



Review on characteristics of metakaolin-based geopolymer and fast setting

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Abstract

The setting of metakaolin-based geopolymer depends on the raw materials and mix proportions. Setting, when material is cured at room temperature, takes about 1 day and is longer than setting time of Portland cement. For the fast setting of geopolymers, some studies increased the curing temperature or used raw materials with high CaO content. Also, Ca²⁺ and Mg²⁺ compounds were used as additives. Setting can be easily controlled and accelerated by adding Ca²⁺ compounds. However, it has been reported that knowledge of the reaction mechanism and final products between Ca²⁺ and geopolymers is still limited. In this study, we investigated the characteristics of metakaolin-based geopolymers and methods for fast setting of geopolymers, and made hypotheses about the reaction mechanism between Ca²⁺ and geopolymers.

Keywords Metakaolin · Metakaolin-based geopolymer · Setting · Fast setting · Calcium

1 Introduction

Geopolymers are inorganic binders that are set at room temperature or low temperatures, and are synthesized by combining natural pozzolanic materials and amorphous aluminosilicates, such as coal ash and metakaolin, with alkali activators, such as water glass, NaOH, or KOH [1–3]. The structure of a geopolymer is composed of disorderly connected Si tetrahedrons with part of their Si cations substituted by Al, and a charge imbalance arising from these cation substitutions is compensated by alkali earth metals contained in alkali activators [4]. When compared to Portland cement, geopolymers are known to exhibit better mechanical properties, such as superior initial compressive strength, thermal resistance, and water permeability, as well as good chemical characteristics, such as acid resistance and immobilization of toxic elements [1, 5–10]. Also, in contrast to cement, its manufacturing does not need a

high-temperature sintering process, thereby generating less carbon dioxide [1].

While Portland cement is set by the hydration reaction, curing of geopolymers is achieved by polymerization of aluminate and silicate species [1]. As mentioned above, geopolymers are cured at room temperature or low temperatures, but it takes longer to reach the final setting than in the case of Portland cement [11]. In general, it takes at least 1 day for fly ash-based geopolymers to reach the initial setting at room temperature while it takes about a day for metakaolin-based geopolymers to reach the final setting at room temperature [12–16].

Thus far, there have been various attempts to shorten the setting time of geopolymer, for example, by increasing the curing temperature [17, 18], using raw materials with higher CaO content [19–21], or adding various compounds such as Ca²⁺ and Mg²⁺ [12, 22–24]. Among all the methods above, the simplest is considered to be increasing the curing temperature. However, the high curing temperature and resultant fast curing may lead to a decrease in the apparent density and compressive strength of geopolymer [25], and this approach is not applicable in environments where the temperature cannot be controlled. Alternatively, it is possible to produce geopolymers using raw materials with high CaO content. Previous studies have reported that this approach may reduce the setting time because C–(A)–S–H gel is generated along with the geopolymer, but sufficient evidence of

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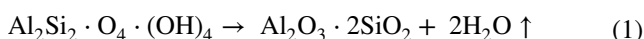
the mechanism has not been provided [19, 20]. Meanwhile, this approach involves a fast setting, and thus it is necessary to find ways to improve the workability of the compound [1]. Also, it is difficult to control the setting time as desired.

In this light, adding additives is considered to be a more practical approach in terms of control the setting time. Adding Ca^{2+} compounds to geopolymers is known to promote fast setting and improve their compressive strength [12, 26]. However, the reaction mechanism and final reaction products associated with this approach have not been clearly revealed and are still subject to debate. This arises from different manufacturing conditions of geopolymer binders, e.g., raw material types, mix proportions, alkali activators, and curing conditions. Meanwhile, recent studies have attempted to add $\text{Ca}(\text{OH})_2$ to metakaolin-based geopolymers that have a pure aluminosilicate system to conduct NMR and X-ray pair distribution function analyses [12, 27]. Both studies reported that Ca^{2+} promoted the dissolution of metakaolin, and a geopolymer was generated along with a C–(A)–S–H gel. However, these studies failed to reveal the effect of this C–(A)–S–H gel on the curing behavior of the geopolymer [12, 27].

In this study, results from relevant previous research papers were analyzed to examine research trends regarding the characteristics of metakaolin-based geopolymers, methods for shortening the setting time, and hypotheses about the reaction mechanism between Ca^{2+} and geopolymers.

2 Characteristics of metakaolin

When kaolin clay (kaolinite, dickite, nacrite, halloysite) that is composed of Si tetrahedrons and Al octahedrons alternately stacked at a ratio of 1:1 is sintered at 500–800 °C, dehydroxylation occurs by the following reactions, thereby leading to the formation of metakaolin [28, 29]. If the temperature is increased further, metakaolin is transformed into mullite and cristobalite [30, 31].



During the sintering process, 6-coordinated Al atoms turn into 4- or 5-coordinated Al atoms. Here, it is known that as more Al atoms are subject to this transition, metakaolin becomes accordingly more reactive [32]. The sintering temperature is determined by the purity and crystallinity of kaolin [33]. Meanwhile, when irradiated with X-ray beams, metakaolin is identified to be amorphous [34]. However, in a study where the structure of metakaolin was analyzed using energy-filtered transmission electron microscopy (EF-TEM), a cycle of about 14 Å was observed along the c^* -axis of the kaolinite structure [35]. This means that the formation of metakaolin did not lead to complete destruction of the

kaolinite structure. Simply put, some structural periodicity remained [35]. Metakaolin is mainly composed of 44–73% of SiO_2 and 15–47% of Al_2O_3 [36].

Different studies conducted ^{27}Al and ^{29}Si MAS NMR to examine the molecular electronic structure of metakaolin and relevant structural models [37–41]. In ^{27}Al MAS NMR spectra of metakaolin, it was found that three peaks overlapped; the first peak found at 49–80 ppm corresponds to 4-coordinated Al atoms, the second peak at 35–40 ppm corresponds to 5-coordinated Al atoms, and the third peak at –5 to 15 ppm corresponds to 6-coordinated Al atoms (Fig. 1a) [37, 40, 41]. A broad peak width, as observed here, is indicative of a high degree of disorder in the structure of metakaolin. In ^{29}Si MAS NMR spectra, a single broad peak centered at about -100 ppm was observed (Fig. 1b) [38, 40, 41]. This peak represents both the ($\text{Q}^4(2\text{Al})$) unit where Si is connected through bridging oxygens to two Al atoms and the ($\text{Q}^4(0\text{Al})$) unit where only Si atoms are connected without being connected with Al atoms [39]. This broad peak width is known to be associated with metakaolin having a flattened silicon conformation [41].

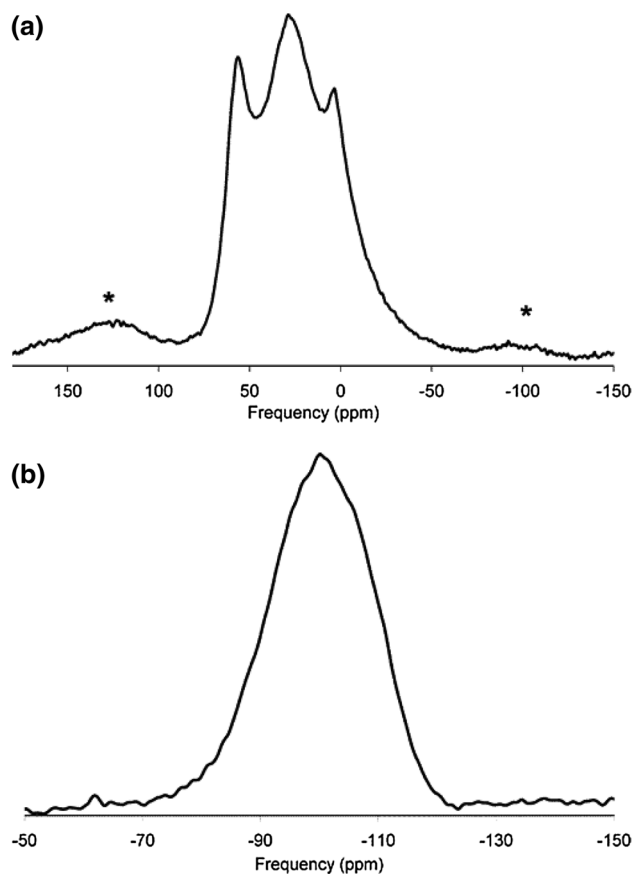


Fig. 1 **a** ^{27}Al MAS-NMR spectra of metakaolin [37], **b** ^{29}Si MAS NMR spectra of typical metakaolin [38]

The average particle size of metakaolin is reported to be 1–38 μm , and the average specific surface area is about 2.2–22 m^2/g [36].

3 Metakaolin-based geopolymer

3.1 Reaction mechanism of metakaolin-based geopolymer

The reaction mechanism of metakaolin-based geopolymers is largely divided into four stages (Fig. 2) [1, 42]. The first stage is a process where metakaolin is dissolved by alkali activators to release silicate species and aluminate species, thereby turning 5- or 6-coordinated Al atoms into 4-coordinated Al atoms [1, 14, 37, 42]. The second stage is a process where those released species react with silicates from alkali activators to generate aluminosilicate oligomers [1, 42]. The third stage is a process where those aluminosilicate oligomers are turned into aluminosilicate gel through polymerization and gelation [1, 42]. The final stage is a curing process, and the setting time is determined depending on the mix proportion, curing conditions, and presence of impurities [1, 42].

Metakaolin-based geopolymers may transform into a zeolite phase that has a relatively simpler structure depending on the Si/Al ratio and curing conditions [1, 42, 43]. It has been reported that when sealed and stored at warm temperatures, metakaolin-based geopolymers with low Si/Al ratios may transform into sodalite, faujasite, gismondine, Linde type A(LTA) zeolite, etc. [1, 42, 43].

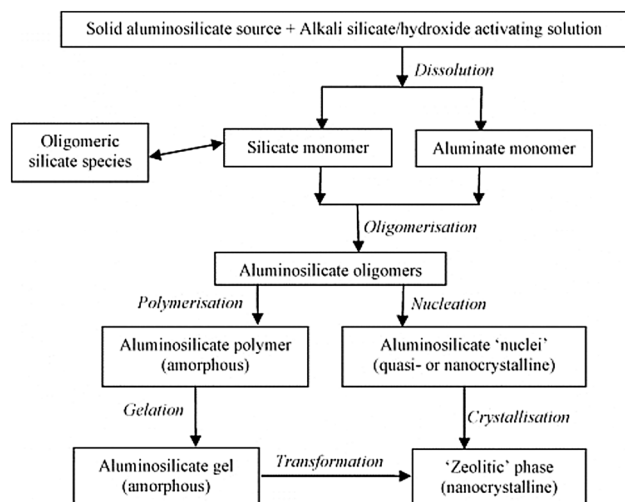


Fig. 2 Schematic outline of the reaction processes involved in geopolymerization [42]

3.2 Compressive strength and microstructural characteristics of metakaolin-based geopolymer

The compressive strength of geopolymers is highly correlated with the Si/Al ratio. Some studies reported that metakaolin-based geopolymers exhibited high compressive strength with a specific Si/Al ratio [39, 44, 45] (Fig. 3). Duxson et al. (2005) fabricated metakaolin-based geopolymers with a Si/Al ratio of 1.15, 1.40, 1.65, 1.90, and 2.15, and measured their compressive strength. To sum up, the compressive strength tended to increase with increasing Si/Al ratio. According to the previous study, this observation was attributed to the fact that an increase in the Si content led to an increase in the number of Si–O–Si bonds, which are stronger than Si–O–Al and Al–O–Al bonds [2, 39, 44]. Meanwhile, the compressive strength was the highest when the Si/Al ratio was 1.95 (Fig. 3). ^{27}Al MAS NMR analysis results showed that the content of unreacted metakaolin was higher in a geopolymer specimen with a Si/Al ratio of 2.15 than in one with a Si/Al ratio of 1.95 [37, 44]. Accordingly, it was reported that this unreacted portion of metakaolin acted as defects in the geopolymer structure and negatively affected the compressive strength [37, 44].

SEM analysis results showed that metakaolin-based geopolymers with low Si/Al ratios (≤ 1.40) had a coarse microstructure with a low degree of connectivity and were mostly composed of small and large pores, as shown in Fig. 4a, b [44]. Geopolymers with high Si/Al ratios ($1.65 \geq$) were found to have a more uniform and finer microstructure than those with low Si/Al ratios. Also, the microstructure of the former was more smoothly connected, as shown in Fig. 4c–e [44].

Other studies measured and compared the compressive strength of metakaolin-based geopolymers while varying

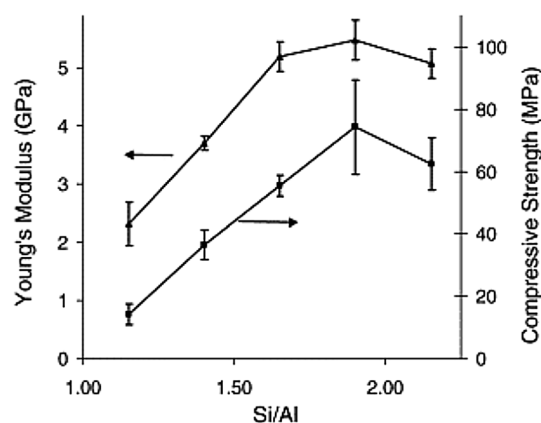
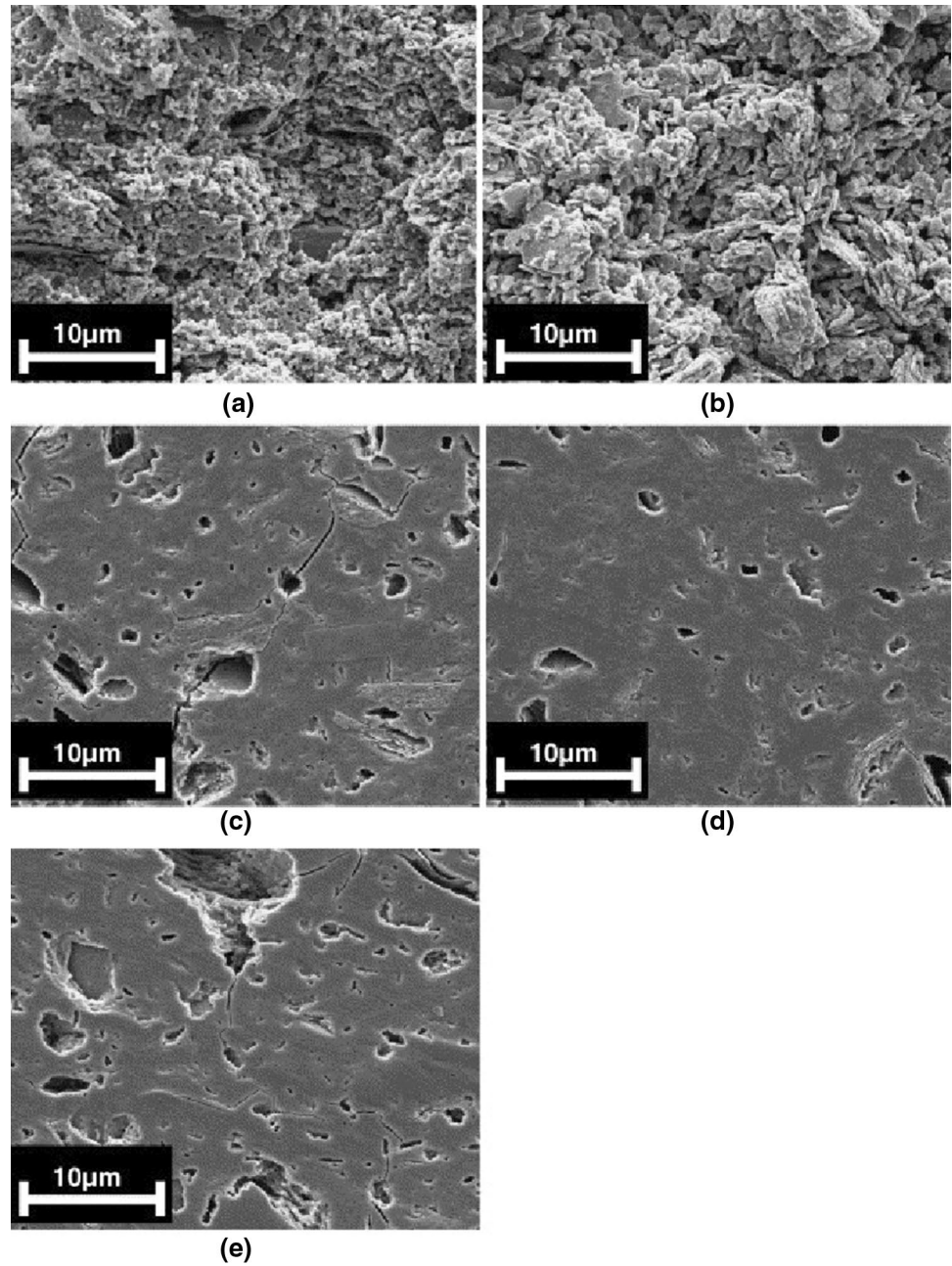


Fig. 3 Young's moduli (filled triangle) and ultimate compressive strengths (filled square) of geopolymers. Error bars indicate the average deviation from the mean over the six samples measured [44]

Fig. 4 SEM micrographs of Na-geopolymers: Si/Al ratio of **a** 1.15, **b** 1.40, **c** 1.65, **d** 1.90, and **e** 2.15 [44]



the curing temperature (20–100 °C) [17]. The 1-day, 3-day, and 7-day compressive strength of geopolymers tended to increase with increasing curing temperature and finally peaked at a specific temperature, as shown in Fig. 5 [17]. An increase in the curing temperature facilitates chemical reactions, promotes the dissolution of metakaolin, and accelerates the reaction of geopolymers, thereby increasing the initial compressive strength. However, beyond the critical limit, microcracks and shrinkage occur, eventually deteriorating the compressive strength of geopolymers.

3.3 Chemical characteristics of metakaolin-based geopolymer

XRD analysis results revealed that metakaolin-based geopolymers resulted in two types of diffraction patterns, which corresponded to crystalline materials that were contained in metakaolin as impurities (quartz, anatase, muscovite, etc.) and aluminosilicate amorphous materials (Fig. 6) [46–49]. The amorphous material peak was centered at 2θ of 27°–30°, which was about 5°–8° higher than that of the metakaolin

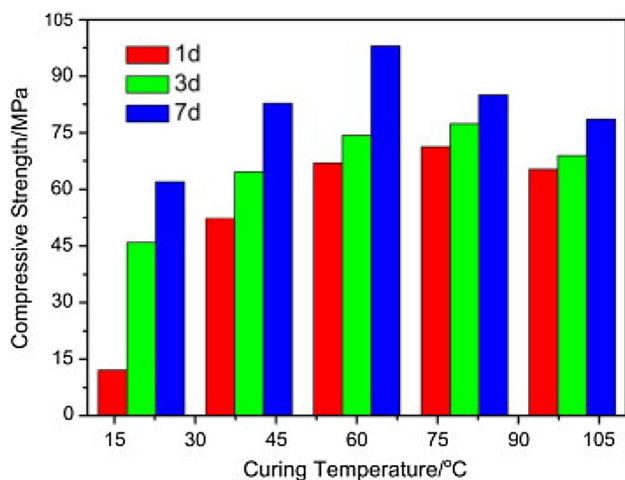


Fig. 5 Influence of curing temperatures on the compressive strength [17]

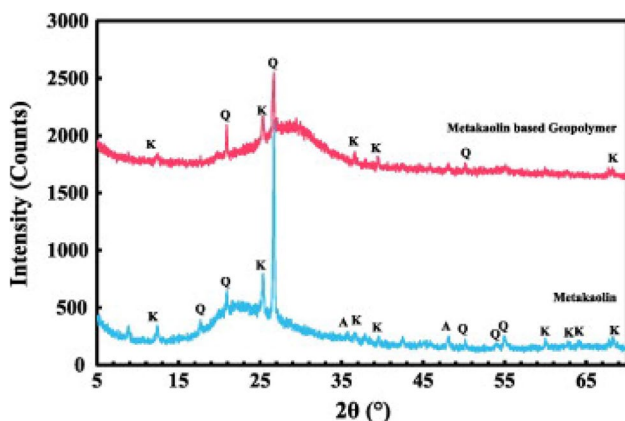


Fig. 6 XRD pattern of metakaolin and metakaolin-based geopolymer (K Kaolinite, Q Quartz, A Anatase) [49]

peak at 2θ of 22° (Fig. 6) [46, 47, 49]. The shape and center of this peak remained the same despite variations in the Si/Al ratio and curing temperature [46, 47]. Geopolymer reaction products are amorphous, and thus it is typical that new crystalline materials are not formed during the reaction. However, as mentioned above, when the Si/Al ratio is low (Si/Al = 1.15 or 1.25), crystalline materials, such as faujasite and zeolite, are generated [47, 50].

The chemical bonding structure of molecules that comprise metakaolin-based geopolymers was analyzed using FT-IR [51]. Bands indicative of Si–O stretching vibration (1022 cm^{-1}) and Si–O–Al vibration (778 cm^{-1}) were found at a lower wavenumber in the geopolymer than in metakaolin. This means that a reorganization occurred in the Si environment during the geopolymer reaction, thereby affecting the microstructure (Fig. 7) [4, 51, 52]. Other bands observed near 3315 cm^{-1} and 1645 cm^{-1} were attributed to adsorption

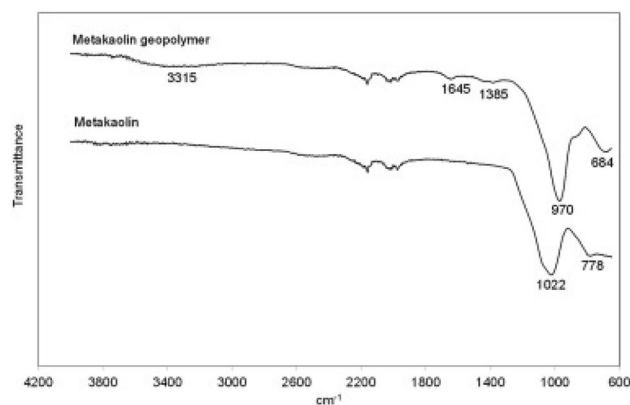


Fig. 7 FT-IR spectra of metakaolin and metakaolin-based geopolymer [51]

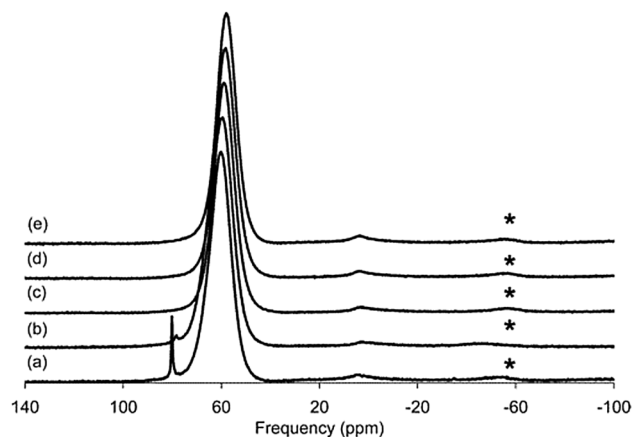


Fig. 8 ^{27}Al MAS NMR spectra of Na-geopolymers with Si/Al ratios of a 1.15, b 1.40, c 1.65, d 1.90, and e 2.15. Asterisk indicates spinning sidebands [37]

water [4]. Other studies have measured and compared the IR spectra of geopolymers while varying the curing temperature ($20\text{--}100^\circ\text{C}$) and Si/Al ratio ($1.25\text{--}2.0$) [46, 50]. The resultant IR spectra of geopolymers were not affected by the increasing curing temperature [46]. Also, when the Si/Al ratio was higher, Si–O stretching vibration was represented at a higher wave number [50].

Given that XRD and FT-IR analyses alone cannot precisely analyze the structure of a geopolymer, which is mainly composed of amorphous materials, MAS NMR was applied in multiple studies [37–39, 51, 52]. In the ^{27}Al MAS NMR analysis of metakaolin-based geopolymers, a peak centered at about 50 ppm was observed, which was narrower than the metakaolin peak (Fig. 8a). According to the studies, this was attributed to the development of a higher degree of order in the Al structure during the geopolymer reaction, and thus 5- or 6-coordinated Al atoms transformed into 4-coordinated Al atoms [37, 39]. In the ^{29}Si MAS NMR analysis, a broad

peak was observed, which resembled the metakaolin peak, but this peak was known to represent all types of $Q^4(mAl)$ ($m=0, 1, 2, 3, 4, 5$) units, in contrast to the metakaolin peak representing only two units, i.e., $Q^4(2Al)$ and $Q^4(0Al)$ units (Fig. 9a) [38, 39].

Duxson et al. (2005) conducted ^{27}Al and ^{29}Si MAS NMR analyses of metakaolin-based geopolymers with Si/Al ratios of 1.15, 1.40, 1.65, 1.90, and 2.15 [37, 38]. Regardless of the varying Si/Al ratio of geopolymers, the resultant ^{27}Al MAS NMR peaks remained almost the same in terms of peak width and center [37]. When the Si/Al ratio was 1.40 or lower, a small peak was observed at 80 ppm, and this was considered to originate from $Al(OH)_4^-$ (aq), as shown in Fig. 8 [37]. Meanwhile, the center of the ^{29}Si MAS NMR peak tended to move toward a lower chemical shift with an increasing Si/Al ratio. Also, the peak increasingly became broader and asymmetric, as shown in Fig. 9 [38].

4 Fast setting of geopolymer

4.1 Methods for shortening the setting time of geopolymer

The setting behavior of the geopolymer is known to be affected by the chemical composition of the used raw materials, alkali activators, curing temperature, silica modulus, target Si/Al ratio, W/S ratio, etc. [15]. In general, it takes at least 1 day for fly ash-based geopolymers to reach the initial setting at room temperature, and thus those materials are cured at lower temperatures, e.g., 40–80 °C [15, 16]. Metakaolin-based geopolymers may be cured at room temperature, and it takes about 15–20 h to reach the final setting [12–14]. It is faster than fly ash-based geopolymers in reaching the final setting at room temperature; however, it takes

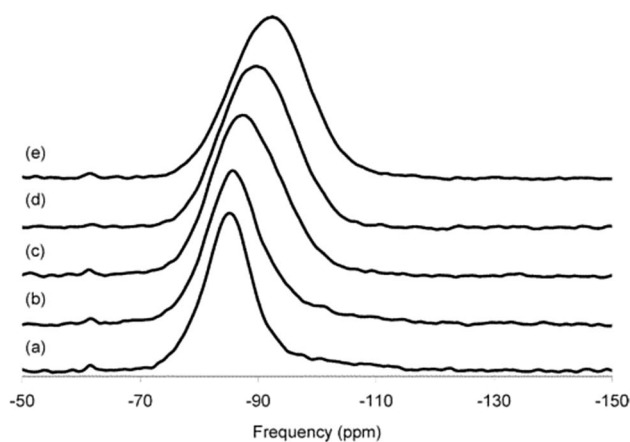


Fig. 9 ^{29}Si MAS NMR spectra of Na-geopolymers with Si/Al ratios of **a** 1.15, **b** 1.40, **c** 1.65, **d** 1.90, and **e** 2.15 [38]

five to seven times longer than 2–3 h of curing time required for Portland cement.

There are largely three methods for shortening the setting time of geopolymers, as follows. The first method is to use raw materials with high CaO content. A previous study measured the setting time of geopolymer made from fly ash with various CaO contents. As a result, it was found that the higher the CaO content of fly ash was, the shorter the setting time became [19]. The setting time of fly ash-based geopolymers was measured to be about 2 min when the CaO content of the used fly ash was about 22.5%.

The second method is to add Ca^{2+} or Mg^{2+} compounds to geopolymers or substitute part of raw materials with them. In a previous study, it was found that the addition of 0.4 mol of $Ca(OH)_2$ to metakaolin-based geopolymers shortened the setting time from 15 h to less than 1 h [12]. It was also reported that when CaO was added to metakaolin-based geopolymers at a ratio of 4% by weight, the setting time was found to decrease from 20 to 4 h [22]. In another study, the effect of metakaolin partially substituted by CaO on the setting time of geopolymers was examined. When 30% of metakaolin was substituted, the initial setting time was shortened from about 3.5 h to 30 min [23]. Lee and Deventer (2002) fabricated geopolymers by setting the ratio of fly ash to kaolinite to 9.0, and Ca^{2+} compounds ($CaCl_2$, $Ca(OH)_2$, $CaCO_3$, and CaO) and Mg^{2+} compounds ($MgCl_2$, $Mg(NO_3)_2$, and MgO) were added as additives [24]. It was reported that 0.08764 mol of the respective additives was dissolved in distilled water and added. $CaCO_3$ among Ca^{2+} compounds and $MgCl_2$ among Mg^{2+} compounds were the most effective in improving fast setting performance [24].

The third method is to increase the curing temperature and thus accelerate the geopolymer reaction. It was found that the setting time was shortened from 4 to 2 h by increasing the curing temperature of fly ash-based geopolymers from 65 to 80 °C [18]. In metakaolin-based geopolymers as well, the setting time was shortened in proportion to the increasing curing temperature. To be more specific, the setting time was measured to be about 22 h when cured at room temperature, but it was significantly reduced to less than 20 min when cured at 100 °C [17].

4.2 Chemical characteristics of geopolymer containing Ca^{2+} compounds

XRD, SEM/EDS, and NMR analyses were conducted to examine the chemical properties of geopolymers that contained Ca^{2+} compounds. XRD analysis results showed that the varying $Ca(OH)_2$ content resulted in different crystalline phases. When 15% of $Ca(OH)_2$ was added to metakaolin-based geopolymers, new crystalline phases, i.e., C–(A)–S–H gel and calcite, were formed [39]. The formation of C–(A)–S–H gel was attributed to the reaction between

$\text{Ca}(\text{OH})_2$ and a sodium silicate solution, which eventually precipitated [53] and calcite was formed due to carbonation because the geopolymers had not been stored in vacuum [39]. When 30% of $\text{Ca}(\text{OH})_2$ was added, C–(A)–S–H gel was not formed, and only portlandite was formed [54]. This observation indicated that the added $\text{Ca}(\text{OH})_2$ was not fully reacted, but some of it remained. A recent study fabricated metakaolin-based geopolymers with a CaO/SiO_2 ratio of 0.75, 1.5, and 2.25 by adding $\text{Ca}(\text{OH})_2$ [27]. X-ray diffraction analysis results showed that in all three specimens to which $\text{Ca}(\text{OH})_2$ was added, diffraction patterns for C–S–H gel were observed. In specimens with a CaO/SiO_2 ratio of 1.5 and 2.25, patterns for monocarboaluminate and portlandite were found (Fig. 10) [27]. The formation of monocarboaluminate was attributed to carbonation [27].

Meanwhile, it was found that the microstructure of geopolymers containing Ca^{2+} compounds was densified by the formation of C–(A)–S–H gel. SEM/EDS analyses were conducted on a metakaolin-based geopolymer with 20% of its metakaolin substituted by granulated blast-furnace slag powder with a CaO content of 43 wt%. As a result, phase separation between the geopolymer phase and C–(A)–S–H gel was found (Fig. 11) [55]. It was reasoned that the formed C–(A)–S–H gel acted as a micro-aggregate to fill the micropores of the geopolymer, thereby refining and densifying its microstructure [55]. Similar results were reported when part of fly ash was substituted by CaO [26]. With more CaO substitution, the overall microstructure became dense, and there were fewer unreacted fly ash particles, as shown in Fig. 12a, c [26]. Similarly, it was reasoned that the microstructure became denser by the formation of C–(A)–S–H gel with the addition of Ca^{2+} , but quantitative evidence for the mechanism was not provided [26].

As can be seen from different XRD and SEM/EDS analysis results, different reaction products of Ca^{2+} and

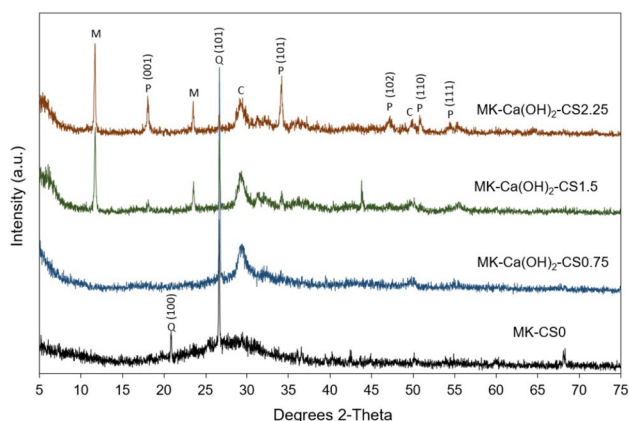


Fig. 10 X-ray diffraction (XRD) patterns for prepared metakaolin-based geopolymers with various content of calcium. (C C–S–H gel, M monocarboaluminate, P portlandite, Q quartz) [27]

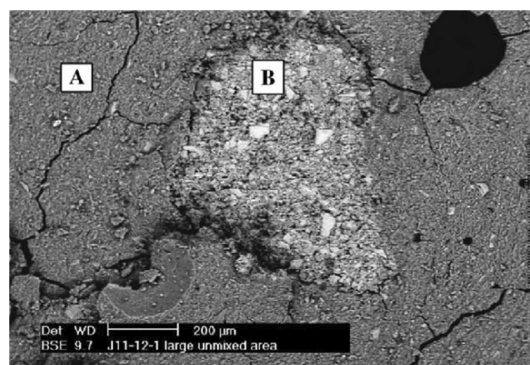


Fig. 11 SEM micrograph of Matrix 8 (20% slag, $M_s=2.0$) at 14 days. Identification of different phases: **a** geopolymeric binder with low content of calcium; **b** calcium silicate hydrate with a small proportion of aluminum [55]

geopolymers have been reported from study to study. This is because C–(A)–S–H gel, which has been reported as one of the reaction products, is amorphous or a poorly ordered crystalline, which is difficult to be detected using X-ray techniques. Another reason is that Ca^{2+} ions tend to be combined with the geopolymer structure [54].

Meanwhile, a study based on solid-state MAS NMR analyses reported that Ca^{2+} ions facilitated the dissolution of raw materials of geopolymers. Chen et al. (2018) fabricated metakaolin-based geopolymers with a mole ratio of $\text{CaO}:\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{H}_2\text{O}$ of 0.4:1:1:4:12.1 by adding $\text{Ca}(\text{OH})_2$ and conducted ^{27}Al MAS NMR analysis on them [12]. It was found that the addition of $\text{Ca}(\text{OH})_2$ facilitated the dissolution of metakaolin by alkali activators, thereby increasing the rate and degree at which 5- or 6-coordinated Al atoms turned into 4-coordinated Al atoms (Fig. 13). Also, salicylic acid/methanol (SAM) and hydrochloric acid (HCl) extraction methods were carried out, and the resultant residues were subjected to a ^{29}Si MAS NMR analysis in an attempt to identify the final reaction products. Here, SAM extraction is a process where C–(A)–S–H gel is removed while HCl extraction is a method for removing geopolymers [56, 57]. The resultant ^{29}Si MAS NMR peak was deconvoluted into multiple peaks, each of which corresponded to C–(A)–S–H gel, geopolymers, and unreacted metakaolin (Fig. 14) [12]. The study, however, is still limited to reveal how the formation of C–(A)–S–H gel directly affected the setting behavior of geopolymers.

4.3 Hypothesis about the final reaction products of Ca^{2+} -added geopolymers and reaction mechanism

As explained above, Ca^{2+} ions accelerate the setting rate of geopolymers, but the governing mechanism has not been clearly elucidated because the resultant final

Fig. 12 **a** Microstructure of the non-calcium added and **b** 1% and **c** 3% CaO-added geopolymers cured at ambient temperature [26]

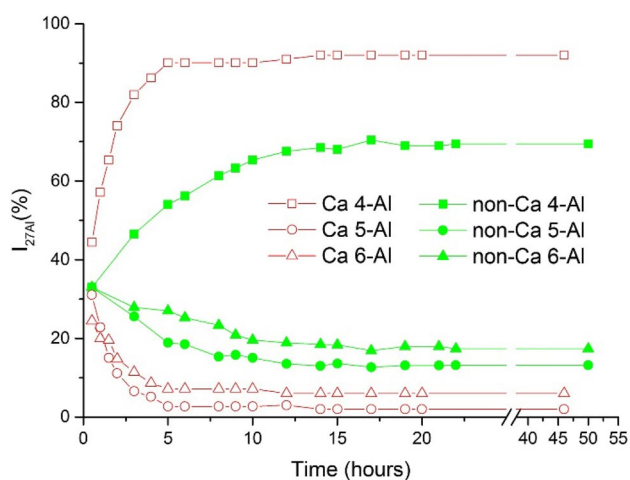
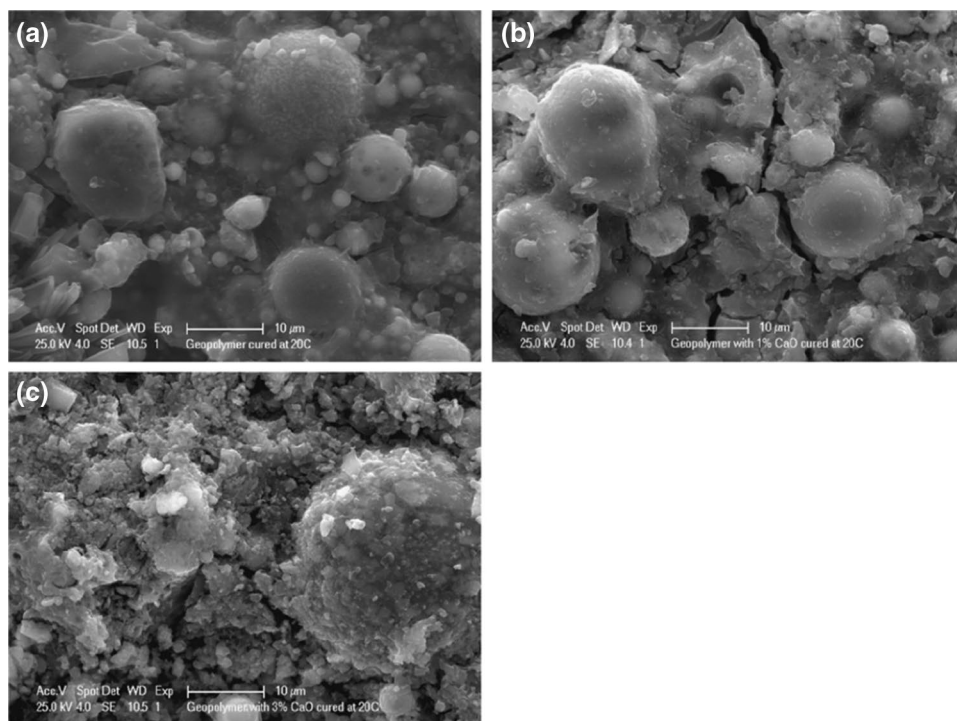


Fig. 13 Percentage changes of 4-, 5-, and 6-coordinated Al with time for calcium mix (open symbols) and non-calcium mix (filled symbols), from the lower field ^{27}Al NMR (7.04 T) [12]

reaction products have been reported differently by different authors. This is considered to be because the main raw materials of geopolymers contain a large amount of amorphous material, and the final reaction products are amorphous as well. Also, fly ash has a relatively complex chemical structure, and it contains not only amorphous materials but also various types of crystalline materials. This may also add to the difficulty in identifying the governing mechanism. Although ambiguity remains as to how

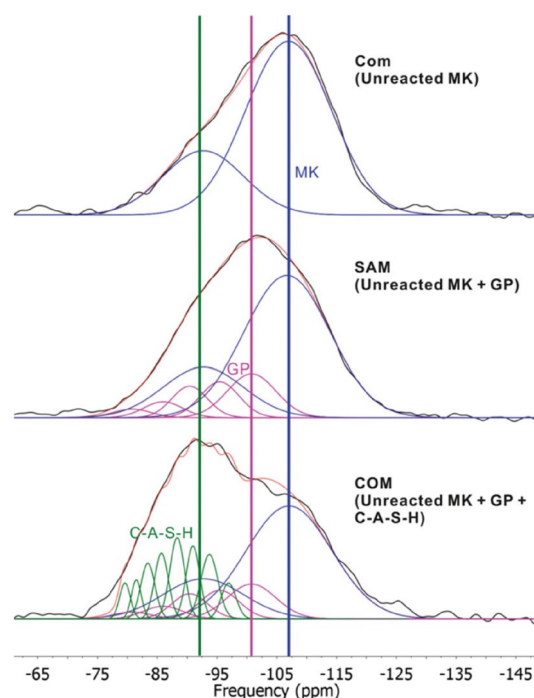


Fig. 14 Deconvolution of ^{29}Si solid-state spectra of residues from combined (bottom), SAM (middle), and HCl (top) extractions for a mix with calcium at 15 h, showing peaks assigned to metakaolin (MK), C–A–S–H and geopolymer gel (GP) [12]

it works, the following three major hypotheses are largely supported [12, 24, 26, 58, 59].

The first hypothesis is that the formation of C–(A)–S–H gel consumes H₂O, which leads to a localized increase in pH and thus facilitates the dissolution of the raw materials [26, 59]. The second hypothesis is that, as in the hydration reaction of Portland cement, the generation of C–(A)–S–H gel directly improves the setting performance [59]. The third hypothesis is that the C–(A)–S–H gel acts as a nucleation site where geopolymers can form [24, 26, 27, 58, 59]. These hypotheses have been proposed in different studies, but quantitative evidence for them has not provided.

5 Conclusions

In this study, results from relevant previous research papers were analyzed to examine the mechanical and chemical properties of metakaolin-based geopolymers, methods for shortening the setting time, and hypotheses about the reaction mechanism between Ca²⁺ and geopolymers. It was found that metakaolin-based geopolymers exhibited high compressive strength and a denser microstructure with a specific Si/Al ratio. The compressive strength tended to increase in proportion to the increasing curing temperature, but beyond a critical temperature, it decreased due to microcracks and shrinkage. Various methods for shortening the setting time of geopolymers were proposed, including using raw materials with high CaO content, adding various types of additives, such as Ca²⁺ and Mg²⁺ compounds, and increasing the curing temperature. Ca²⁺ ions were reported to be highly effective in improving fast setting performance, but only different hypotheses about the formation of C–(A)–S–H gel have been provided without sufficient quantitative evidence regarding the governing mechanism and final reaction products. Therefore, going forward, more research is needed to quantitatively identify how Ca²⁺ ions affect the setting performance of geopolymers in a precise manner. Once the reaction mechanism between Ca²⁺ ions and geopolymer is clearly elucidated, it will be possible to easily control the setting behavior of geopolymers. This will make the material available for a wider scope of applications.

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