Turkish Journal of Civil Engineering, 2024, 47-64, Paper 787, ***Research Article***

Optimization of Hybrid Microwave Curing Approach Based On the Performance of Metakaolin-Based Geopolymer Mortars

Yiğit Alper ATALAY[1]
Tolga AYDIN[2]
Zeynep BAŞARAN BUNDUR[3*]
Pozhhan MOKHTARI[4]
Mehmet Ali GÜLGÜN[5]
Zoubeir LAFHAJ[6]

ABSTRACT

Geopolymer binders have been highlighted due to their low carbon emission during production and processing. While metakaolin and F-type fly ash are commonly used as raw materials for aluminosilicate-based geopolymers, the long heat-curing requirements for hardening and strength development still pose challenges. This paper investigates the possible use of a hybrid microwave curing technique to design a set-on-demand approach to reduce the duration of heat curing in metakaolin-based geopolymer. The experimental design was established for samples with three different molar ratios (MR; 1.3,1.5, and 1.7) containing metakaolin, fly ash, and silica fume. Samples were subjected to 3 different curing regimes: oven curing, microwave (MW) curing, and hybrid curing (a combination of optimized microwave and oven curing). The performance evaluation was based on compressive strength, dimensional stability, and alkali leaching (efflorescence). Implementing only MW curing resulted in a significant decrease in compressive strength

Note:
- This paper was received on October 12, 2023 and accepted for publication by the Editorial Board on June 14, 2024.
- Discussions on this paper will be accepted by January 31, 2025.
- https://doi.org/10.18400/tjce.1322047

1 Ozyegin University, Civil Engineering Department, Istanbul, Türkiye
alper.atalay@ozu.edu.tr - https://orcid.org/0000-0002-2296-1940

2 Ozyegin University, Civil Engineering Department, Istanbul, Türkiye
tolga.aydin@ozu.edu.tr - https://orcid.org/0009-0007-7699-7889

3 Ozyegin University, Civil Engineering Department, Istanbul, Türkiye
zeynep.basaran@ozyegin.edu.tr - https://orcid.org/0000-0003-1398-4021

4 University of Illinois, Material Science and Engineering, Urbana, USA
mokhtari@illinois.edu - https://orcid.org/0000-0002-0425-0483

5 Sabancı University, Faculty of Engineering and Natural Sciences, Istanbul, Türkiye
mehmet.gulgun@sabanciuniv.edu.tr - https://orcid.org/0000-0002-7096-6252

6 Civil Engineering Department, Centrale Lille, Lille, France
zoubeir.lafhaj@gmail.com - https://orcid.org/0000-0003-1985-9176

* Corresponding author

compared to their counterpart oven-cured samples. The reduction of compressive strength was more pronounced at lower molar ratios. The design of a hybrid curing approach where a portion of oven curing was replaced by MW resulted in a higher strength development than those only cured with MW. Similarly, the efficiency of hybrid curing was more pronounced in samples having MR of 1.5 and 1.7. Using MW curing in the geopolymer binders did not affect the alkali leaching; however, it increased the material's drying shrinkage. Results showed that replacing a portion of oven curing with microwave curing in a hybrid approach can increase the operation speed and the hardening rate without significantly decreasing compressive strength.

Keywords: Geopolymer, metakaolin, microwave curing, strength, shrinkage.

1. INTRODUCTION

Geopolymers are aluminosilicate-based sustainable building materials with a low carbon footprint during production and processing [1–3]. Some additional advantages of geopolymer binders over Ordinary Portland Cement (OPC) are higher compressive strengths, superior resistance to chemical attacks, freeze-thaw resistance, and higher temperature resistance [4–6]. Such properties have also led to geopolymers being considered as possible matrices for special applications such as hazardous/nuclear waste stabilization and solidification.

The raw materials for geopolymer binders can be provided entirely from aluminosilicate-rich by-products or naturally-resourced materials, such as calcined clays, with limited further processing [7–10]. Since the geopolymer composition generally involves by-product materials and natural resources, their production is efficient in raw material and energy consumption compared to OPC binders [2,11]. While geopolymer binders provide significant advantages in terms of sustainability, the cost of alkali activators such as sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_2) limit their use to smaller volume operations [7].

It is known that a properly designed mix of high calcium-contained, alkali-activated binders can harden at room temperature, which makes them usable in the field. However, low-calcium geopolymer binders require additional time or heat, creating a disadvantage for *in-situ* applications. Without an external energy source such as heat, the polymerization reaction in low-calcium, i.e., metakaolin-based geopolymer, will be prolonged [12,13]. In general, heat and curing can be obtained in conventional ovens. Herein, the thermal energy is transferred from the surface to the core section of the material through convection, conduction, and heat radiation due to the different thermal gradients occurring in the material.

Despite certain advantages, the practical applications of geopolymers have been limited by the long maintenance time and slow strength development. Technologies that enable rapid strength development are of great interest in geopolymers. Recently, microwave curing (MW) was found to be an alternative heat curing method to improve the polymerization reaction rate [12,14–17]. In MW applications, microwaves can penetrate the matrix to generate heat throughout the volume of the material [14,18–20]. Microwave energy is delivered directly to the material through molecular interaction with the electromagnetic field. The electromagnetic energy is then converted to thermal energy. The curing process in a traditional oven causes water to evaporate from the surface of the treated materials quickly. Hence, uniform heating is difficult to achieve due to the high thermal gradient, resulting in

significant energy loss through heat conduction and convection in the heated materials [21]. MW provides an essential advantage in reducing the duration of heat curing, and it may even eliminate the need for heat curing if the binder system contains sufficient calcium oxide.

On the contrary, microwave heating induces the rise of temperature due to the absorption of heat by polar molecules to create position-independent localized heating spots, which is favorable for the formation of uniform volumetric heating. Besides, MW provides superior benefits to traditional heating, such as shortening the reaction time, improving reaction kinetics, lowering heat, enabling uniform heating, and higher energy efficiency [21–23]. While the material must be kept around 60 to 100 °C for an extended curing period in conventional oven curing, MW can provide a rapid temperature increase within seconds. However, improper microwave irradiation can cause surface cracking in geopolymers, reducing structural strength. Therefore, it is critical to understand the principles of microwave heating in developing geopolymer strength and how the process affects the key properties of geopolymers [24].

While MW can be applied to geopolymer ceramics, the application of such a method to building materials is still challenging because of the dimensions of the elements produced. Previously, Somaratna et al. [19] investigated the influence of MW on NaOH-activated, fly-ash-based mortars. It was found that MW applied for 120 min resulted in compressive strength comparable to those samples cured at 75 °C for 48 h. It was found that the compressive strength of the mortar samples was directly related to the total microwave energy absorbed during the first MW application when free water was present in the system [19]. However, applying MW for 120 min is still challenging for building materials. This study was followed using MW again for fly-ash-based geopolymers activated by Na_2SiO_2 and NaOH [12]. The study evaluated using MW and oven curing (OC) at higher temperatures in less than 60 minutes. The microwave-cured samples showed relatively higher compressive strength than those kept in the oven for 120 min [12]. The promising applicability of MW led the researchers to implement this technique in novel applications such as 3D printing. MW also effectively improved the buildability of slag-based alkali-activated material in 3D printing applications [25].

The MW method was validated in literature as an alternative curing method for alkali-activated material, mostly having slag as a primary precursor. This study investigated the effects of MW on strength and dimensional stability in metakaolin-based geopolymers. In addition, it was aimed at optimizing the duration of curing, enabling ease of application. The outcomes of this study can be applied to advance new processes, such as the 3D printing of geopolymers. The main goal of this study was to implement MW technology in metakaolin-based geopolymer mortars to reduce the duration of heat curing for geo-polymerization. The feasibility of MW was assessed in terms of compressive strength, dimensional stability, and alkali leaching. The significance of this research can be listed as (1) proposing a novel approach to trigger rapid hardening in metakaolin-based geopolymer with a short-term MW (less than 45 min); (2) establishing an optimized curing procedure; (3) reducing the total energy input in developing geopolymers and (4) investigating the effects of MW on alkali leaching and free shrinkage of the geopolymer binders.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials

The primary raw materials used for the experiment were commercial metakaolin, silica fume, and F-type fly ash. Metakaolin was purchased from Kaolin Industrial Minerals Inc. Trade, Istanbul, Turkey. The fly ash was obtained from Cates Electric (Zonguldak, Turkey), and the commercial silica fume was purchased from Dost Kimya Inc. Trade, Istanbul, Turkey. Table 1 lists the chemical compositions of the raw materials used in the mixes. The data for metakaolin and fly ash was obtained by quantitative X-ray diffraction (XRD) analysis conducted with a BRUKER D8 Advance X-ray diffractometer (Karlsruhe, Germany). The XRD analysis of the minerals was conducted at angles from 10 to 90° 2θ at a step size of 0.02° in 2θ.

Table 1 - Composition of metakaolin, Type F fly ash, and silica fume

Element	Weight %		
	Metakaolin	**Fly Ash**	**Silica Fume**
SiO_2	56.1	55.8	98.1 (Amorph)
Al_2O_3	40.2	26.0	-
Fe_2O_3	0.8	6.44	-
CaO	0.2	1.68	-
MgO	0.2	2.33	-
SO_3	-	0.18	-
Na_2O	-	1.87	-
K_2O	0.5	3.86	-
Na Eq.	0.24	4.41	-
Free CaO	N/S	0.08	-
LOI	1.5	2.61	1.81

The manufacturer provided the chemical composition of silica fume. The average particle sizes of the raw materials were determined by a Mastersizer 2000 particle size analyzer with a Hydro MU 2000 (Malvern, Worcestershire, United Kingdom) wet dispersion unit. Figure 1 summarizes the particle size distributions for metakaolin and fly ash. The average particle size of silica fume was less than 25 µm. Amongst all materials used, silica fume had the smallest particle size, whereas metakaolin and fly ash had relatively similar gradation curves.

The alkaline activating solution was formulated using a commercially available sodium silicate solution composed of 26.5 wt% SiO_2, 10.6 wt% Na_2O, and 62.9 wt% H_2O having a molar ratio (MR, $nSiO_2/nNa_2O$) of 2.6. The sodium silicate solution was then mixed with 8 M sodium hydroxide (NaOH) solution to obtain the desired molar ratios (MR) of the

activating solution. Table 2 summarizes the relative proportions of the mixed ingredients. At last, mortar samples were prepared using standard sand according to the norm EN 196-1.

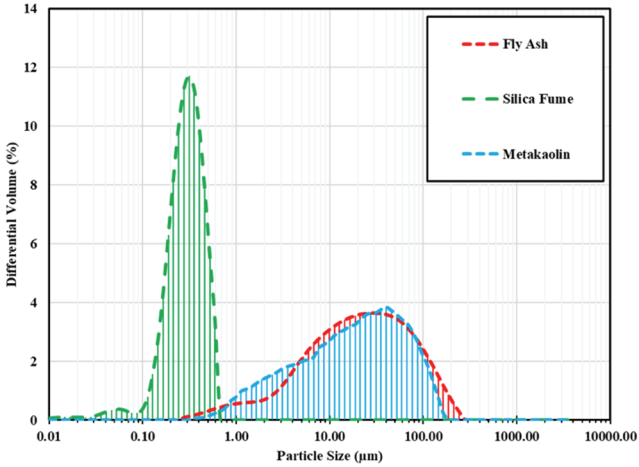

Figure 1 - Particle size distribution of Metakaolin and Fly Ash

Table 2 - Material proportions of blended geopolymers. FA: Fly Ash; MK: Metakaolin; SF: Silica Fume; MR: Molar Ratio; sol/b: Solution to binder ratio; w/b: Water to binder ratio

Sample Name	Binder (g)			Activating Solution (mL)		MR	sol/b	w/b	SiO_2/Al_2O_3	SiO_2/Na_2O
	FA	MK	SF	NaOH (8M)	Na_2SiO_3					
MK_5_1.3	180	390	30	105	255	1.3	0.62	0.4	3.31	7.01
MK_10_1.3	180	360	60	105	255	1.3	0.62	0.4	3.62	7.21
MK_15_1.3	180	330	90	105	255	1.3	0.62	0.4	3.98	7.42
MK_5_1.5	180	390	30	92	280	1.5	0.62	0.4	3.36	7.18
MK_10_1.5	180	360	60	92	280	1.5	0.62	0.4	3.68	7.39
MK_15_1.5	180	330	90	92	280	1.5	0.62	0.4	4.04	7.60
MK_5_1.7	180	390	30	70	300	1.7	0.62	0.4	3.40	7.69
MK_10_1.7	180	360	60	70	300	1.7	0.62	0.4	3.72	7.91
MK_15_1.7	180	330	90	70	300	1.7	0.62	0.4	4.09	8.13

2.2. Sample Preparation and Methodology

Nine mix compositions containing metakaolin, fly ash, and silica fume were prepared within the scope of this study. The weight % of the fly ash was kept at 30 wt% of the total binder content. A portion of the metakaolin in the binder was replaced by silica fume (5,10, and 15 wt. %). The formulated mixtures were designed to initiate hardening by providing the required heat of curing due to their low calcium oxide (CaO) contents (< 5% by weight) [26,27]. The activator solution to binder ratio (sol/b), including the water content in the activating solution, was kept at 0.60 ± 0.02, and the water to binder ratio (w/b) was held at 0.40. Mortar samples were prepared according to ASTM C305-14 [28]. Since the designed material system was aimed at 3D printing applications, the binder-to-sand ratio was kept at 1:1.5 [29].

The samples were cast in 40 x 40 x 160 mm molds. For all samples, three different curing regimes were applied: The duration and power of the microwave were determined by preliminary evaluations of its effects on hardening and workability. The microwave curing power and time were selected considering their impact on the geopolymers. Samples were kept in a humid environment under ambient conditions (70% RH at 23 ˚C).

2.3. Mechanical Performance Tests

The mechanical performance of the geopolymer mortars was determined by compressive strength tests. The mechanical performance was measured 3, 7, and 28 days after casting. The compressive strength was measured according to standard EN 196-1 [30]. The performance tests were done on triplicate samples.

2.4. Drying Shrinkage in Geopolymer Mortars

The dimensional stability and resistance against drying shrinkage in geopolymer mortars were assessed according to the ASTM C596-18 standard [31]. Geopolymer samples were cast in 50 x 50 x 285 mm molds. Six samples were cast from each mix. A set of samples were directly put in the oven for curing. Another set was subjected to hybrid curing. The samples were kept in a humid environment for three days after heat curing, as stated in section 2.2. After three days, the samples were removed from the curing chamber and submerged in the lime water for 24 hours, as stated in the standard. Then, the samples were removed from lime water, and the length and weight measurements were taken as t=0 [31]. The samples were kept in a 50% RH environment at 23 ˚C for 16 weeks. Periodic length measurements were taken at the 4^{th}, 7^{th}, 11^{th}, $18^{th,}$ 25^{th} days, and 8^{th} and 16^{th} weeks. Each measurement was taken from triplicates of samples.

2.5. Alkali Leaching in Geopolymer Mortars

The occurrence of alkali leaching (i.e., efflorescence) in geopolymer mortar was determined by 40x40x160 mm samples. A set of samples were directly put in an oven for curing. Another group was subjected to hybrid curing. The samples were kept in a humid environment for 28 days after heat curing. Then, the samples were placed in distilled water and kept in an open-air atmosphere at ambient conditions (60 ± 5 % RH at 23 ˚C) until the water evaporated completely. The initial evaluation was done by visual inspection. Once all the water was evaporated, the leached product produced on the top and bottom surfaces of the samples was scratched, and the material was collected from the sample. The weight of the total leached material was recorded for each sample. A qualitative XRD X-ray diffraction (XRD) analysis was done for the leached products with a BRUKER D8 Advance X-ray Diffractometer (Karlsruhe, Germany). The samples were placed and compacted into a sample holder, and analysis was conducted at angles from 10 to 90° 2θ at a step size of 0.02° 2θ.

3. RESULTS AND DISCUSSION

3.1. Compressive Strength

The initial evaluation of MW curing was done regarding compressive strength tests. Figure 2 compares the compressive strength of metakaolin-based geopolymers at different MRs and cured under various conditions. The MR and degree of heat input highly influenced the compressive strength of the metakaolin-based geopolymer systems.

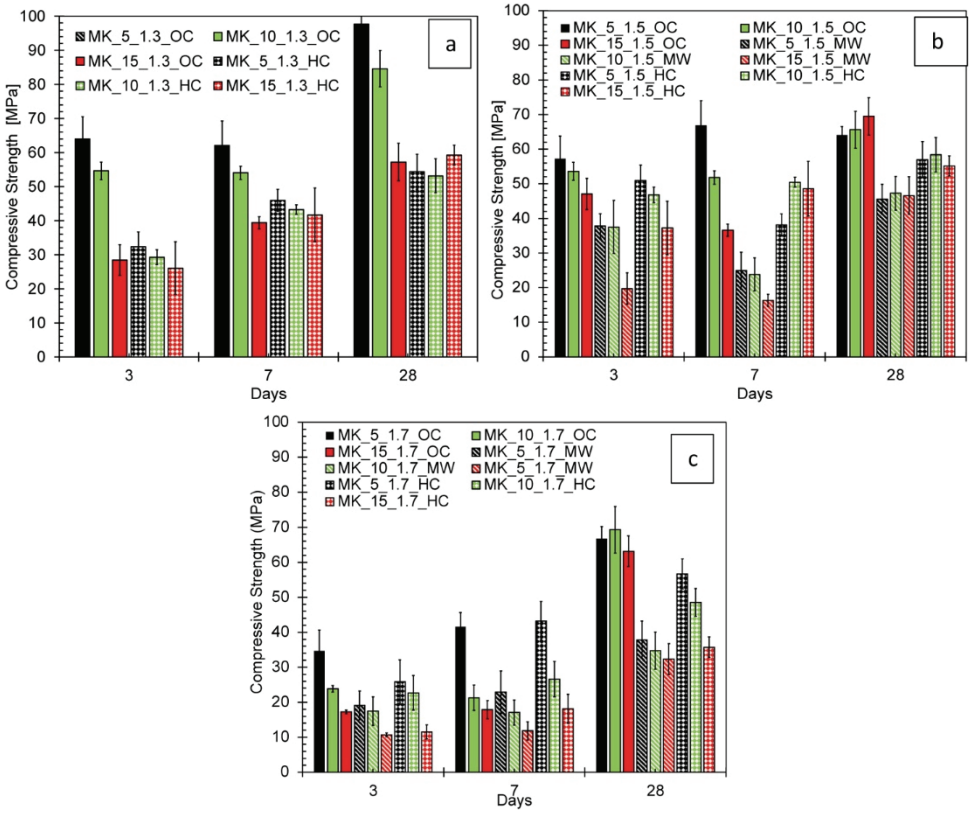

Figure 2 - Compressive strength of geopolymer mortars (a) MR: 1.3 (b) MR:1.5 (c) MR:1.7. OC: Oven Curing; MW: Microwave Curing; HC: Hybrid Curing. *The samples were not hardened with only microwave curing*

While MR is an important factor in compressive strength, the highest strength values were recorded with oven curing regardless of all MR ratios; this indicates that both MR and curing methodology are decisive factors. Even with oven curing, increasing silica fume dosage was more pronounced at 28 days and decreased the compressive strength at 3 and 7 days. This can be attributed to the pozzolanic nature of silica fume [32]. In addition, achieving a strength increase at 28 days in the MK_15 sample (15% silica fume) required an MR of 1.5 or higher.

This shows that the system should have higher moles of Na_2O to form N-A-S-H in a silica-rich environment.

Only MW curing reduced the compressive strength compared to the oven-cured counterpart samples. Theoretically, MW curing at 800W for 3 minutes should trigger a faster geopolymerization process by increasing the reaction rate [15, 25]. The samples with an MR of 1.5 and 1.7 were hardened after microwave application. This indicated that microwave curing was adequate for accelerating the strength gain of metakaolin-based geopolymer. However, this accelerating effect did not directly lead to increased 3-day compressive strength. Another important point is that MW curing was insufficient to develop strength in the MR_1.3_MW series. The sample with an MR of 1.3 was hardened but did not exhibit any strength. The compressive strength in MR_1.3_MW samples was recorded as "0". This might be due to the extended duration of high-energy microwave heating that can trigger evaporation in pore water, leading to a lower water content before the geopolymerization reaction. This effect results in a denser microstructure and an increasing rate of the hardening process without increasing the strength. A further evaluation must be done to understand the influence of microwave curing on the chemical composition of the geopolymer and establish a methodology to reduce the water loss in the samples.

Further optimization was done by establishing a combined hybrid curing (HC) approach. Herein, the samples were subjected to MW curing for 90 seconds and then kept at 60^{o}C for 30 minutes. This method partially restored the decrease in compressive strength due to only MW curing, particularly for an MR of 1.5. However, HC samples' compressive strength was still lower than their oven-cured counterparts, particularly for samples cured at 3 and 7 days. At 28 days, the decrease in compressive strength for HC compared to OC was 15% for MR 1.5, regardless of the percentage of silica fume replaced. This might have shown that the rapid heat application increased the hardening rate, but the total heat energy applied might not have been sufficient to trigger rapid geoopolymerization. Yet, based on the results obtained, it is concluded that the effective performance features are silica fume replacement, MR, and compressive strength. The silica fume replacement should be kept at 5% if we use an MR of 1.3, whereas increasing the silica fume dosage resulted in higher strength development in oven-cured samples. This trend was different when MW or HC was applied to the material; in this case, increasing MR and silica fume dosage decreased compressive strength. Therefore, further evaluation was done to correlate the curing regime, SiO_2/Al_2O_3, and SiO_2/Na_2O ratios on compressive strength

To correlate the chemical composition to the mechanical properties, further evaluation was done by assessing the influence of SiO_2/Al_2O_3 and SiO_2/Na_2O ratios on compressive strength. Figure 3 summarizes the effect of SiO_2/Al_2O_3 and SiO_2/Na_2O ratios on the compressive strength of geopolymer mortar cured at different temperatures. It was found that there was a direct relationship between the SiO_2/Na_2O ratio and the early age (3 and 7 days) compressive strength of the mortar. Both 3 and 7-day compressive strength of mortar decreased with increasing SiO_2/Na_2O ratio. The reduction in strength could be attributed to the excess silica content that could interfere with the geopolymerization process.

Even though the evaluations indicated that the decrease in compressive strength was more pronounced depending on the SiO_2/Na_2O ratio rather than the SiO_2/Al_2O_3 ratio, a high SiO_2/Al_2O_3 ratio might also adversely affect compressive strength. Wan et al. [33] evaluated the impact of extended SiO_2/Al_2O_3 concentrations on the mechanical properties of

metakaolin-based geopolymers. The results concluded that the optimum SiO_2/Al_2O_3 ratio should be held at 2, and increasing the SiO_2/Al_2O_3 ratio to 3 would significantly decrease the compressive strength. Higher concentrations of Si^{+4} and Al^{+3} could immediately form a gel around the metakaolin particles and prevent their subsequent destruction [34]. This study

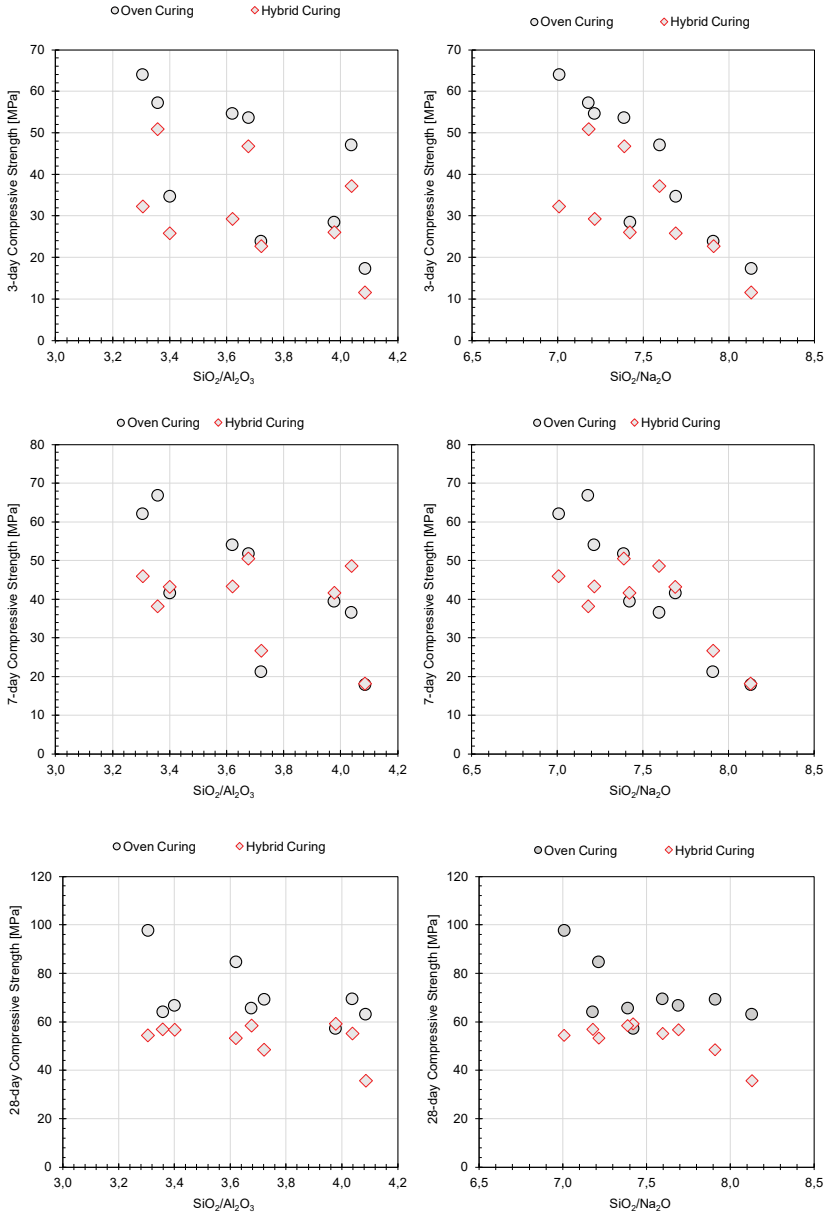

Figure 3 - Relationships between compressive strength and alkali content (a,b) 3 days (c,d) 7 days (e,f) 28 days

held the SiO_2/Al_2O_3 ratio between 3 and 4. Therefore, it was not possible to observe a significant change in the properties due to an increase in SiO_2/Al_2O_3 ratio. However, a lower SiO_2/Al_2O_3 ratio might have led to different outcomes regarding the absolute compressive strength and the effectiveness of the microwave application.

3.2. Dimensional Stability and Drying Shrinkage

Like the OPC binders, geopolymer systems also have a low tensile strength that can result in cracking due to excessive tensile stress developed due to early-age plastic shrinkage strains. Some geopolymer binders may have a higher drying shrinkage than OPC binders since the water does not form the aluminosilicate gel [35]. Higher drying shrinkage means a higher risk of cracking, leading to serviceability or durability problems. Although metakaolin-based geopolymers exhibit superior resistance to thermal shrinkage at temperatures above 700°C compared to OPC binders, they might be susceptible to severe shrinkage cracking at ambient temperatures [36].

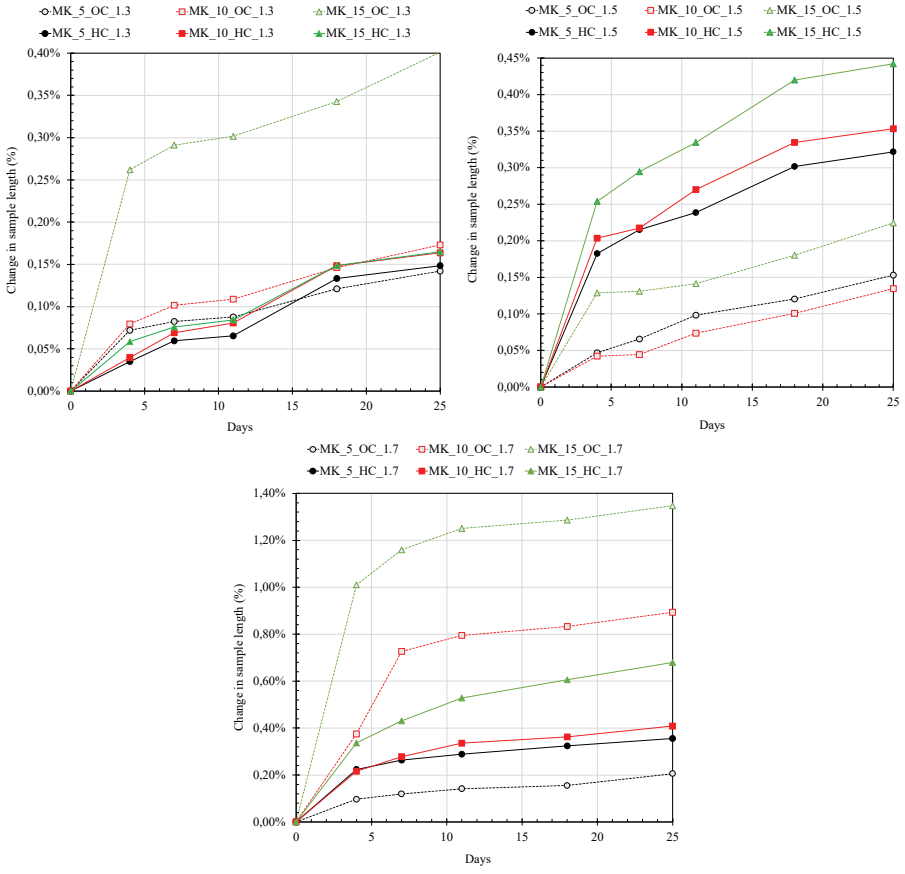

Figure 4 - Time-dependent length change in geopolymer mortars (a) MR: 1.3 (b) MR:1.5 (c) MR:1.7. MK: Metakaolin; OC: Oven Curing; HC: Hybrid Curing

Figure 4 summarizes the percent length changes in metakaolin-based geopolymer mortars cured in OC and HC. Based on the results, increasing the MR resulted in a higher degree of length change. In addition, the heat-cured samples (OC) showed relatively smaller length changes than their microwave-cured counterpart samples (HC). Previous studies indicated that the drying shrinkage of fly ash-based geopolymer concrete mixes cured under ambient conditions could be significantly higher than in OPC-based binders within the range of 1500 µcontrast. The drying shrinkage of heat-cured specimens was recorded in the range of 100 µscript epsilon [37,38]. Volumetric changes in metakaolin-based geopolymers were attributed to drying shrinkage rather than autogenous shrinkage [39]. Like the samples cured under ambient conditions, HC might result in a lower degree of geopolymerization, leaving the mortar mixed with a higher water content even after hardening. The remaining water content may result in a higher degree of evaporation and increase the drying of the material in a hardened state.

3.3. Alkali Leaching

Another performance parameter investigated in this study was alkali leaching (a.k.a efflorescence) in metakaolin-based geopolymers. While alkali leaching in OPC binders occurs with the reaction of soluble Ca^{+2} and CO_2 to form carbonate deposits, geopolymer binders could be much more complicated due to their relatively higher soluble alkali concentrations than OPC [9]. Therefore, alkali leaching could be a more severe issue in geopolymer binders. The known parameters affecting the extent of efflorescence in geopolymer binders can be listed as the reactivity of raw materials, type of alkali, and reaction conditions [40,41]. The alkali leaching in distilled water for the designed metakaolin geopolymers was quantitively assessed by calculating the total weight of collected leached precipitates. Table 3 summarizes the total amount of leached precipitates collected from mortar beams. The results showed that the amount of leaching was directly related to the MR of the alkali-activating solution. Increasing the silica fume content from 5 to 10% decreased the total amount of leached precipitates.

Table 3 - Total alkali leaching content in geopolymer mortars (kg) MK: Metakaolin; OC: Oven Curing; HC: Hybrid Curing

Sample Name	Oven Curing	Hybrid Curing
MK_5_1.3	2.55 ± 0.21	5.39 ± 0.18
MK_10_1.3	1.47 ± 0.19	1.13 ± 0.25
MK_15_1.3	1.39 ± 0.21	2.29 ± 0.21
MK_5_1.5	3.86 ± 0.28	3.82 ± 0.87
MK_10_1.5	1.76 ± 0.17	1.66 ± 0.16
MK_15_1.5	1.57 ± 0.14	2.66 ± 0.08
MK_5_1.7	8.21 ± 0.41	10.38 ± 0.19
MK_10_1.7	5.08 ± 0.59	6.70 ± 0.03
MK_15_1.5	11.78 ± 0.40	6.54 ± 0.22

In geopolymer binders such as those having metakaolin or fly ash as a precursor, the molar ratio SiO_2/Al_2O_3 is an essential indicator of the reactivity in the binder and microstructural features of the gel formed. Figure 5 presents the relationship between the SiO_2/Na_2O and SiO_2/Al_2O_3 ratios on the total alkali leaching. Our results showed that increasing the SiO_2/Na_2O ratio increased leaching. However, the relationship between alkali leaching and SiO_2/Al_2O_3 was more complex since there was no consistent trend between the total alkali leaching and SiO_2/Al_2O_3 ratio. A previous study found that the systems with a lower SiO_2/Al_2O_3 ratio, in other words, higher concentrations of Al_2O_3, will promote a higher degree of dissolution, which might decrease the ion binding capacity of the gel and lead to a higher degree of leaching [42, 43]. Our results indicated that the influence of the SiO_2/Al_2O_3 ratio was more pronounced in samples having a higher MR (i.e., MR=1.7). This effect on leaching can be correlated with the amount of drying shrinkage in samples. The samples with a higher alkali leaching also demonstrated a higher degree of plastic shrinkage. The loss of reaction phases in the material resulted in a change in volumetric dimension.

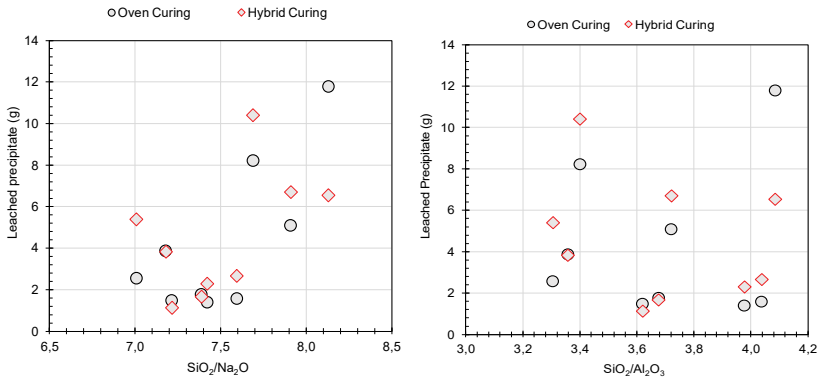

Figure 5 - Relationship between total alkali leaching from the sample and the alkali content in the mix (a) SiO_2/Na_2O and (b) SiO_2/Al_2O_3

Another critical factor affecting alkali leaching could be the temperature applied during the curing process. It was found that microwave curing did not significantly affect the total amount of leaching. In geopolymer binders, heat curing promotes the reaction and dissolution of oxides in the precursor, resulting in a faster geo-polymerization reaction [44]. Kani et al. [45] observed that alkali leaching could be reduced when the curing temperature was increased above 65°C. Heat curing can increase the gel formed with a higher density and a higher amount of captured Na^+.

Finally, an evaluation was done to characterize the chemical composition of the leached precipitate, and Figure 6 presents the XRD diffractograms for geopolymer binders. The leached precipitate was mainly a mix of sodium carbonate (Na_2CO_3) and quartz (SiO_2), which shows that the leaching was due to effloresce. This indicates that the main binding phase Na-A-S-H in the geopolymer is converted to carbonate Na_2CO_3 through carbonation. Thus, the dimensional change observed in Section 3.2 can also be related to carbonation-induced and plastic shrinkage. This may also cause a decrease in compressive strength since the main binder phase is carbonated and tends to leach from the sample.

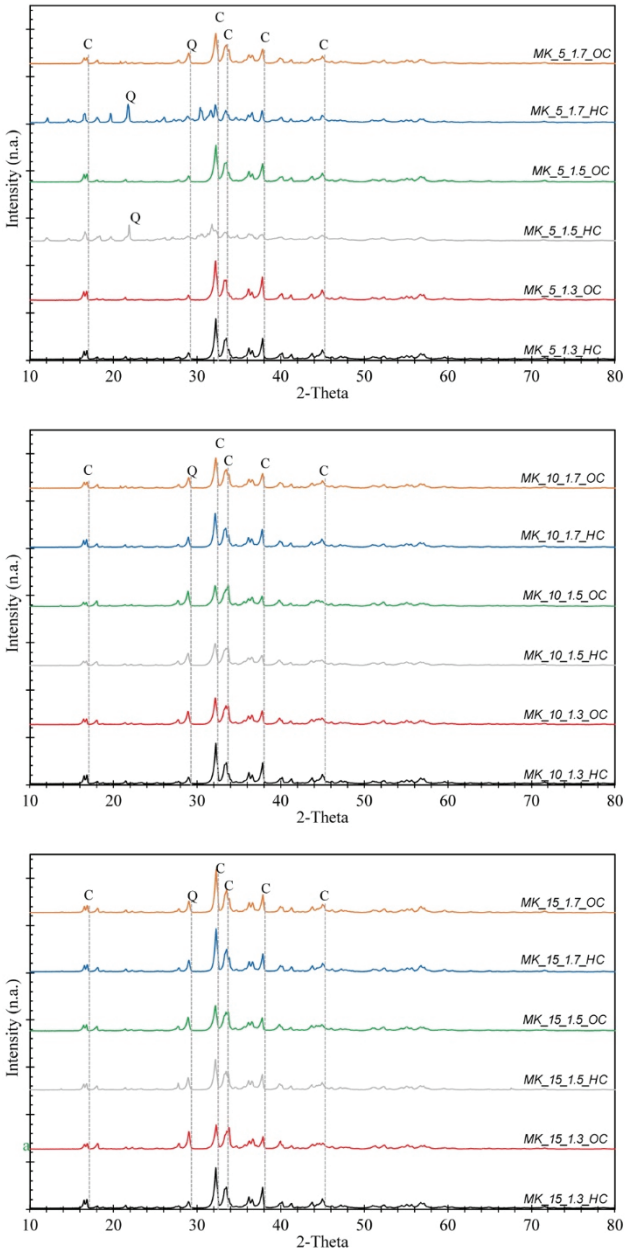

Figure 6 - X-ray diffractograms from leached contents obtained from geopolymer containing 5% silica fume by weight of cement (a) 5% silica fume replacement (b) 10% silica fume replacement (c) 15% silica fume replacement MK: metakaolin; OC: oven curing; HC: hybrid curing. C: sodium carbonate (PDF:70-8045): Q: quartz (PDF 82-0512).

4. CONCLUSION

This study aimed to develop a microwave curing technique to design a set-on-demand approach to improve the hardening rate in metakaolin-based geopolymer in a shorter time frame. The outcomes of the experimental evaluations indicated that only microwave curing reduced the compressive strength of metakaolin-based geopolymers. The curing scheme has been optimized to adapt heat and microwave curing to a hybrid system. Throughout the literature, the MW curing approach was only proposed for slag-based geopolymers, which can already react at room temperature. Herein, the challenge is to adapt this technology to low calcium oxide binders where heat curing is required. Hybrid curing (HC) resulted in a 75% decrease in curing time in metakaolin-based geopolymers. Even though this decrease seems insignificant in lab-scale cast specimens, HC will provide an important advantage in special applications such as 3D printing or precast elements.

- Only MW curing resulted in a significant decrease in compressive strength compared to the counterpart oven-cured samples. The reduction of compressive strength was more pronounced at lower molar ratios (MR: 1.3). This was attributed to the sudden evaporation of the water phase, limiting the further geo-polymerization reaction.
- The design of a hybrid curing approach where a portion of oven curing was replaced by MW resulted in a higher strength development than those only cured with MW. Similarly, the efficiency of hybrid curing was more pronounced in samples having MR of 1.5 and 1.7. The 28-day compressive strength of hybrid cured geopolymer mortars was 90% and 75% of the oven-cured counterpart samples for MRs 1.5 and 1.7, respectively.
- The results indicated a direct relationship between the SiO_2/Na_2O ratio and the early-age compressive strength of geopolymer mortar. The strength reduction was attributed to excess silica content that can interfere with geopolymerization.
- Implementing the hybrid curing approach increased the drying shrinkage of the geopolymer mortar, but it did not affect the alkali leaching in the material. The increased drying shrinkage was attributed to water loss because of the applied rapid microwave energy.
- The alkali leaching was found to be directly affected by the molar ratio of the alkaline solution, increasing the molar ratio and SiO2/Al2O3 ratio, thereby reducing the system's ion binding capacity.
- This optimization of hybrid curing decreased the duration of the required heat treatment of the mortar, leading to an advantage in special field applications such as 3D printing.

Acknowledgment

This research was conducted with financial assistance from the Scientific and Technical Research Council (TUBITAK) of Turkey (Project No: MAG-119N246) and Campus France (Project No: 44804RM).

Author Contributions

YAA and TA: conceptualizing the work, experimental analysis, data curation and analysis, methodology, drafting the plots and tables, and writing the original draft. PM: Developing the microwave concept, XRD data curation, and analysis. MAG: Developing the microwave concept and reviewing the original draft. WK, DK, and ZL: data analysis, review, and editing. ZBB: conceptualizing the work, funding acquisition, project management, administration, methodology, supervision, resources, and writing-review and editing. All authors contributed to the article and approved the submitted version.

Conflict of Interest

The authors declare no conflict of interest.

References

[1] K. Chen, Q. Liu, B. Chen, S. Zhang, L. Ferrara, W. Li, Effect of raw materials on the performance of 3D printing geopolymer: A review, Journal of Building Engineering 84 (2024) 108501. https://doi.org/10.1016/j.jobe.2024.108501.

[2] Y.H.M. Amran, R. Alyousef, H. Alabduljabbar, M. El-Zeadani, Clean production and properties of geopolymer concrete; A review, J Clean Prod 251 (2020) 119679. https://doi.org/10.1016/j.jclepro.2019.119679.

[3] N. Akhtar, T. Ahmad, D. Husain, A. Majdi, M.T. Alam, N. Husain, A.K.S. Wayal, Ecological footprint and economic assessment of conventional and geopolymer concrete for sustainable construction, J Clean Prod 380 (2022) 134910. https://doi.org/10.1016/j.jclepro.2022.134910.

[4] B. Zhang, Durability of low-carbon geopolymer concrete: A critical review, Sustainable Materials and Technologies 40 (2024) e00882. https://doi.org/10.1016/j.susmat.2024.e00882.

[5] P. Zhang, X. Han, S. Hu, J. Wang, T. Wang, High-temperature behavior of polyvinyl alcohol fiber-reinforced metakaolin/fly ash-based geopolymer mortar, Compos B Eng 244 (2022) 110171. https://doi.org/10.1016/j.compositesb.2022.110171.

[6] W. Tu, M. Zhang, Behaviour of alkali-activated concrete at elevated temperatures: A critical review, Cem Concr Compos 138 (2023) 104961. https://doi.org/10.1016/j.cemconcomp.2023.104961.

[7] M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, Cem Concr Res 41 (2011) 1232–1243. https://doi.org/10.1016/j.cemconres.2010.11.012.

[8] K. Sankar, A. Sutrisno, W.M. Kriven, Slag-fly ash and slag-metakaolin binders: Part II—Properties of precursors and NMR study of poorly ordered phases, Journal of the American Ceramic Society 102 (2019) 3204–3227. https://doi.org/10.1111/jace.16224.

[9] K. Sankar, P. Stynoski, G.K. Al-Chaar, W.M. Kriven, Sodium silicate activated slag-fly ash binders: Part I – Processing, microstructure, and mechanical properties, Journal of the American Ceramic Society 101 (2018) 2228–2244. https://doi.org/10.1111/jace.15391.

[10] K. Sankar, P. Stynoski, W.M. Kriven, Sodium silicate activated slag-fly ash binders: Part III—Composition of soft gel and calorimetry, Journal of the American Ceramic Society 102 (2019) 3175–3190. https://doi.org/10.1111/jace.16219.

[11] R. Bajpai, K. Choudhary, A. Srivastava, K.S. Sangwan, M. Singh, Environmental impact assessment of fly ash and silica fume based geopolymer concrete, J Clean Prod 254 (2020) 120147. https://doi.org/10.1016/j.jclepro.2020.120147.

[12] A. Graytee, J.G. Sanjayan, A. Nazari, Development of a high strength fly ash-based geopolymer in short time by using microwave curing, Ceram Int 44 (2018) 8216–8222. https://doi.org/10.1016/j.ceramint.2018.02.001.

[13] F. Puertas, S. Martínez-Ramírez, S. Alonso, T. Vázquez, Alkali-activated fly ash/slag cements, Cem Concr Res 30 (2000) 1625–1632. https://doi.org/10.1016/S0008-8846(00)00298-2.

[14] P. Chindaprasirt, U. Rattanasak, S. Taebuanhuad, Role of microwave radiation in curing the fly ash geopolymer, Advanced Powder Technology 24 (2013) 703–707. https://doi.org/10.1016/j.apt.2012.12.005.

[15] R. Prommas, T. Rungsakthaweekul, Effect of Microwave Curing Conditions on High Strength Concrete Properties, Energy Procedia 56 (2014) 26–34. https://doi.org/10.1016/j.egypro.2014.07.128.

[16] M. Nadeem, E. Ul Haq, F. Ahmed, M. Asif Rafiq, G. Hameed Awan, M. Zain-ul-Abdein, Effect of microwave curing on the construction properties of natural soil based geopolymer foam, Constr Build Mater 230 (2020). https://doi.org/10.1016/j.conbuildmat.2019.117074.

[17] J. Tan, J. Cai, L. Huang, Q. Yang, M. Mao, J. Li, Feasibility of using microwave curing to enhance the compressive strength of mixed recycled aggregate powder based geopolymer, Constr Build Mater 262 (2020). https://doi.org/10.1016/j.conbuildmat.2020.120897.

[18] E.T. Thostenson, T.W. Chou, Microwave processing: fundamentals and applications, Compos. Part A: Appl. Sci. Manuf. 30 (1999) 1055–1070.

[19] J. Somaratna, D. Ravikumar, N. Neithalath, Response of alkali activated fly ash mortars to microwave curing, Cem Concr Res 40 (2010) 1688–1696. https://doi.org/10.1016/j.cemconres.2010.08.010.

[20] S. Das, A.K. Mukhopadhyay, S. Datta, D. Basu, Prospects of microwave processing: An overview, 2009.

[21] Y. Sun, P. Zhang, J. Hu, B. Liu, J. Yang, S. Liang, K. Xiao, H. Hou, A review on microwave irradiation to the properties of geopolymers: Mechanisms and challenges, Constr Build Mater 294 (2021) 123491. https://doi.org/10.1016/j.conbuildmat.2021.123491.

[22] Z. Dong, H. Ma, W. Feng, Y. Nie, H. Shi, Achieving superior high-strength geopolymer via the synergistic effect of traditional oven curing and microwave curing, Constr Build Mater 357 (2022) 129406. https://doi.org/10.1016/j.conbuildmat.2022.129406.

[23] A.A. Shubbar, M. Sadique, P. Kot, W. Atherton, Future of clay-based construction materials – A review, Constr Build Mater 210 (2019) 172–187. https://doi.org/10.1016/j.conbuildmat.2019.03.206.

[24] E.T. Thostenson, T.-W. Chou, Microwave processing: fundamentals and applications, Compos Part A Appl Sci Manuf 30 (1999) 1055–1071. https://doi.org/10.1016/S1359-835X(99)00020-2.

[25] S. Muthukrishnan, S. Ramakrishnan, J. Sanjayan, Effect of microwave heating on interlayer bonding and buildability of geopolymer 3D concrete printing, Constr Build Mater 265 (2020) 120786. https://doi.org/10.1016/j.conbuildmat.2020.120786.

[26] A. Noushini, A. Castel, The effect of heat-curing on transport properties of low-calcium fly ash-based geopolymer concrete, Constr Build Mater 112 (2016) 464–477. https://doi.org/10.1016/j.conbuildmat.2016.02.210.

[27] A. Noushini, F. Aslani, A. Castel, R.I. Gilbert, B. Uy, S. Foster, Compressive stress-strain model for low-calcium fly ash-based geopolymer and heat-cured Portland cement concrete, Cem Concr Compos 73 (2016) 136–146. https://doi.org/10.1016/j.cemconcomp.2016.07.004.

[28] ASTM International, ASTM C305-14 Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes andMortars of Plastic Consistency, West Conshohocken, 2014. https://doi.org/10.1520/C0305-14.2.

[29] B. Panda, C. Unluer, M.J. Tan, Investigation of the rheology and strength of geopolymer mixtures for extrusion-based 3D printing, Cem Concr Compos 94 (2018) 307–314. https://doi.org/10.1016/j.cemconcomp.2018.10.002.

[30] European Standarts, EN 196-1: Methods of testing cement - Part 1: Determination of strength, 2016.

[31] ASTM, ASTM C 596-18 Standard Test Method for Drying Shrinkage of Mortar Containing Hydraulic Cement, West Conshohocken, PA, USA, 2018.

[32] B. Li, A. Gao, Y. Li, H. Xiao, N. Chen, D. Xia, S. Wang, C. Li, Effect of silica fume content on the mechanical strengths, compressive stress–strain behavior and microstructures of geopolymeric recycled aggregate concrete, Constr Build Mater 384 (2023) 131417. https://doi.org/10.1016/j.conbuildmat.2023.131417.

[33] Q. Wan, F. Rao, S. Song, R.E. García, R.M. Estrella, C.L. Patiño, Y. Zhang, Geopolymerization reaction, microstructure and simulation of metakaolin-based geopolymers at extended Si/Al ratios, Cem Concr Compos 79 (2017) 45–52. https://doi.org/10.1016/j.cemconcomp.2017.01.014.

[34] M.S. Muñiz-Villarreal, A. Manzano-Ramírez, S. Sampieri-Bulbarela, J.R. Gasca-Tirado, J.L. Reyes-Araiza, J.C. Rubio-Ávalos, J.J. Pérez-Bueno, L.M. Apatiga, A. Zaldivar-Cadena, V. Amigó-Borrás, The effect of temperature on the geopolymerization process of a metakaolin-based geopolymer, Mater Lett 65 (2011) 995–998. https://doi.org/10.1016/j.matlet.2010.12.049.

[35] M. Mastali, P. Kinnunen, A. Dalvand, R. Mohammadi Firouz, M. Illikainen, Drying shrinkage in alkali-activated binders – A critical review, Constr Build Mater 190 (2018) 533–550. https://doi.org/10.1016/j.conbuildmat.2018.09.125.

[36] P. Duan, C. Yan, W. Zhou, W. Luo, Thermal Behavior of Portland Cement and Fly Ash–Metakaolin-Based Geopolymer Cement Pastes, Arab J Sci Eng 40 (2015) 2261–2269. https://doi.org/10.1007/s13369-015-1748-0.

[37] I. Khan, T. Xu, A. Castel, R.I. Gilbert, M. Babaee, Risk of early age cracking in geopolymer concrete due to restrained shrinkage, Constr Build Mater 229 (2019). https://doi.org/10.1016/j.conbuildmat.2019.116840.

[38] S. Wallah, Creep behaviour of fly ash-based geopolymer concrete, , Civ. Eng. Dimens. 12 (2) (2010) 73–78 12 (2010) 73–78.

[39] T. Yang, H. Zhu, Z. Zhang, Influence of fly ash on the pore structure and shrinkage characteristics of metakaolin-based geopolymer pastes and mortars, Constr Build Mater 153 (2017) 284–293. https://doi.org/10.1016/j.conbuildmat.2017.05.067.

[40] F. Škvára, S. Pavlasová, L. Kopecký, L. Myšková, L. Alberovská, 3rd International Symposium on Non-traditional Cement and Concrete, in: High Temperature Properties of Fly Ash-Based Geopolymers, 2008: pp. 741–750.

[41] Z. Zhang, J.L. Provis, A. Reid, H. Wang, Fly ash-based geopolymers: The relationship between composition, pore structure and efflorescence, Cem Concr Res 64 (2014) 30–41. https://doi.org/10.1016/j.cemconres.2014.06.004.

[42] P. Duxson, G.C. Lukey, F. Separovic, J.S.J. van Deventer, Effect of Alkali Cations on Aluminum Incorporation in Geopolymeric Gels, Ind Eng Chem Res 44 (2005) 832–839. https://doi.org/10.1021/ie0494216.

[43] M. Criado, A. Fernández-Jiménez, A. Palomo, Alkali activation of fly ash: Effect of the SiO2/Na2O ratio. Part I: FTIR study, Microporous and Mesoporous Materials 106 (2007) 180–191. https://doi.org/10.1016/j.micromeso.2007.02.055.

[44] N. Granizo, A. Palomo, A. Fernandez-Jiménez, Effect of temperature and alkaline concentration on metakaolin leaching kinetics, Ceram Int 40 (2014) 8975–8985. https://doi.org/10.1016/j.ceramint.2014.02.071.

[45] E. Najafi Kani, A. Allahverdi, J.L. Provis, Efflorescence control in geopolymer binders based on natural pozzolan, Cem Concr Compos 34 (2012) 25–33. https://doi.org/10.1016/j.cemconcomp.2011.07.007.