* **2016**, *9*, 767. [CrossRef]
- Zhang, F.; Zhang, L.; Liu, M.; Mu, C.; Liang, Y.N.; Hu, X. Role of alkali cation in compressive strength of metakaolin based geopolymers. *Ceram. Int.* 2017, 43, 3811–3817. [CrossRef]
- Provis, J.L.; Van Deventer, J.S.J. Direct measurement of the kinetics of geo-polymerisation by in-situ energy dispersive X-ray diffractometry. J. Mater. Sci. 2007, 42, 2974–2981. [CrossRef]
- 40. Davidovits, J. Geopolymers and geopolymeric materials. J. Therm. Anal. Calorim. 1989, 35, 429–441. [CrossRef]
- 41. Bauer, A.; Berger, G. Kaolinite and smectite dissolution rate in high molar KOH solutions at 35 and 80 °C. *Appl. Geochem.* **1998**, *13*, 905–916. [CrossRef]
- Provis, J.L.; Lukey, G.C.; Van Deventer, J.S.J. Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results. *Chem. Mater.* 2005, 17, 3075–3085. [CrossRef]
- Yunsheng, Z.; Wei, S.; Zongjin, L. Composition design and microstructural characterization of calcined kaolin-based geopolymer cement. *Appl. Clay Sci.* 2010, 47, 271–275. [CrossRef]
- 44. Sun, W.; Zhang, Y.; Lin, W.; Liu, Z. In situ monitoring of the hydration process of K-PS geopolymer cement with ESEM. *Cem. Concr. Res.* **2004**, *34*, 935–940. [CrossRef]
- 45. Bewa, C.N.; Tchakouté, H.K.; Fotio, D.; Rüscher, C.H.; Kamseu, E.; Leonelli, C. Water resistance and thermal behavior of metakaolin-phosphate-based geopolymer cements. *J. Asian Ceram. Soc.* **2018**, *6*, 271–283. [CrossRef]
- Yalghuz, M.R. Investigation of Geopolymer Mortar Production and Durability Using Different Type of Materials. Master's Thesis, YOKSIS Electronic Theses and Dissertations Center, Eskişehir Technical University, Eskişehir, Turkey, 2020.
- 47. Toniolo, N.; Boccaccini, A.R. Fly ash-based geopolymers containing added silicate waste. A review. *Ceram. Int.* **2017**, *43*, 14545–14551. [CrossRef]
- 48. Zivica, V. Effects of type and dosage of alkaline activator and temperature on the properties of alkali-activated slag mixtures. *Constr. Build Mater.* **2007**, *21*, 1463–1469. [CrossRef]
- 49. Shi, C.; Jiménez, A.F.; Palomo, A. New cements for the 21st century: The pursuit of an alternative to Portland cement. *Cem. Concr. Res.* **2011**, *41*, 750–763. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.