

Enhancing Early Strength Development of Alkali-Activated Slag through Preheating of Materials

Cemal KARAASLAN*¹ ORCID 0000-0002-8993-7566

¹Iğdir University, Faculty of Engineering, Department of Civil Engineering, Iğdir, Türkiye

Geliş tarihi: 22.06.2023

Kabul tarihi: 25.12.2023

Atf şekli/ How to cite: KARAASLAN, C., (2023). Enhancing Early Strength Development of Alkali-Activated Slag through Preheating of Materials. Cukurova University, Journal of the Faculty of Engineering, 38(4), 1129-1138.

Abstract

Alkali-activated cements have gained attention as sustainable alternatives to Portland cement-based concretes. This study aims to enhance the early strength development of alkali-activated slag (AAS) mortars by preheating the alkali activator, ground granulated blast furnace slag, and aggregates to temperatures reaching up to 65°C before their utilization. Preheating at 50°C enhances both early and ultimate strength of AAS, compared to specimens that were not subjected to preheating. Similarly, preheating at 65°C results in a substantial increase in early strength but leads to some strength reduction after three days. SEM and FTIR analyses reveal that preheating at 50°C improves the interfacial transition zone between paste and aggregate, reduces microcracks, and promotes alkali activation. Furthermore, FTIR analysis confirms the occurrence of hydration reactions in AAS upon contact with water.

Keywords: Alkali-activated slag, Preheating of materials, Early age concrete, Heat curing, Water resistance

Malzemelerin Isıtılarak Kullanılması ile Alkali-Aktive Cürufların Erken-dönem Dayanım Gelişimlerinin İyileştirilmesi

Öz

Alkali ile aktive edilmiş çimentolar, Portland çimentosu esaslı betonlara sürdürülebilir alternatifler olarak dikkat çekmektedir. Bu çalışmada, alkali aktivatör, öğütülmüş granüle yüksek fırın cürufu ve agreganın 65°C'ye kadar ısıtılması yoluyla alkali ile aktive edilmiş cüruf (AAS) esaslı harçların erken yaştaki dayanım gelişimlerinin iyileştirilmesi amaçlanmıştır. Ön ısıtmaya tabi tutulmayan AAS ile kıyaslandığında, 50°C'lik ön ısıtma, AAS'nin hem ilk günlerdeki hem de nihai dayanımını artırırken 65°C'lik ön ısıtma, AAS'nin ilk saatlerdeki dayanımını önemli derecede artırırken 3 günden sonraki dayanımlarda bir miktar düşüşlere sebep olmuştur. 50°C'lik ön ısıtmanın hamur ile agrega arasındaki bağı arttırdığı, mikro çatlakları azaltarak daha yoğun bir matris oluşturduğu ve alkali aktivasyonu ilerlettiği SEM ve FTIR analizlerinden anlaşılmaktadır. Ayrıca FTIR analizleri, suyla temas eden AAS'lerde hidrasyon reaksiyonlarının gerçekleştiğini göstermektedir.

Anahtar Kelimeler: Alkali-aktive cüruf, Malzemelerin ön-ısıtılması, Erken dayanımlı betonlar, Isıl kür, Suya dayanıklılık

*Sorumlu yazar (Corresponding Author): Cemal KARAASLAN, cemal.karaaslan@igdir.edu.tr

1. INTRODUCTION

Concrete, one of the most widely used construction materials, traditionally relies on Portland cement as its primary binder. However, the growing interest in sustainable and environmentally friendly alternatives has paved the way for the development of alkali-activated cements (AACs). In recent years, AACs have gained considerable attention due to their potential to offer enhanced performance and reduced carbon footprint compared to Portland cement-based concretes [1]. This has prompted researchers and engineers to explore and compare the properties and characteristics of AACs with those of conventional concretes. Alkali-activated slag (AAS) is a type of alkali-activated cementitious material that utilizes blast furnace slag as its main precursor. Blast furnace slag is a byproduct of the iron and steel industry and contains a high content of reactive compounds, such as calcium, silicon, and aluminum [2]. When activated with alkaline solutions, typically a combination of sodium hydroxide and sodium silicate, the slag undergoes a chemical reaction that results in the formation of a hardened matrix. This matrix exhibits cementitious properties and provides strength and durability to the AAS. One of the key advantages of AAS is its ability to utilize industrial waste materials, contributing to sustainable construction practices. AAS offers several desirable characteristics, including high early strength, good chemical resistance, and low carbon footprint compared to traditional Portland cement-based materials [3,4].

AAS/geopolymer binders require heat curing to achieve sufficient mechanical properties, typically ranging from a few hours to a few days, with curing temperatures usually falling between 40°C and 90°C [5,6]. Geopolymers produced with high calcium content binders, in other words alkali-activated cements, have been shown to reach acceptable strength levels within reasonable timeframes at room temperatures [7]. However, heat curing has been found to accelerate the strength development and improve the mechanical properties of alkali-activated cements [8]. It is worth noting that in the conventional method, the

heat curing process for alkali-activated cements (slags) is applied after obtaining the samples. This practice limits the possibility of in-situ casting of alkali-activated slag (AAS) and requires additional energy consumption. On the other hand, preheating the materials before mixing is suggested to offer wider application possibilities for AAS concrete and contribute to reduced energy consumption [9].

Souza et. al. [10] demonstrated that heating the mixture in 3D-printed metakaolin-based geopolymers can yield highly fluid mixtures, allowing for the continuous and rapid production of geopolymer mixtures through a systematic heating process, from pumping to printing. Nguyen et. al. [9] found that preheating fly ash and fine aggregate resulted in geopolymer mortars with higher compressive strength when a larger amount of supplied heat energy was provided. Mazumder and Prasad [11] investigated the effect of preheating in self-compacting geopolymer concretes by mixing fly ash and alkali activator at room temperature and then heating the mixture at 85°C for 15, 20, 25, and 30 minutes before combining it with the aggregate. They determined that the preheated self-compacting geopolymer concrete exhibited 31% higher compressive strength than one cured at 60°C for 48 hours and achieved 99% energy savings.

Motivated by these findings and the limited research available on the pre-heating method for the production of alkali-activated slag (AAS) mortars, the present study aims to investigate the effects of pre-heating the alkaline activator, ground granulated blast furnace slag, and fine aggregate to temperatures reaching up to 65°C. The physical and mechanical properties of the mortars will be examined, and the microstructural changes of the alkali-activated slags will be analyzed using FTIR and SEM/EDX techniques.

2. MATERIALS AND METHODS

2.1. Materials

Ground granulated blast furnace slag, obtained from Iskenderun Iron-Steel Plant, was used as the powder

binder in this study. The chemical composition of the slag is presented in Table 1. Detailed information regarding the particle size distribution,

mineralogical structure, and physical properties of the slag can be found in the study conducted by Danish et. al [12].

Table 1. Chemical composition of slag (wt.%) [12]

Oxides	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	LOI
Slag	35.5	34.2	18.3	0.6	9.7	0.1	0.3	0.4	0.3

LOI: Loss on ignition

For the alkaline activation process, NaOH (98% purity) and Na₂SiO₃ (with a SiO₂/Na₂O weight ratio of 2.04 and SiO₂ content of 24.5%) were utilized. Solid NaOH particles were dissolved in pure water to prepare a 10 M NaOH solution. The fine aggregate used was CEN Standard Sand with a maximum particle size of 2 mm, conforming to TS EN 196-1 [13].

2.2. Specimen Production

The proportions of the alkali-activated mortar mixtures are provided in Table 2. The Na₂SiO₃ to NaOH weight ratio was set at 2.5, the alkaline activator to powder binder weight ratio was 0.60, and the fine aggregate to powdered binder weight ratio was 2.5 [14].

Table 2. Mix proportions

Mix ID	NaOH (g)	Na ₂ SiO ₃ (g)	Slag (g)	Sand (g)	Heating temperature (°C)
PH25	92.6	231.4	540	1350	25
PH50					50
PH65					65

The NaOH solution (10 M) was prepared 24 hours prior to its mixing with the Na₂SiO₃ solution. After the resting period, the NaOH solution was added to the Na₂SiO₃ solution and stirred for 5 minutes. The resulting solution mixture was then placed in a sealed container and placed in a preheated oven at the desired temperature. The standard sand and slag were mixed for 3 minutes, and the mixture was transferred along with the mixing bowl to the oven. After a 2-hour waiting period, the materials were removed from the oven. Subsequently, the alkali activator mixture was added to the solid materials in the mixing bowl and the mixing process continued for 2 minutes. The fresh mixture was immediately cast into 40 mm cube molds. The molds were vibrated 60 times on a vibrating table to eliminate entrapped air voids. Afterward, the surface of the molds was cleaned, and the specimens were left uncovered at the laboratory's room temperature of 25 ± 2°C. Following a 24-hour curing period, the specimens were demolded and left exposed in the laboratory until the testing day. It should be noted that the specimens utilized to determine the 8-hours compressive strength were removed from the mold after 7 hours.

2.3. Experimental Methods

The bulk density and water absorption of the AAS mortar specimens were determined according to the TS EN 12390-7 standard, utilizing the 7-day specimens [15]. It is noteworthy that the properties of AACs can significantly vary with temperature; hence, the specimens were tested without undergoing drying in an oven. The compressive strength of the AAS mortar specimens was evaluated at the 8th hour, as well as on days 1, 3, 7, and 28, using a 20 kN capacity cement compression and flexural testing machine according to the TS EN 196-1 standard [13].

To evaluate the water resistance of preheated AAS mortars, 3-day specimens were submerged in water for 24 hours, followed by a 24-hour period of storage in the laboratory environment. This cycle was repeated once more, and the remaining compressive strengths of the specimens were measured. The change in strength serves as an indicator of the water resistance of AAS mortars. Each data presented in the physical and mechanical test results are the average of four specimens.

The Agilent Cary 630 FTIR (Fourier-Transform Infrared) spectrometer, capable of operating within the wavelength range of 4000-650 cm^{-1} , was employed to observe the molecular bonding structure of AASs. The ZEIS Gemini Sigma 300 scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) were utilized to analyze the microstructure and chemical compositions of the hardened mortar specimens.

3. RESULTS AND DISCUSSION

3.1. Physical Properties

The bulk density and water absorption of AAS mortars are presented in Table 3. The bulk densities of AAS mortars ranges from 2312.8 kg/m^3 to 2318.7 kg/m^3 . It can be observed that the bulk density of AAS is not significantly affected by the preheating process, as these values are quite close to each other. Similarly, the water absorption values of these specimens are also in close proximity. Furthermore, the water absorption levels are found to be very low.

Table 3. Physical properties of AAS mortars

Mix ID	Bulk density (kg/m^3)	Water absorption (%)
PH25	2317.5	0.52
PH50	2318.7	0.46
PH65	2312.8	0.47

It is noteworthy that the PH50 specimens exhibit higher bulk density and lower water absorption compared to the others. This could be attributed to the higher material temperatures, resulting in a more fluid mixture and better compaction in the mold. It may also be a consequence of improved slag activation due to the higher material temperature. The absence of such improvement in the mixture at 65°C can be attributed to its rapid solidification and inadequate compaction in the mold due to the high temperature effect. In fact, attempts were made to produce AAS at temperatures above 65°C; however, the high reactivity of the slag and the instant solidification of the material at high temperatures (Figure 1) hindered the investigation of the effects of temperatures above 65°C.



Figure 1. Solidification of the mixture with a preheating temperature of 75°C during the mixing process

3.2. Compressive Strength

The change in compressive strengths over time in AAS mortars with different preheating temperatures is illustrated in Figure 2. All three AAS mortars achieved approximately 60% of their ultimate strength (considering the 28-day strength) within the first three days and approximately 86-88% within the first seven days. From this perspective, it can be observed that preheating does not make a significant difference. However, when examining the strength development in the first three days, it is evident that preheating significantly contributes to the early strength.

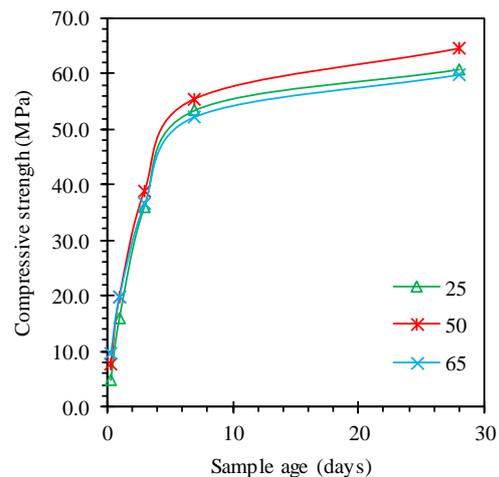


Figure 2. Strength development of AAS mortars

Figure 3 illustrates the strength development of AAS mortars preheated at 50°C and 65°C, along with the relative change in strength compared to the AAS mortar without preheating. It can be observed that preheating at 50°C and 65°C resulted in strength increases of 58.7% and 97.3% in eight hours, and 24.4% and 24.3% in one day, respectively. However, after three days, the influence of preheating on strength diminishes significantly. In terms of contribution to strength, preheating at 65°C is more effective in the initial hours but loses its effect after three days. Indeed, the compressive strengths of this specimen at 7 and 28

days were 2.0% and 1.3% lower, respectively, than the compressive strengths of the specimen not subjected to preheating. In Figure 1, it is evident that the mixture preheated at 75°C solidified before placement. Similarly, as shown in the image provided in Figure 4, the effect of preheating at 65°C led to incomplete consolidation due to rapid solidification during placement. The acceleration of alkali activation and the significant increase in strength in the initial hours can be attributed to the effect of preheating at 65°C, but the inadequate consolidation of samples due to rapid solidification resulted in strength reduction after three days.

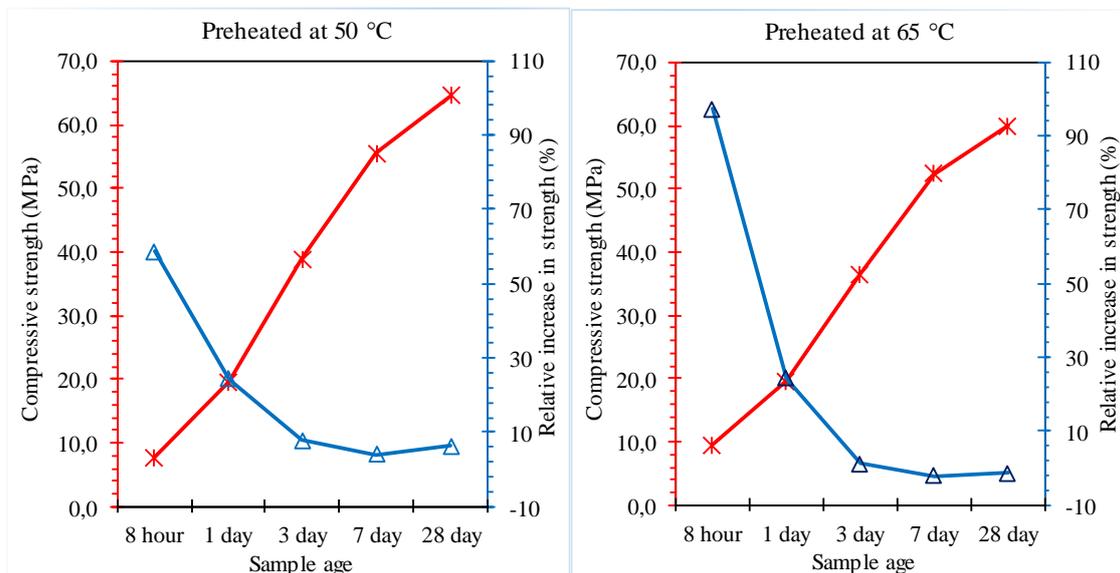


Figure 3. Strength development and the effect of preheating on the strength increase of AAS mortars

On the other hand, preheating at 50°C not only increased the early strength but also resulted in a 6.3% increase in ultimate strength. Considering the contribution to strength, preheating at 50°C provides a significant contribution both in the early stages and at the ultimate strength. The traditional method of thermal curing for AAS/geopolymer concrete requires curing at mild temperatures (40-90°C) for several hours to a few days [16]. This method not only eliminates the possibility of in-situ casting of AAS/geopolymer concrete but also leads to significant energy consumption. The proposed

method will increase the in-situ casting capabilities of AAS/geopolymer concrete by utilizing an asphalt plant commonly used in the construction of hot mix asphalt pavements. This approach will also result in shorter curing times and relatively lower curing temperatures, leading to significant energy savings [11]. Moreover, the utilization of preheated materials in the production of AAS will result in increased early-age strength, enabling early opening to traffic for concrete pavement and providing protection against early frost damage.



Figure 4. Incomplete consolidation of specimens preheated at 65°C.

The SEM images of AAS mortars with preheating temperatures of 25°C and 50°C were observed on 7-day specimens and presented in Figure 5. As shown in Figure 5a, there is less adhesion between the hardened AAS paste and the aggregate in the AAS mortar with a preheating temperature of 25°C. In contrast, the AAS mortar with a preheating temperature of 50°C exhibits better bonding at the paste-aggregate interface. Moreover, when examining the hardened paste regions at the same scale (Figure 5b), wide cracks are observed in the AAS mortar with a preheating temperature of 25°C, while a denser matrix with fine cracks is present in the AAS mortar with a preheating temperature of 50°C.

At higher magnifications (Figure 5c), it can be observed that the reaction products in the AAS mortar with a preheating temperature of 50°C fill the existing cracks, which are evident in the AAS mortar with a preheating temperature of 25°C. This phenomenon explains the higher strength of AAS mortars with a preheating temperature of 50°C. It is well known that a moderate curing temperature improves the mechanical properties and microstructure of alkali-activated cements and geopolymer binders [1,16].

3.3. Water Resistance

Figure 6 presents the remaining compressive strengths of the alkali-activated slag (AAS) mortars after 2 wetting-drying cycles. It can be observed that the compressive strength of AAS mortars subjected to wetting-drying cycles has increased compared to the compressive strength at 3 days. In fact, the compressive strength of these specimens is

slightly higher than that of the specimens cured in dry conditions for the same duration (7 days). The compressive strength of AAS mortars with preheating temperatures of 25°C, 50°C, and 65°C, exposed to wetting-drying cycles, has increased by approximately 14.9%, 18.9%, and 26.0% respectively in 4 days compared to the specimens kept in dry conditions. The higher increase in compressive strength for the AAS mortar with a preheating temperature of 65°C can be attributed to the faster hardening of the mortar at this temperature, preventing the dissolution of certain precipitates (such as Ca^{2+}) in the slag. These precipitates dissolve and react in the aqueous (alkaline) environment, contributing to the observed strength enhancement. It is important to note that these reactions are primarily hydration reactions, with the main product of hydration being the formation of the C-S-H gel. This gel significantly contributes to the increase in strength observed in the AAS mortar.

Figure 7 presents the FTIR spectra of alkali-activated slag (AAS) specimens with preheating temperatures of 25°C and 50°C, as well as AAS subjected to wetting-drying cycles with a preheating temperature of 50°C. It can be observed that these three samples exhibit highly similar FTIR spectra. However, with a preheating temperature of 50°C, the hump at 965 cm^{-1} , which is a significant fingerprint associated with the asymmetric stretching functional group of Si-O-T (T: Si, Al tetrahedral) in AAS/geopolymer materials, becomes more pronounced. This indicates that the alkali activation of slag further progresses due to the heat provided by the preheated materials.

On the other hand, an interesting observation is that the asymmetric stretching vibration band of Si-O-Si (Al) shifts towards a higher wavenumber, specifically from 965 cm^{-1} to 969 cm^{-1} , indicating an increased wave number for the AAS specimens with a preheating temperature of 50°C in a water environment. This shift is attributed to the increase in Si/Al ratio in the reaction products. The released Ca^{2+} ions from unreacted slag particles undergo a reaction with SiO_4^{4-} ions derived from sodium silicate solution, resulting in the formation of C-S-

H gel products and a densified matrix [17,18]. The densification of the matrix contributes to the

strength enhancement observed in Figure 6.

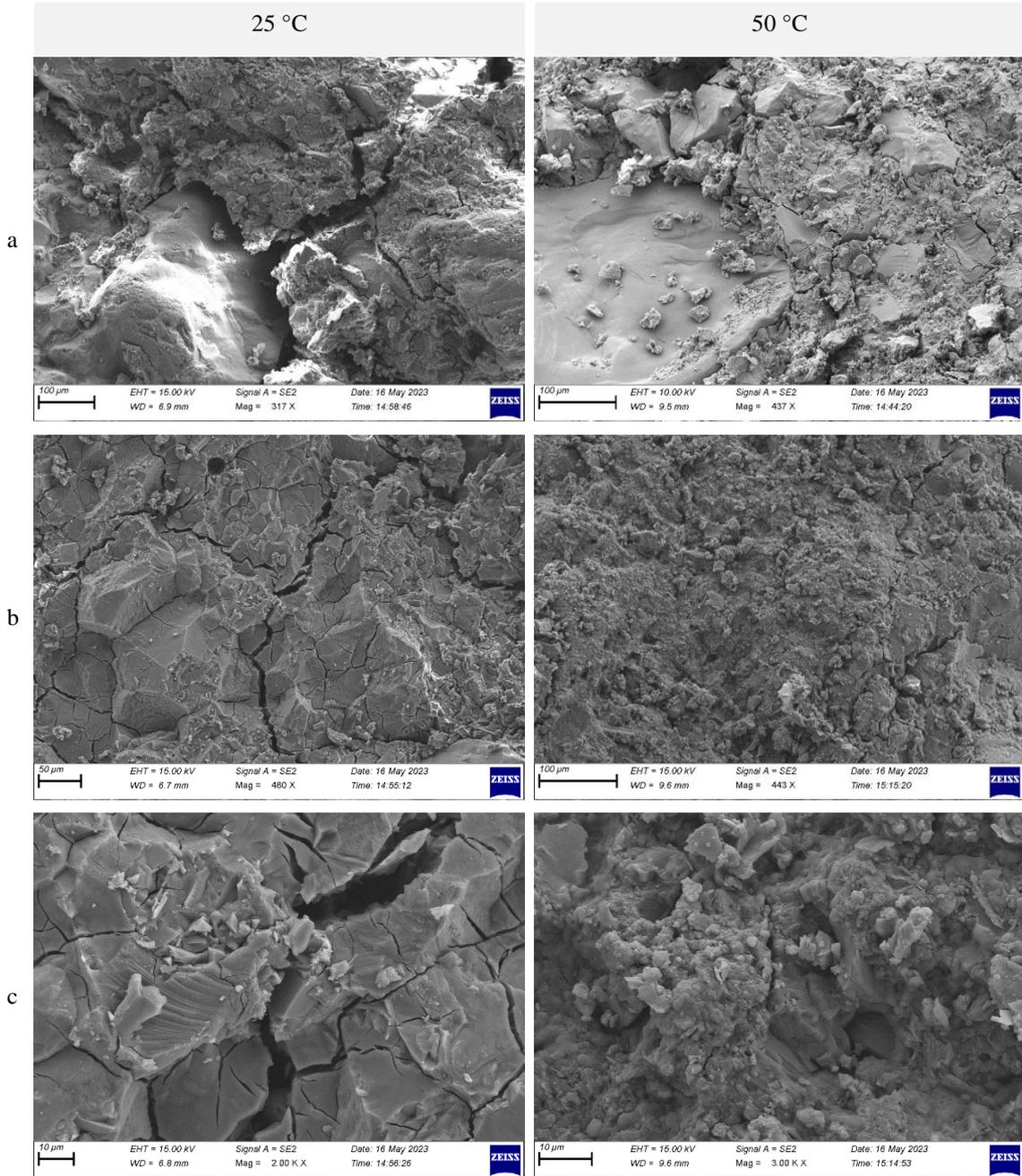


Figure 5. SEM images of AAS mortars with preheating temperatures of 25°C and 50°C

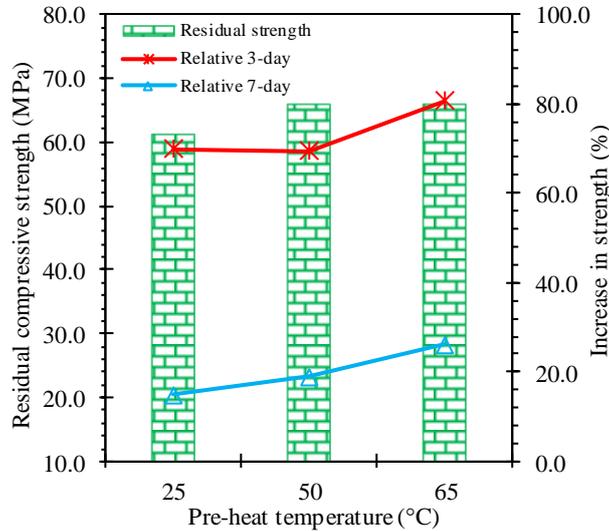


Figure 6. Strength of AAS mortars after wet-dry cycles and the variation of this strength compared to the 3-day and 7-day strengths

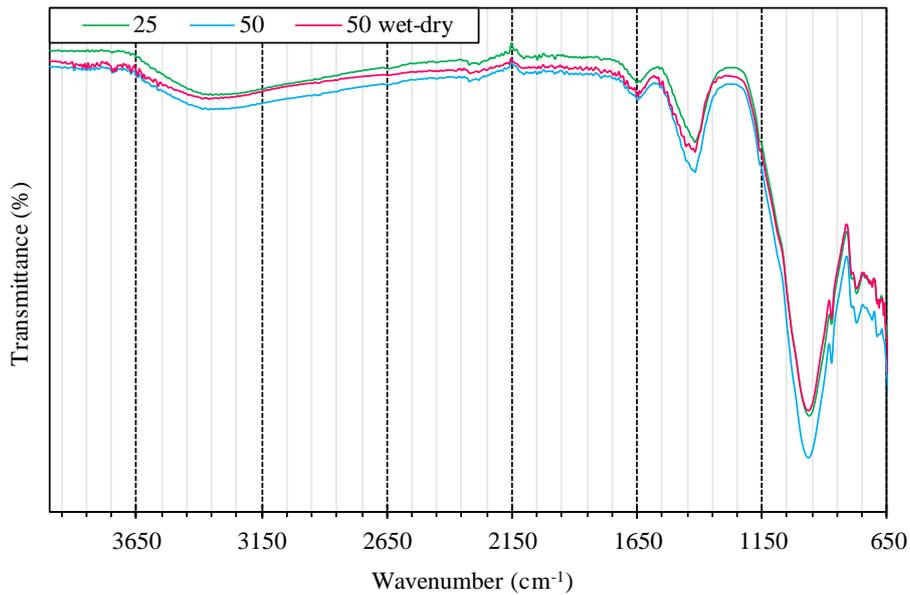


Figure 7. FTIR analysis of AAS specimens with different preheating temperatures and subjected to wetting-drying cycles

The resistance of an alkali-activated cement or geopolymers against water effects is one of the most crucial indicators in determining its suitability as a construction material [19, 20]. The fact that AAS is not negatively affected by water effects highlights its significance as a viable construction material. Its

ability to withstand the detrimental effects of water enhances its potential for structural applications. Additionally, the water resistance of AAS contributes to its long-term durability, making it a promising alternative to traditional cement-based materials in sustainable construction practices.

4. CONCLUSION

In this study, the effects of preheating on the early strength development of alkali-activated slag (AAS) mortars were investigated. The results demonstrated that preheating the materials before mixing significantly influenced the early strength of AAS mortars. Preheating at 50°C resulted in a 58.7% increase in strength within eight hours, and a 6.3% increase in ultimate strength. Preheating at 65°C showed higher early strength in the initial hours but led to strength reduction after three days due to rapid solidification. Microstructural analysis using SEM and FTIR revealed that preheating at 50°C improved the bond between paste and aggregate, reduced microcracks, and promoted enhanced alkali activation, indicating denser matrix formation. Furthermore, FTIR analysis confirmed the occurrence of hydration reactions (resulting in the formation of the C-S-H gel) in AAS mortars upon contact with water.

In conclusion, the utilization of this proposed method not only significantly enhances the early strength development of AAS but also provides better opportunities for in-situ casting of concrete. Additionally, it offers energy savings, making positive contributions to construction practices.

5. REFERENCES

1. Amer, I., Kohail, M., El-Feky, M.S., Rashad, A., Khalaf, M.A., 2021. A Review on Alkali-Activated Slag Concrete. *Ain Shams Engineering Journal*, 12(2), 1475-1499.
2. Erdoğan, T.Y., 2016. *Beton (Concrete)*. METU Press Publishing Company, 6. ed. Ankara, 757.
3. Provis, J.L., 2018. Alkali-Activated Materials. *Cement Concrete Research*, 114, 40-48.
4. Roy, D.M., 1999. Alkali-Activated Cements Opportunities and Challenges. *Cement Concrete Research*, 29(2), 249-254.
5. Yener, E., Karaaslan, C., 2020. Curing Time and Temperature Effect on the Resistance to Wet-Dry Cycles of Fly Ash Added Pumice Based Geopolymer. *Cement Based Composites*, 1(2), 19-25.
6. Rovnaník, P., 2010. Effect of Curing Temperature on the Development of Hard Structure of Metakaolin-Based Geopolymer. *Construction Building Materials*, 24(7), 1176-1183.
7. Karaaslan, C., Yener, E., Bağatur, T., Polat, R., Gül, R., Alma, M.H., 2022. Synergic Effect of Fly Ash and Calcium Aluminate Cement on the Properties of Pumice-Based Geopolymer Mortar. *Construction and Building Materials*, 345, 128397.
8. Bakharev, T., Sanjayan, J.G., Cheng, Y.B., 1999. Effect of Elevated Temperature Curing on Properties of Alkali-Activated Slag Concrete. *Cement Concrete Research*, 29(10), 1619-1625.
9. Nguyen, K.T., Le, T.A., Lee, J., Lee, D., Lee, K., 2017. Investigation on Properties of Geopolymer Mortar Using Preheated Materials and Thermogenetic Admixtures. *Construction Building Materials*, 130, 146-155.
10. Souza, M.T., Simão, L., Moraes E.G., Senff, L., Pessôa, J.R.C., Ribeiro, M.J., Oliveira, A.P.N., 2021. Role of Temperature in 3D Printed Geopolymers: Evaluating Rheology and Buildability. *Materials Letters*, 293, 129680.
11. Mazumder, E.A., Prasad, L.M., 2023. Performance Enhancement of Fly Ash-Based Self Compacting Geopolymer Concrete Using Pre-heating Technique, *Iranian Journal of Science Technology. Transactions of Civil Engineering*, 1-13.
12. Danish, A., Öz, A., Bayrak, B., Kaplan, G., Aydın, A.C., Ozbakkaloglu, T., 2023. Performance Evaluation and Cost Analysis of Prepacked Geopolymers Containing Waste Marble Powder Under Different Curing Temperatures for Sustainable Built Environment. *Resources, Conservation Recycling*, 192, 106910.
13. TS EN 196-1, 2016. *Çimento Deneysel Metotları - Bölüm 1: Dayanım Tayini (Methods of Testing Cement - Part 1: Determination of Strength)*, Ankara.
14. Yang, K.H., Song, J.K., Lee, K.S., Ashour, A.F., 2009. Flow and Compressive Strength of

- Alkali-Activated Mortars, *ACI Materials Journal*, 106(1), 50-58.
15. TS EN 12390-7, 2010. Beton - Sertleşmiş Beton Deneylemleri - Bölüm 7: Sertleşmiş Betonun Yoğunluğunun Tayini (Testing Hardened Concrete - Part 7: Density of Hardened Concrete), Ankara.
 16. Suwan, T., Fan, M., Braimah, N., 2016. Internal Heat Liberation and Strength Development of Self-Cured Geopolymers in Ambient Curing Conditions. *Construction Building Materials*, 114, 297-306.
 17. Zhang, Z., Zhu, Y., Zhu, H., Zhang, Y., Provis, J.L., Wang, H., 2019. Effect of Drying Procedures on Pore Structure and Phase Evolution of Alkali-Activated Cements. *Cement Concrete Composites*, 96, 194-203.
 18. Cao, R., Zhang, S., Banthia, N., Zhang, Y., Zhang, Z., 2020. Interpreting the Early-Age Reaction Process of Alkali-Activated Slag By Using Combined Embedded Ultrasonic Measurement, Thermal Analysis, XRD, FTIR and SEM. *Composites Part B: Engineering*, 186, 107840.
 19. Tchadjié, L.N, Djobo, J.N.Y., Ranjbar, N., Tchakouté, H.K., Kenne, B.B.D., Elimbi, A., Njopwouo, D., 2016. Potential of Using Granite Waste as Raw Material for Geopolymer Synthesis. *Ceramics International*, 42(2), 3046-3055.
 20. Karaaslan, C., Yener, E., Bağatur, T., Polat, R., 2022. Improving the Durability of Pumice-Fly Ash Based Geopolymer Concrete with Calcium Aluminate Cement. *Journal of Building Engineering*, 59, 105110.