- Technical Paper -

INFLUENCE OF ALKALI METAL TYPES IN THE ACTIVATOR ON THE MECHANICAL PROPERTIES OF GEOPOLYMER MORTARS

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ABSTRACT

This study investigates the effects of LiOH, NaOH, and KOH as alkali activators on geopolymer mortar properties using GGBS, FA, and silica fume as binders. LiOH showed delayed setting and lower compressive strength due to Li_2SiO_3 formation and limited SiO_2 extraction. NaOH achieved the highest strength through effective polymerization, while KOH performed moderately. XRD analysis highlighted the impact of alkali metal ions on microstructure. Further research is required to optimize LiOH-based geopolymers.

Keywords: geopolymer, alkali metal ion, activator, mechanical properties, micro analysis

1. INTRODUCTION

As environmental issues and the importance of resource recycling are emphasized, geopolymer has gained attention as a carbon-neutral and sustainable construction material. Davidovits defined the three-dimensional aluminosilicate structure and named it "geopolymer" [1]. Unlike cement, geopolymers do not rely on clinker and instead harden through the reaction between aluminosilicate precursors and alkali activators. Due to this characteristic, geopolymers are classified as a type of alkali-activated material (AAMs) and are increasingly recognized as eco-friendly construction materials [2]. Particularly, their ability to use industrial by-products such as fly ash (FA) and ground granulated blast-furnace slag (GGBS) as primary raw materials highlights their potential as sustainable construction materials [3].

However, structures or construction cases utilizing geopolymers remain rare. This is attributed to practical limitations such as the availability of materials, lack of market competitiveness, a short development history, and the absence of design and testing standards [4]. Additionally, performance limitations such as excessively short setting times and excessive shrinkage are cited as drawbacks, underscoring the need for continuous research on geopolymers [5]. The mechanical and microstructural properties of geopolymers vary significantly depending on their composition and curing condition, with the type and characteristics of the activator exerting a particularly strong influence.

In geopolymer research, hydroxides such as NaOH and KOH are commonly used as alkali activators, and silicate-based activators such as sodium silicate (Na_2SiO_3) are sometimes added. Hydroxide ions promote the dissolution of aluminosilicates during the polymerization process, while silicates supplement the main components of the geopolymer gel, enhancing its strength and durability. Alkali metal ions maintain the electrical balance of the geopolymer gel, and the type of metal ions in the activator is a crucial factor determining the properties of geopolymers [6]. For instance, Na+ has been reported to induce polymerization reactions more efficiently than K+ due to its smaller ionic size [6].

However, optimizing geopolymer performance with a limited range of activators has its limitations. Therefore, research on the single use or combined use of different materials as activators is a key factor in improving the mechanical properties and durability of geopolymers, thus suggesting their practical applicability.

Lithium, an alkali metal, is utilized in various industries such as batteries, metallurgy, ceramics, and glass. Particularly, lithium slag, an industrial by-product of lithium carbonate production, is primarily composed of SiO_2 and Al_2O_3, similar to GGBS, but with lower CaO content [7]. While some studies have evaluated the applicability of lithium slag in geopolymers, cases where lithium ions are used as alkali activators are rare. Lithium, which has the smallest ionic radius, was theoretically suggested to promote the polymerization reaction in geopolymers more effectively than sodium ions. However, there is also concern that its relatively lower alkalinity might reduce the solubility of the precursor [6], and research clearly elucidating the specific effects of lithium remains insufficient.

Therefore, this study investigates the effects of lithium ions on the geopolymer system by using LiOH, NaOH, and KOH as alkali activators, analyzing the relationship between the characteristics of alkali metal ions and the mechanical properties of geopolymers. GGBS and FA, identified as the principal binders of geopolymers, were used, and silica fume (SF) was

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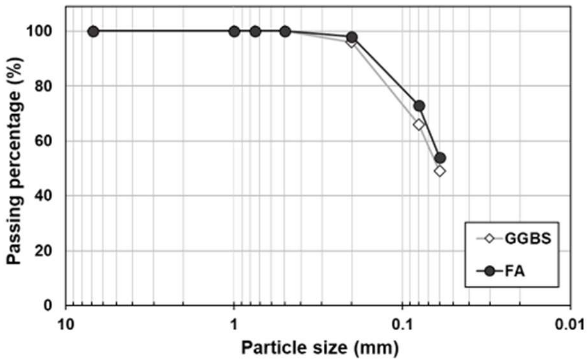


Fig. 1 Particle size distribution of GGBS and FA

Table 1 Properties of binder

Binder	Chemical composition (wt. %)				Specific Gravity (g/cm^3)
	CaO	SiO_2	Al_2O_3	Fe_2O_3	
GGBS	55.85	31.17	13.92	0.73	2.9
FA	26.19	38.84	19.52	2.87	2.3
SF	0.02	99.00	0.30	0.05	2.2

* GGBS: Ground Granulated Blast-furnace Slag, FA: Fly Ash, SF: Silica Fume

Table 2 Mixture of geopolymer mortar (weight ratio)

ID	GGBS	FA	SF	Sand	Alkaline activator			
					Water	LiOH	NaOH	KOH
Li	0.383	0.432	0.124	0.996	0.400	0.036		
Na	0.383	0.432	0.124	0.996	0.400		0.060	
K	0.383	0.432	0.124	0.996	0.400			0.084

employed as an additional source of silica to assess changes in specimen characteristics according to the activator. The flowability, setting time, and compressive strength of the geopolymer mortar were measured, and microstructural analysis was conducted using gravimetric analysis, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

2. TEST PROGRAMS

2.1 Materials

In this study, the binder was a mixture of GGBS, FA, and SF. The chemical composition of the binders was obtained through EDX (energy dispersive X-ray) analysis for GGBS and FA and XRD (X-ray diffraction) analysis for SF, as presented in Table 1. Fig. 1 shows the particle size distribution curve of the binder. Fine aggregate was quartz sand with a specific gravity of 2.65 g/cm^3 and a particle size of 0.25–0.6 mm.

To investigate the properties of geopolymer mortar according to different alkali metal types in activators, LiOH, NaOH, and KOH were used. The hydroxides were industrial-grade products with a purity of over 98%, and their molar masses were 23.95 g/mol, 40.00 g/mol, and 56.11 g/mol, respectively. LiOH, NaOH, and KOH were used in powder, bead, and flake forms, respectively, with the beads being approximately 5 mm and the flakes approximately 10 mm in size. The alkali activators were prepared by dissolving hydroxides in water to achieve a concentration of 3.75 M in a beaker. To eliminate the influence of heat generated during the dissolution of hydroxides, the activators were prepared at least 24 hours before mixing.

2.2 Specimens

Table 2 shows the mix proportions of the geopolymer mortar in weight ratios. The variable is the type of alkali metal, and the binder ratios were set to achieve a compressive strength of 40 MPa or higher at 28 days of curing. The composition of the binder was set as a volumetric ratio of GGBS: FA: SF = 0.35: 0.5: 0.15. The water-to-binder ratio was set at 0.4 by weight, and the sand-to-binder ratio was set at 1.0 by volume. The names of the specimens were labeled using the atomic symbols of the alkali metals, Li, Na, and K, to indicate which activator was used.

The mixing of the geopolymer mortar was conducted using a small mixer. First, the binder and fine aggregate were dry-mixed for 30 seconds, after which the alkali activator was added at a constant rate, and mixing was continued for 2 minutes. The mortar was then poured into molds to create test specimens.

Two types of specimens were prepared: cubic and prism forms. To measure the compressive strength of geopolymer mortar based on the alkali metal, cubic specimens of 40 × 40 × 40 mm^3 were produced following ASTM C109. The specimens were cast into molds, cured at room temperature for 24 hours, and then demolded. They were subsequently cured unsealed in a temperature-controlled and humidity-controlled chamber at 20°C and 65% relative humidity.

2.3 Test methods

Within the scope of this study, the objective is to examine the mechanical properties of geopolymer mortar based on the types of LiOH, NaOH, and KOH. Therefore, the properties such as table flow, setting time, and compressive strength, which may emerge from polymerization reactions that vary according to the type of alkali metal ion, were investigated and analyzed using gravimetric analysis, XRD, and SEM.

The workability of the mortar in its fresh state was evaluated by measuring the table flow. Using an automatic table flow apparatus referenced from ASTM C230, 25 impacts were applied over 15 seconds, and the longest and shortest diameters of the spread were measured. The average value was calculated to compare the characteristics of the mix.

The setting time of the mortar was measured using a Vicat apparatus according to ASTM C191.

Plastic molds with a lower diameter of Φ80 mm, an upper diameter of Φ70 mm, and a height of 40 mm was used. Immediately after mixing, the mortar was poured into the mold, and the needle was dropped at different positions at 10-minute intervals. The readings on the apparatus were recorded. The time when the distance between the needle and the base plate reached 4 mm was recorded as the initial setting time, and the time at 39.5 mm was recorded as the final setting time.

The mechanical properties of the geopolymer mortar were primarily evaluated through compressive strength. The test was conducted at curing ages of 3, 7, and 28 days, referencing ASTM C1928. A material testing machine with a capacity of 200 kN (Quasar 200, Galdabini Cesare S.p.A., Varese, Italy) was used for the test in Fig. 5, applying a loading rate of 0.8 MPa/s. The average compressive strength of three cubic specimens was reported as the final result.

The gravimetric analysis method was used to compare the ability of alkali metal activators to dissolve SiO_2, a key component in the geopolymer polymerization process, from the binder. This was intended to analyze the results of table flow and setting time measurements. Solutions of 200 ml with a concentration of 3.75 M for LiOH, NaOH, and KOH were prepared in 250 ml glass beakers using distilled water, and 22.53 g of silica fume was added. The mixtures were stirred at 250 rpm for 12 hours using a magnetic stirrer. The solutions were then filtered using filter paper with a pore size of 5 μm. To precipitate SiO_2, 7.81 ml of hydrochloric acid was added to 10 ml of the filtered solution. Once precipitates formed, they were filtered out using filter paper and washed with distilled water to remove soluble salts. The precipitated SiO_2 was dried, and its mass was measured to a precision of 0.01 g. Additionally, the precipitated SiO_2 was examined using SEM to confirm its crystalline structure.

XRD analysis was performed to relatively compare the amounts of polymerization reaction products in the geopolymer paste regions using different alkali metal activators. Samples were ground into a powder using a mortar and pestle and passed through a 75 μm (200 mesh) sieve. The analysis was conducted using the SmartLab 9 kW instrument by Rigaku Corporation (Tokyo, Japan). The crystalline phase composition of the samples was examined within the range of 10–70 degrees (2Θ) using a Cu Kα detector at a scanning speed of 3 deg/min and a step size of 0.02.

SEM analysis was performed to investigate the microstructure and polymerization reaction products through images of the cross-section of the alkali-activated mortar. As a pre-treatment, the samples were coated with platinum at a thickness of 2 nm for 60 seconds. The equipment used was the HITACHI SU7000 (Tokyo, JAPAN), set at an accelerating voltage of 10 kV and a spot intensity of 30.

3. TEST RESULTS

3.1 Table flow

Table 3 shows the graph of the table flow measurement results and the state at the end of the test for geopolymer mortar with different alkali activators. Fig. 2 (a)-(c) shows a photo of the test after completion.

Table 3 Table flow of geopolymer mortar

Alkaline activator	LiOH	NaOH	KOH
Average Table flow (mm)	139	151.5	190.5
Activator viscosity (mPa·s)	2.530	2.043	1.411
Cation size (pm)	76	102	128
Cation Charge density (10^{10}×C/m^3)	8.70	3.61	0.58

(a) LiOH (b) NaOH (c) KOH

Fig. 2 Images of table flow results

The length of all specimens was measured after 25 impacts. The table flow values of mortar using LiOH, NaOH, and KOH were 139 mm, 151.5 mm, and 190.5 mm, respectively. These results, as shown in Table 3, exhibited a positive correlation with the size of metal ions and a negative correlation with charge density.

In this study, hydroxides in the form of MOH with different alkali metals were used as alkali activators. When these ionic compounds dissolve in water to form an aqueous solution, the viscosity of the solution can vary depending on the concentration and type of dissolved ions [8]. The concentration of the activators was consistently set at 3.75 M, with each containing the alkali metals Li, Na, or K. The size of alkali metal ions and their charge density are inversely proportional. Higher charge density leads to stronger interactions with other ions, influencing the solubility and bonding strength of substances. Consequently, the viscosity of the activators used was found to decrease in the order of Li > Na > K [9]. Furthermore, the viscosity of the 3.75 mol concentration used in the experiment was found to be 2.530 mPa·s, 2.043 mPa·s, and 1.411 mPa·s for LiOH, NaOH, and KOH, respectively. In a geopolymer system, using a high-viscosity activator can affect the workability of the mix, depending on its properties. The viscosity of the activator can vary with concentration or the ratio of components, such as Na_2SiO_3/NaOH. Previous studies showed that the viscosity of the activator affected the non-setting characteristics of the mortar, and as the content of sodium silicate increased from 4% to 8%, the viscosity of the activator increased, resulting in a decrease in flow from 165 mm to 158 mm [10]. Therefore, the table flow was observed to decrease in the order of Li < Na < K, corresponding to the type of alkali metal used.

3.2 Setting time

Table 4 shows the graph of the setting time measurement results for geopolymer mortar with different alkali activators. The mortar set in the order of Na-K-Li. The initial setting times for Li, Na, and K were measured at approximately 210 minutes, 80 minutes, and 120 minutes, respectively, while the final setting times were approximately 330 minutes, 150 minutes, and 210 minutes, respectively. Additionally, the time from initial to final setting was approximately 120 minutes, 70 minutes, and 90 minutes for Li, Na, and K, respectively. Despite the smaller ionic size of Li+ compared to Na+, geopolymer with LiOH exhibited the slowest entry into the initial setting and the slowest overall setting speed.

The setting of a geopolymer system occurs through the polymerization reaction of silicate and alumina dissolved from the precursor [11]. Such polymerization reactions can be accelerated by increasing the concentration of the activator, thereby shortening the setting time. The polymerization reaction is also influenced by the type of alkali metal. In geopolymer systems, Na+, with a smaller ionic size, is known to form zeolite crystals more rapidly than K+ [12].

However, the setting time measurements showed that despite the smaller size of Li+ compared to Na+, it required more time to set. Geopolymers generally exhibit shorter setting times compared to OPC composites. Thus, studies have been conducted to use additives to delay setting. These retarders delay setting by altering or blocking the sequence of chemical reactions, thereby inhibiting polymerization.

Silicates dissolved by the activator can react with metal cations to form silicates in the form of M_2SiO_3. While Na_2SiO_3 and K_2SiO_3 dissolve back into ions in water, Li_2SiO_3 remains in crystalline form due to its insolubility in water [13]. This reduces the concentration of silicate ions freely available within the matrix, thereby limiting the availability of silicate necessary for the polymerization reaction. Since silicate is the main reactant in forming the geopolymer gel through the polymerization reaction, the presence of Li_2SiO_3 in molecular form consequently restricts the supply of silicate that can participate in the reaction. The reduction in reactive silicate may slow the polymerization rate, acting as a cause for the delayed setting of the geopolymer. Therefore, the delay in setting observed in geopolymers using Li is presumed to be due to the decrease in reactive silicate resulting from the formation of lithium silicate.

3.3 Compressive strength

Fig. 3 presents the compressive strength measurement results for geopolymer mortar with different alkali activators. The compressive strength of the mortar was measured at curing ages of 3, 7, and 28 days. For all specimens, the compressive strength increased with the curing age. The 28-day compressive strength was measured as 28.32 MPa, 49.66 MPa, and 40.56 MPa for Li, Na, and K, respectively, following the order of Na-K-Li. This trend was consistent for the compressive strength at 3 and 7 days.

In previous studies, the compressive strength of fly ash–based geopolymer concrete was investigated according to the type of hydroxide activator, and the 3-day strength exhibited a similar trend: NaOH (37.3 MPa) – KOH (15.0 MPa) – LiOH (7.8 MPa) [14].

Table 4 Setting time of geopolymer mortar

Alkaline activator	LiOH	NaOH	KOH
Initial Setting (min)	210	80	120
Final Setting (min)	330	150	210

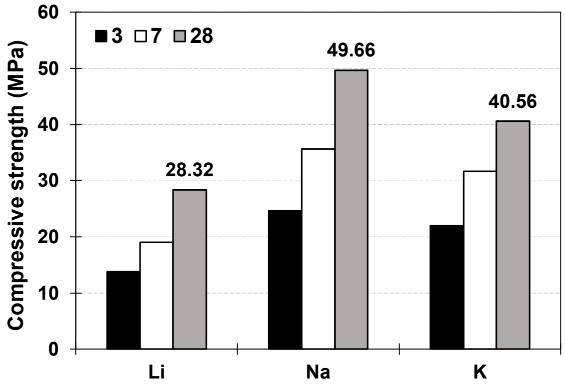


Fig. 3 Compressive strength of geopolymer mortar

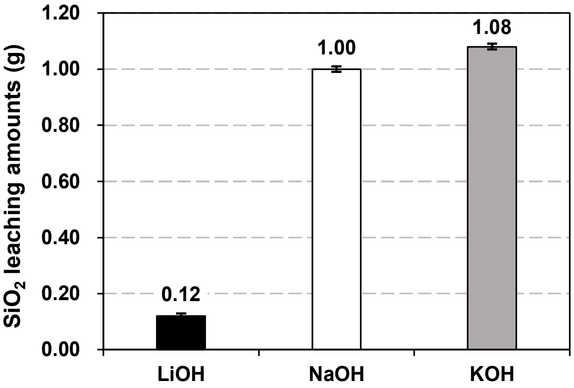


Fig. 4 Amounts of leached SiO_2 on activator

The compressive strength of geopolymer increases depending on the ratio and concentration of the binder and activator, as well as the curing temperature and duration. The increase in the concentration of the activator raises the hydroxide ion content in the matrix, promoting the chemical dissolution of the binder and the polymerization reaction, thereby forming a denser internal structure [15]. In this study, since the mixing ratio and concentration were fixed and curing was conducted under the same conditions, the variation in compressive strength with curing age is considered to be influenced by the type of alkali metal in the activator.

Additionally, the compressive strength of geopolymer mortar was higher with faster setting rates. The rapid setting rate in geopolymer systems indicates that the internal structure quickly develops, resulting in relatively high early strength. Similar trends have been observed in previous study. In previous studies, it was found that when the calcium content within the matrix is low, the reactivity decreases, leading to a reduced formation of amorphous Ca-Al-Si gel. This delay in the polymerization rate results in lower strength [16]. Within the scope of this study, the observed trends in compressive strength are presumed to be due to delayed setting caused by different polymerization reaction

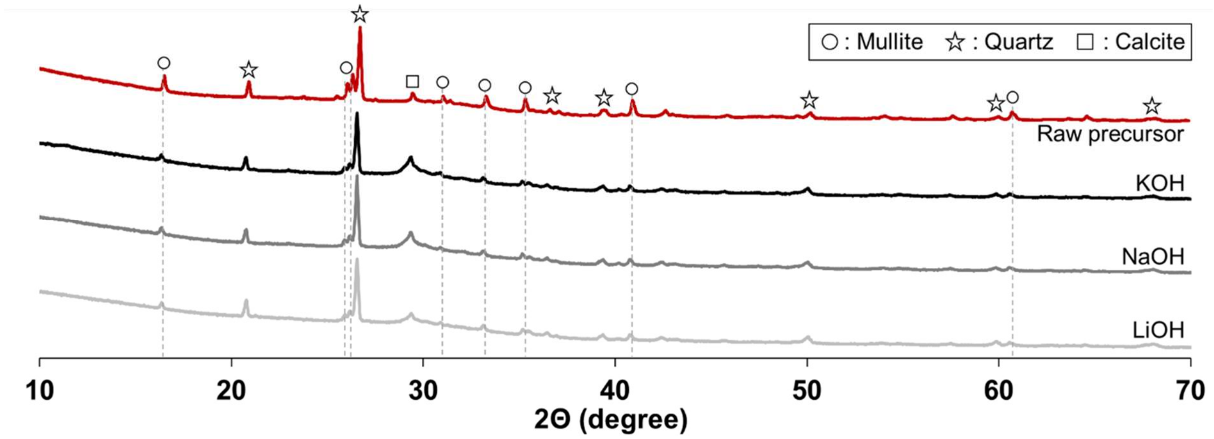
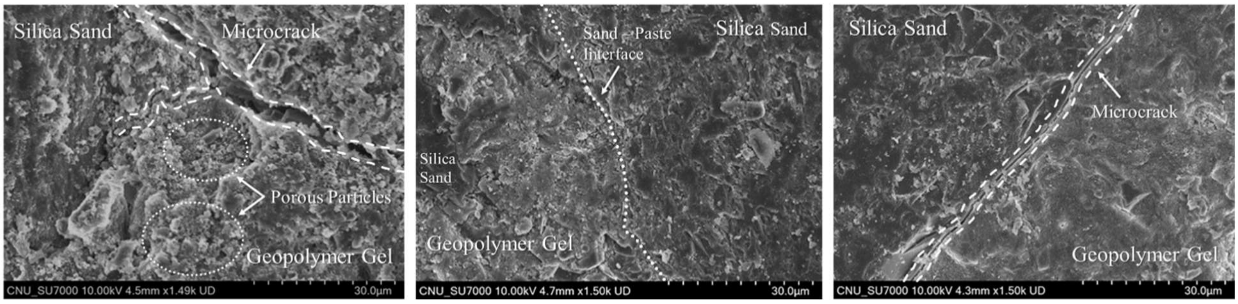


Fig. 5 XRD results of geopolymer mortar



(a) LiOH (b) NaOH (c) KOH

Fig. 6 SEM images of geopolymer mortar

characteristics associated with the metal ions of the activator.

3.4 Gravimetric analysis

Fig. 4 presents the amount of SiO_2 precipitated through gravimetric analysis and the SEM images. The amounts of extracted SiO_2 were measured as 0.12 g, 1.00 g, and 1.08 g for LiOH, NaOH, and KOH, respectively.

Geopolymers primarily develop strength through the polymerization reaction of Si components [11]. If the amount of Si extracted from the binder is insufficient, the gel may not grow adequately, making it difficult to achieve high strength. Therefore, based on the gravimetric analysis results, the low Si extraction capability of LiOH may delay the polymerization reaction when silica fume is used as a binder, resulting in reduced strength in the geopolymer mortar.

3.5 XRD

Fig. 5 presents the XRD results as a graph for the paste region of 28-day alkali-activated mortar according to the type of alkali metal. Common peaks for mullite, quartz, and calcite were observed in the graph. Mullite and quartz were analyzed as crystalline phases because they do not dissolve from FA [17]. Calcite ($CaCO_3$) was measured as it already existed in the GGBS. The absence of any other distinct peaks is due to the polymerization products being amorphous, which appear as a broad, flat background over a wide range [18].

Specifically, mullite observed between approximately 16° and 61° is a silicate mineral with a chemical structure of either $3Al_2O_3 \cdot 2SiO_2$ or $2Al_2O_3 \cdot SiO_2$. The mullite contained in the binder dissolved due to the activator and was utilized in the formation of the alkali-activated gel. This is evident from the reduction in the mullite peak after activation compared to the graph of the inactivated binder shown in Fig. 5. However, the decrease in the mullite peak intensity did not vary significantly with the type of activator. Therefore, it is considered that the alkali metal ions in the activator do not have a significant effect on the dissolution of FA.

3.6 SEM

Fig. 6 (a)–(c) shows the SEM images of alkali-activated mortar. In the images, the relatively dark regions represent quartz, while the bright areas indicate the paste region. In the mortar activated with LiOH, microcracks were observed between the quartz and paste regions, and within the paste, small particle forms along with numerous voids between them were noted. These small particles, which did not coalesce into a single gel, are believed to have delayed the setting time of the mortar.

This is attributed to the strong bonding caused by the high charge density of Li+. In the mortar activated with NaOH, the paste region exhibited superior homogeneity compared to the other specimens, and microcracks between the quartz and paste were not prominently observed. For the mortar activated with KOH, although the paste region was similar to that of NaOH, microcracks were observed at the interface between the quartz and paste, which is believed to have resulted in a lower compressive strength compared to NaOH.

4. CONCLUSIONS

This study investigated the effects of using LiOH, NaOH, and KOH as activators on the mechanical properties of geopolymer mortar. The main findings and conclusions are as follows:

1. The table flow decreased in the order of Li-Na-K. This was closely related to the size and charge density of the alkali metal ions.
2. In the setting tests, the mortar set more quickly in the order of Na-K-Li. In the geopolymer using LiOH, the formation of insoluble Li_2SiO_3 delayed the polymerization reaction.
3. The alkali-activated mortar with LiOH had the lowest amount of leached SiO_2 in gravimetric analysis. The microcracks and loose structure observed in SEM analysis resulted in lower compressive strength.

As a result of this study, it was confirmed that the characteristics of ions in the alkali activator have a significant influence on the mechanical properties and microstructure of alkali-activated mortar. Although the Li+ ion has the smallest ionic radius, it exhibited lower values in most mechanical properties due to its inhibitory effect on the polymerization reaction. This indicates that there is no linear relationship between ion size and mechanical properties as expected from previous studies. Given the microcracks and pores observed in SEM analysis, sufficient consideration is required when using LiOH as an activator. However, since mechanical performance may vary depending on the chemical composition and mix proportions of the binder, further investigation through additional experiments is necessary. Moreover, because micromechanical relationships exert an influence, precise, controlled-environment studies are required to clearly elucidate these relationships.

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