Available online at www.sciencedirect.com

ScienceDirect

Cement and Concrete Research 37 (2007) 512–518

Cement and Concrete Research

Kinetics of geopolymerization: Role of Al_2O_3 and SiO_2

P. De Silva *, K. Sagoe-Crenstil, V. Sirivivatnanon

CSIRO Manufacturing and Infrastructure Technology, 14 Julius Avenue, Riverside Corporate Park, North Ryde, NSW 2113, Australia

Received 19 June 2006; accepted 11 January 2007

Abstract

The early-stage reaction kinetics of metakaolin/sodium silicate/sodium hydroxide geopolymer system have been investigated. The setting and early strength development characteristics, and associated mineral and microstructural phase development of mixtures containing varying SiO_2/Al_2O_3 ratios, cured at 40 °C for up to 72 h, were carefully studied. It was observed that setting time of the geopolymer systems was mainly controlled by the alumina content. Essentially, the setting time increased with increasing SiO_2/Al_2O_3 ratio of the initial mixture. Up to a certain limit, the SiO_2/Al_2O_3 ratio was also found to be responsible for observed high-strength gains at later stages. An increase in the Al_2O_3 content, i.e. for low SiO_2/Al_2O_3 ratio, led to products of low strength, accompanied by microstructures with increased amounts of Na–Al–Si-containing “massive” phases (grains). EDAX analyses showed that the SiO_2/Al_2O_3 ratios of geopolymer gel phases were quite similar to those of the starting mixtures, but with an overall lower Na content. Most importantly, this study clearly demonstrates that the properties of resulting geopolymer systems can be drastically affected by minor changes in the available Si and Al concentrations during synthesis.

Keywords: Inorganic polymers; Kinetics; Microstructure; Mechanical properties

1. Introduction

During the last decade, considerable research efforts have been directed towards the development of inorganic geopolymers, due to the wide range of potential applications for these materials. Several reports can be found in the literature on the synthesis, properties and applications of geopolymers [1–4]. In general, inorganic geopolymers can be synthesized by alkali activation of materials rich in SiO_2 and Al_2O_3. The mechanism involves the dissolution of Al and Si in the alkali medium, transportation (orientation) of dissolved species, followed by a polycondensation, forming a 3D network of silico-aluminate structures. According to Davidovits [5], these structures can be of three types: poly(sialate) (–Si–O–Al–O–), poly(sialate–siloxo) (Si–O–Al–O–Si–O) and poly(sialate–disiloxo) (Si–O–Al–O–Si–O–Si–O). The setting (hardening) of geopolymer is believed to be due to the polycondensation of hydrolysed aluminate and silicate species. The typical geopolymer composition is generally expressed as $nM_2O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$, where M is an alkali metal.

Dissolution, hydrolysis and condensation reactions of metakaolin in alkaline conditions (with high and low Si/Al ratios) have been discussed in detail by number of authors [6,7]. The dissolution and hydrolysis reactions can be written as:

$$Al_2O_3 + 3H_2O + 2OH^- \rightarrow 2[Al(OH)_4]^-$$

$$SiO_2 + H_2O + OH^- \rightarrow [SiO(OH)_3]^-$$

$$SiO_2 + 2OH^- \rightarrow [SiO_2(OH)_2]^{2-}$$

The presence of $[SiO_2(OH)_2]^{2-}$ ions is preferred to $[SiO(OH)_3]^-$ in very high alkaline conditions. Condensation can occur between aluminate and silicate species or silicate species themselves, depending on the concentration of Si in the system. With mixtures with low Si/Al ratios (=1), condensation predominantly occurs between aluminate and silicate species, resulting in mainly poly(sialate) polymer structures. Likewise, when the Si/Al ratio increases (>1), the silicate species formed as a result of the hydrolysis of SiO_2, tend to condense among themselves to form oligomeric silicates. These oligomeric silicates in turn condense with $Al(OH)_4^{4-}$, forming a rigid 3D

---

* Corresponding author. Tel.: +61 2 9739 2346; fax: +61 2 9739 2319.
E-mail address: pre.desilva@acu.edu.au (P.D. Silva).

0008-8846/$ - see front matter. Crown Copyright © 2007 Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2007.01.003

network of polymer structures [poly(sialate–siloxo) and poly (sialate–disiloxo)]. The rate of condensation between silicate species is believed to be slower than that between aluminate and silicate species [6,8,9].

The synthesis of geopolymers with predictable performance is not straightforward, mainly because the type, composition and reactivity of the raw materials play a major part in controlling the chemistry of resulting geopolymers, and hence the properties [3]. Metakaolin is a good source of Al_2O_3 and SiO_2, and is highly reactive with alkaline activators, and therefore it can be used in understanding the fundamentals of geopolymerization. The effects of initial SiO_2/Al_2O_3 ratios on the compressive strength and microstructure of alkali-activated metakaolin systems have been reported by several authors [10–13]. Typically, better strength properties are reported for mixtures with SiO_2/Al_2O_3 ratios in the range of 3.0–3.8 with an Na_2O/Al_2O_3 ratio of about 1. Changes in the SiO_2/Al_2O_3 ratio beyond this range have been found to result in low-strength systems [12,13]. These initial ratios can be expected to change when materials other than metakaolin are used as the Al_2O_3 and SiO_2 source.

Investigations into the underlying chemistry of the processes of setting, hardening and the pattern of strength development of geopolymer mixtures at the very early stage of geopolymerization, based on any kind of raw materials, is however rare in the literature. Such understanding is indeed important in the development of any kind of binder, especially so for geopolymer formation, which can be extremely sensitive to the type of raw materials used in its processing. This study is aimed at achieving some fundamental understanding of the role of Al and Si on the reaction kinetics of geopolymerization.

Previous work by Stevenson and Sagoe-Crenstil [12] discussed the effect of various SiO_2/Al_2O_3 ratios on the final strength of alkali-activated metakaolin systems cured at 80 °C for 2 h. This study extends the work of Stevenson and Sagoe-Crenstil on heat-cured systems by determining early-age properties of geopolymer mixtures cured at much lower temperatures, to simulate processing at ambient conditions as opposed to conventional heat-cured conditions, which has been widely investigated [10–12]. The effect of SiO_2/Al_2O_3 ratios on setting, strength development, geopolymer gel phase composition and microstructure development will be looked at in detail.

2. Materials and experimental procedure

Metakaolin was obtained by calcining kaolin (Commercial Minerals, Australia, 47.3 wt.% SiO_2, 35.7 wt.% Al_2O_3, 3.1 wt.% other minerals). Laboratory-grade NaOH and sodium silicate (8.9 wt.% Na_2O, 28.7 wt.% SiO_2, 62.5 wt.% H_2O) were used as alkaline activators.

Two series of mixture formulations with varying SiO_2/Al_2O_3 ratios (changing either SiO_2 or Al_2O_3 content) but with constant H_2O and Na_2O contents, as given in Table 1, were prepared. The H_2O/Na_2O ratio of the mixture formulations was kept at 13.6, which was slightly higher than that used by Stevenson and Sagoe-Crenstil [12], which was 12. This was to provide good workability (especially with low SiO_2/Al_2O_3 ratios) and to lower the rate of reaction, therefore making it easier to observe early-stage development. Mixture compositions were chosen to cover the best SiO_2/Al_2O_3 ranges for metakaolin geopolymers reported in the literature, and to represent step changes in molar ratios. Further expansion of selected range was restricted by the type of raw materials, especially sodium silicate, which itself contained 62.5% water.

Samples were identified according to the variable (Si or Al) being tested and its molar ratio to Na_2O, i.e. samples Si38, Si34, Si30 and Si25 (the Si series) assessed the effect of Si at constant concentrations of Na_2O, Al_2O_3 and H_2O. Similarly, samples Al06, Al07, Al08, Al10 and Al12 (the Al series) assessed the effect of Al at constant concentrations of Na_2O, SiO_2 and H_2O. With both series, as shown in Table 1, the SiO_2/Al_2O_3 ratio was changed by changing the amount of either Si or Al. These initial mixture compositions are also marked in the Na_2O–Al_2O_3–SiO_2–H_2O phase equilibrium diagram shown in Fig. 1. Compositions of metakaolin and class F fly ash (another common raw material used in geopolymer synthesis) are also shown.

The total water in a system includes water from NaOH, sodium silicate and extra added water. In the preparation of mixtures, solid NaOH was first dissolved in sodium silicate solution, followed by the addition of water if necessary. The solution was cooled to room temperature before mixing with metakaolin. Mixtures were cast in 30 mm diameter by 50 mm high cylindrical containers that were sealed to prevent water loss, which were subsequently cured at 40 °C at 95% RH. Care was taken to minimize the time between sample preparation and curing for all the mixtures. Samples were tested for compressive

Table 1
Mixture formulations

Sample	Initial composition	SiO_2/Al_2O_3 (molar ratio)	Al_2O_3/Na_2O (molar ratio)	SiO_2/Na_2O (molar ratio)	H_2O/Na_2O (molar ratio)	Final setting time (min)
Si38	$Na_2O.1.0Al_2O_3.3.8SiO_2.13.6H_2O$	3.81	1.0	3.8	13.6	155
Si34	$Na_2O.1.0Al_2O_3.3.4SiO_2.13.6H_2O$	3.41	1.0	3.4	13.6	70
Si30	$Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	3.0	13.6	46
Si25	$Na_2O.1.0Al_2O_3.2.5SiO_2.13.6H_2O$	2.50	1.0	2.5	13.6	30
Al06	$Na_2O.0.6Al_2O_3.3.0SiO_2.13.6H_2O$	5.01	0.6	3.0	13.6	220
Al07	$Na_2O.0.7Al_2O_3.3.0SiO_2.13.6H_2O$	4.28	0.7	3.0	13.6	180
Al08	$Na_2O.0.8Al_2O_3.3.0SiO_2.13.6H_2O$	3.76	0.8	3.0	13.6	58
Al10	$Na_2O.1.0Al_2O_3.3.0SiO_2.13.6H_2O$	3.00	1.0	3.0	13.6	46
Al12	$Na_2O.1.2Al_2O_3.3.0SiO_2.13.6H_2O$	2.50	1.2	3.0	13.6	30

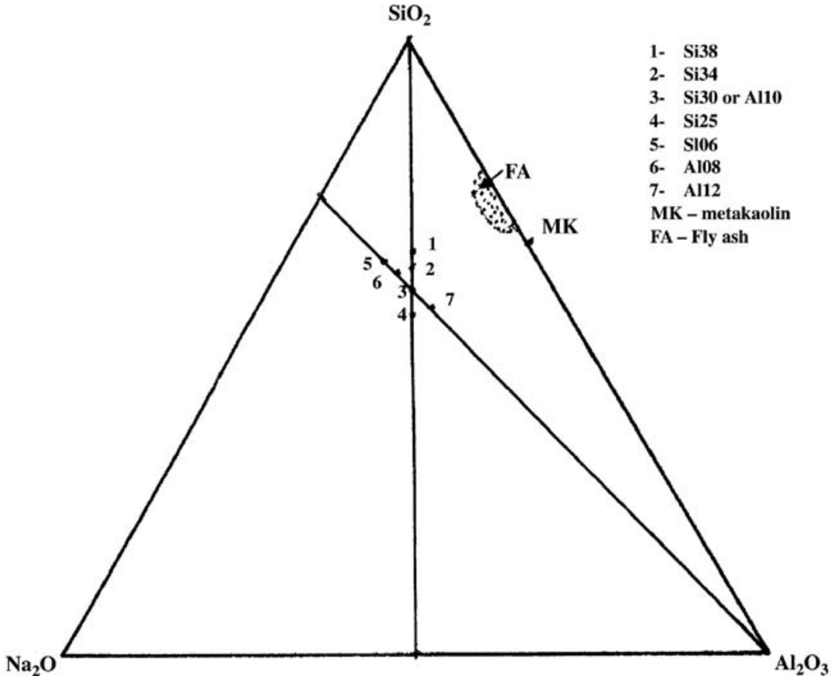


Fig. 1. $Na_2O–Al_2O_3–SiO_2–H_2O$ phase equilibrium diagram showing initial mixture compositions.

strength at different curing times (0.5, 1, 2, 4, 8, 24 and 72 h). The average value of three measurements was considered as the reported strength of the compact. Portions of these samples were kept in a freezer prior to solid phase analysis.

It is important to mention that a higher curing temperature of 60 °C was also tried with above mixture formulations, however for most of the mixtures, no significant change in strength was observed between about 1 and 24 h of curing. This was due to the acceleration of the geopolymer reaction at this higher curing temperature. Therefore, a lower curing temperature (40 °C), at which measurable early-stage changes could be detected, was adopted in this study.

The development of microstructure and geopolymer phases was observed by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Polished and fracture samples coated with carbon were used in the SEM study, and compositional analysis of phases was carried out using electron dispersive X-ray analysis (EDAX).

Final setting times of the mixtures at 40 °C were measured using a Vicat Needle C191-04 — the apparatus used for determining the setting time of cement.

3. Results

3.1. Setting time and subsequent strength development

Table 1 also shows the setting times of both the Si and Al series. It can be seen that for both series, final setting times decreased with decreasing SiO_2/Al_2O_3 molar ratio (increasing Al content).

The compressive strength development of samples Si38, Si34, Si30 and Si25, and samples Al06, Al08, Al10 and Al12 up to 72 h are shown in Figs. 2 and 3, respectively. It is clear that the initial composition (mainly SiO_2/Al_2O_3) had a significant effect on the setting times and strength development of the systems. Considering the Si series (Fig. 2a), the mixture with the lowest Si content (Si25) gained measurable strength within

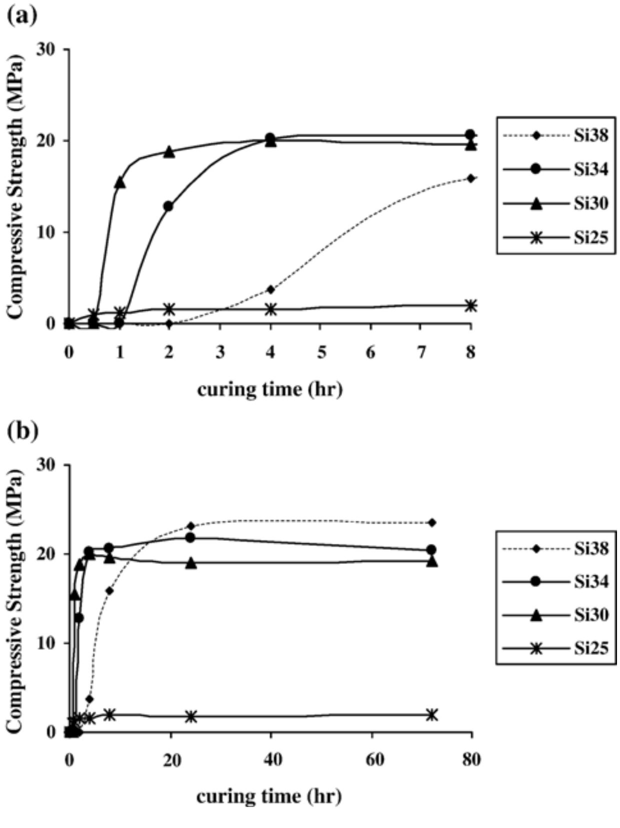


Fig. 2. Compressive strength development of mixtures with different SiO_2 contents (a) up to 8 h, (b) up to 72 h.

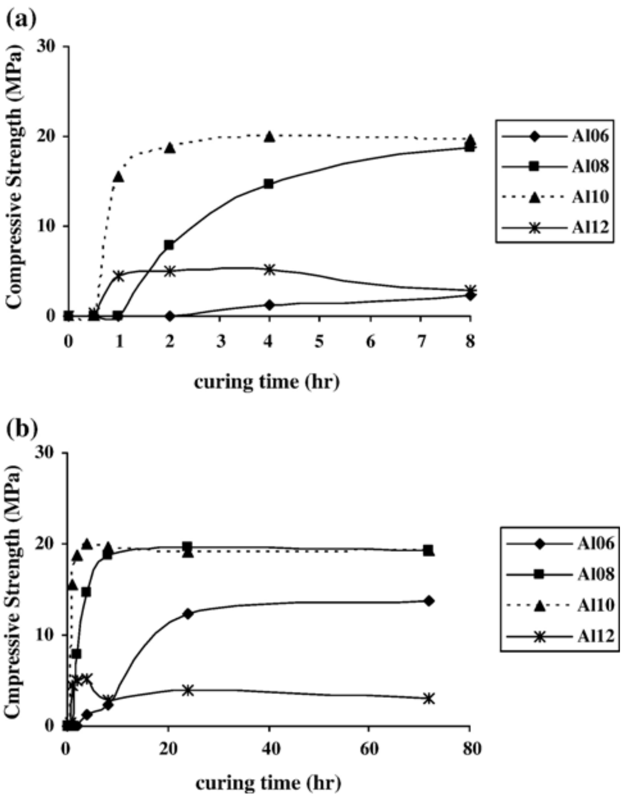


Fig. 3. Compressive strength development of mixtures with different Al_2O_3 contents (a) up to 8 h, (b) up to 72 h.

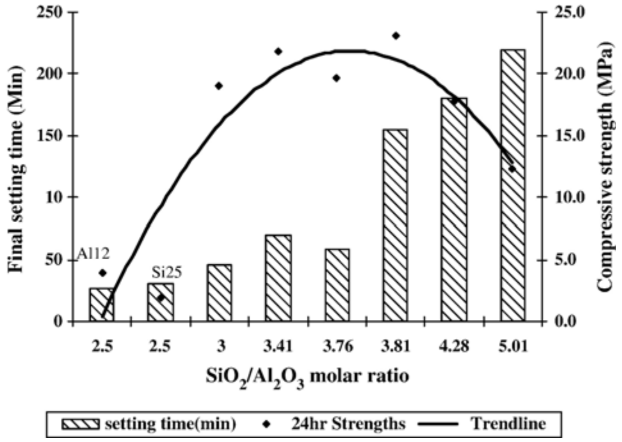


Fig. 4. Final setting times and variation of 24-h compressive strength with respect to SiO_2/Al_2O_3 (molar ratio) at a constant H_2O/Na_2O ratio of 13.6.

the first half an hour of curing. The times taken to attain measurable strength increased with increasing Si in the initial formulation, i.e. for systems Si30, Si34 and Si38, these times were roughly 1, 2 and 4 h, respectively. These values reflect well the measured setting times of these mixtures. When the Si/Al in the initial composition was increased, longer setting and hardening times were observed.

Once setting had occurred, strength continued to increase in all the mixtures but at different rates. The rate of strength development seemed to be highest for Si38 and lowest for Si25. At 24 h, strength development was in the order of Si38 > Si34 > Si30 ≫ Si25 (Fig 2b). It should be noted that the SiO_2/Al_2O_3 ratio of these mixtures were 3.8, 3.4, 3.0 and 2.5, respectively. Although it took the longest time to set, the strength development of Si38 seemed to stabilize after 24 h of curing.

A similar trend in strength development was observed with the Al series, in which the Al content was changed at constant SiO_2, Na_2O and H_2O concentrations. As shown in Fig. 3a, the time taken to gain measurable strength decreased with increasing Al content in the mixtures. These times were approximately 0.5, 1, 2 and 4 h for Al12, Al10, Al08 and Al06, respectively, and these reflect the final setting times of these mixtures. At 24 h, Al10 and Al08 had similar strength and the highest values in the series, while Al12 had the lowest (Fig 3b). It is interesting to note that Al06 did not have the highest strength, even though it contained the highest SiO_2/Al_2O_3 ratio (5.01). It is apparent, therefore, that there is an optimum SiO_2/Al_2O_3 ratio that is favorable for producing high-strength geopolymers.

Fig. 4 shows the variation in setting times and 24-h strengths of both series of mixtures, with respect to SiO_2/Al_2O_3 ratio. Accordingly, the most favorable SiO_2/Al_2O_3 molar ratio for strength development in the geopolymer systems investigated was in the range of 3.4–3.8. For this, the Al_2O_3/Na_2O ratio was in the range of 0.8–1.0, which is in good agreement with the findings of previous studies [11–13]. However, it should be noted that the final setting time of Al08 was much shorter than that of Si38, even though they had similar SiO_2/Al_2O_3 ratios (3.76 and 3.81, respectively). Apart from that, they had different Al_2O_3/Na_2O and SiO_2/Na_2O_3 ratios, which could be a reason for the difference in the setting times of these mixtures but needs further investigation.

The main inference from the above results is that, while Al appears to play a major role in controlling the setting characteristics of $Na_2O–Al_2O_3–SiO_2–H_2O$ geopolymer systems, the later-age strength characteristics depend more on the Si content in a system.

3.2. Phase development by XRD

The phase and microstructure development of the geopolymer mixtures were studied using XRD and SEM techniques.

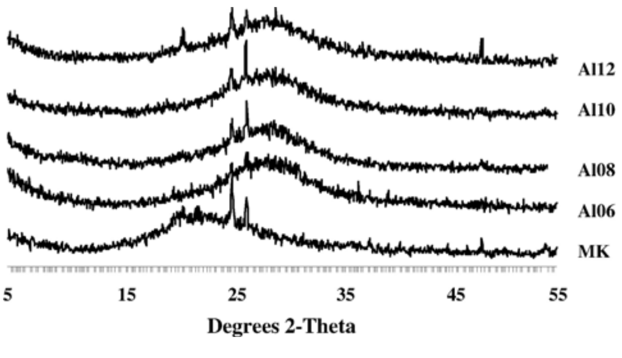


Fig. 5. XRD patterns of samples with different Al_2O_3 contents after 24-h curing.

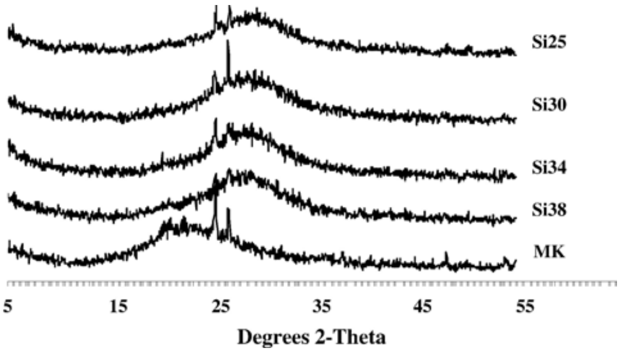
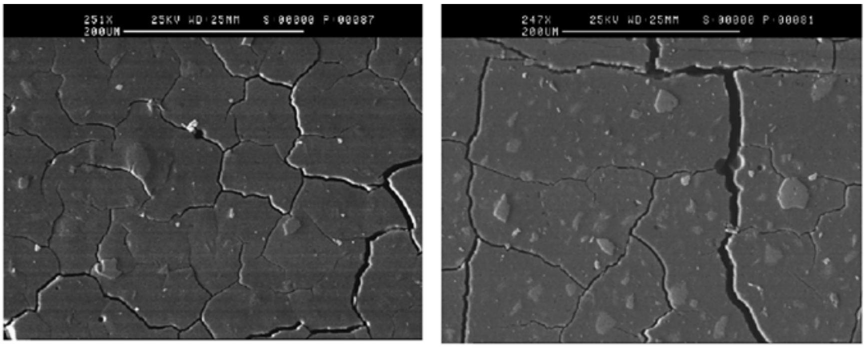
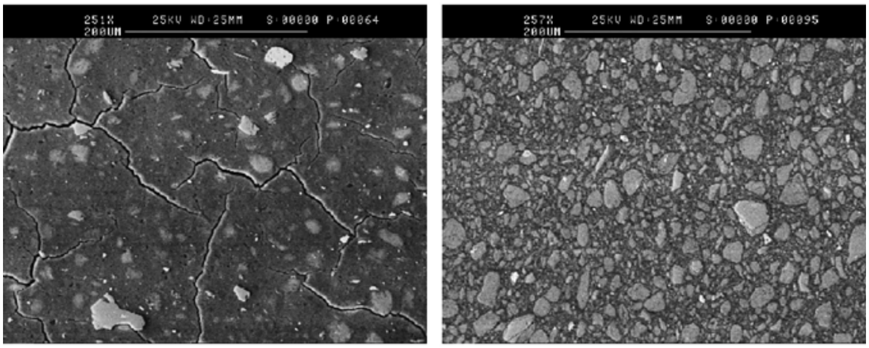


Fig. 6. XRD patterns of samples with different SiO_2 contents after 24-h curing.

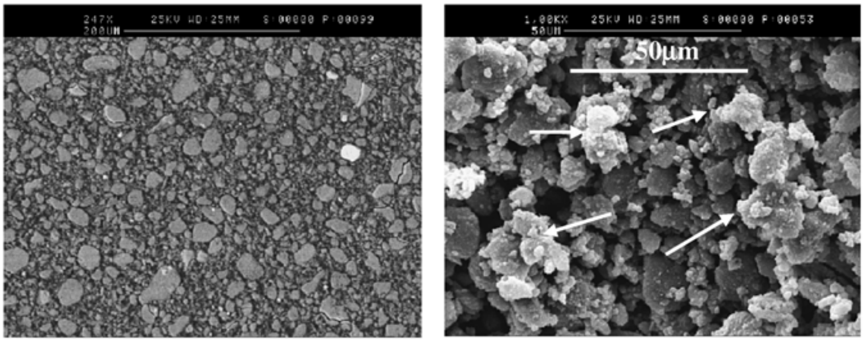
The XRD patterns of the Al and Si series at 24-h curing are shown in Figs. 5 and 6, respectively. The XRD pattern of metakaolin (MK), which is an amorphous material, consists of a broad peak centred around 22° 2θ. The presence of the sharp peaks in the metakaolin trace was due to the presence of trace quartz and TiO_2 in the original clay. When reacted with sodium silicate/NaOH, the position of the centre of the original broad peak of metakaolin shifted from 22° to 28° 2θ, which is characteristic of geopolymer systems [14]. This broad peak was present for all mixtures and was fairly consistent, regardless of the Al (Fig. 5) or Si (Fig. 6) content. However, it is interesting to note (Fig. 5) that when the Al content in the initial composition increased (decrease of Si), a few sharp peaks began to appear in the XRD patterns, especially for Al12 ($SiO_2/Al_2O_3 = 2.5$), suggestive of a potential amorphous to crystalline transition associated with changing SiO_2/Al_2O_3 ratio. As the peaks were not fully developed, the XRD identification of crystalline phase (s) in Al12 was unsuccessful. However, according to chemical analysis by EDAX, Al12 was found to consist mostly of Na–Al–Si-containing "massive" phases (grains).



(a) Al06 ($SiO_2/Al_2O_3 = 5.01$) (b) Si38 ($SiO_2/Al_2O_3 = 3.8$)



(c) Si30 ($SiO_2/Al_2O_3 = 3$) (d) Al12 ($SiO_2/Al_2O_3 = 2.5$)



(e) Si25 ($SiO_2/Al_2O_3 = 2.5$) (f) Al12 ($SiO_2/Al_2O_3 = 2.5$)

Fig. 7. SEMs of (a-3) polished sections and (f) fracture surface of samples (arrows indicating Na–Al–Si grains) with different SiO_2/Al_2O_3 molar ratios.

The above pattern of phase development change was not observed in the Si series (Fig. 6), however according to the EDAX analysis, Si25 ($SiO_2/Al_2O_3=2.5$) was also found to consist mostly of Na–Al–Si-containing grains. These grains (phases) were absent in mixtures of higher SiO_2/Al_2O_3 ratios (e.g. Si38). Clearly, at this stage of the study there is not enough evidence to confirm a possible amorphous to crystalline transition associated with decreasing SiO_2/Al_2O_3 ratio, and this is to be further investigated. However, it is apparent that low SiO_2/Al_2O_3 ratios favor Na–Al–Si-containing grains.

It is also worth recalling that both Si25 and Al12, which had SiO_2/Al_2O_3 ratios of 2.5, showed the lowest 24-h strength.

3.3. Microstructure development

SEM images of polished samples of Al06, Si38, Si30, Si25 and Al12 with corresponding SiO_2/Al_2O_3 molar ratios of 5.01, 3.8, 3.0, 2.5 and 2.5, respectively, are presented in Fig. 7. A significant change in microstructure, especially homogeneity, was associated with changing SiO_2/Al_2O_3 ratio. As shown, the microstructures of Al12 (Fig. 7d) and Si25 (Fig. 7e), which exhibited the lowest strengths, were highly inhomogeneous and the matrixes were full of loosely structured grains of different sizes (5–15 μm). This was further evident in the microstructure of the fracture surface of Al12 (Fig. 7f). EDAX analysis revealed that most of these grains contained Na, Al and silicon, and could possibly be responsible for the sharp peaks shown in the XRD patterns. Very few unreacted metakaolin particles could be identified.

The microstructures of mixtures with higher SiO_2/Al_2O_3 ratios (Al06, Si38 and Si30) (Fig. 7a, b and c) were completely different two those of Al12 and Si25 (Fig. 7d and e). In these, a grainy structure was still apparent, but the matrixes were evidently more dense and homogeneous. Improvement in microstructural homogeneity is conventionally a strong indication of higher strength, as observed for Si38 and Si30. However, there was no clear evidence in the microstructure of Al06 to explain the lower strength values observed for this sample, compared to Si38 and Si30, even though its microstructure appeared very homogeneous.

EDAX spot analyses on the dense (geopolymer) areas of Al06, Si38 and Si30 showed that they contained Na, Al and Si, but at a different ratio to the original composition (Table 2). The results presented are an average of 3–4 analyses. The SiO_2/Al_2O_3 ratio of the geopolymer phase was somewhat consistent with that of the original, but both Al_2O_3/Na_2O and SiO_2/Na_2O ratios were much higher in the resulted geopolymer phase. In other words, all the Na added at mixing was not necessarily incorporated in the geopolymer phase. The values measured by EDAX are generally indicative of the amount of Na incorporated into the geopolymer network structure. The presence of low concentrations of Na in the geopolymer (gel) phase has also been noted in other studies [11,15].

Table 2
Elemental compositions of geopolymer (GP) phases

Sample	SiO_2/Al_2O_3 (molar ratio)	Al_2O_3/Na_2O (molar ratio)	SiO_2/Na_2O (molar ratio)
Al06	Original 5.01, GP 5.45	Original 0.6, GP 1.22	Original 3.0, GP 6.65
Si38	Original 3.81, GP 3.86	Original 1.0, GP 1.65	Original 3.8, GP 6.45
Si30	Original 3.0, GP 3.08	Original 1.0, GP 1.59	Original 3.0, GP 4.97

4. Discussion

The results presented in this study provide an insight into the early reaction kinetics of geopolymer formation. Given that geopolymer formation is basically dissolution and hydrolysis, followed by a condensation process that takes place in an $Na_2O–Al_2O_3–SiO_2–H_2O$ system, the concentrations of Na and Si determine the type of hydrolysed ion and the path of the condensation process, and hence the chemistry and properties of the resulting geopolymer. In a system with a high Si concentration, condensation starts with the formation of oligomeric silicates, leading to [poly(sialate–siloxo) and poly(sialate–disiloxo)] 3D rigid polymeric structures. Low Si concentration results poly(sialate) polymer structures [6].

The SiO_2/Al_2O_3 ratios considered in this study ranged from 2.5 to 5.01. Considering the fact that the Al component of metakaolin tends to dissolve more easily than the silicon component [6], and the relatively lower Si present in the $SiO_2/Al_2O_3=2.5$ system, it is possible that more $Al(OH)_4^{4-}$ species were available for condensation in this system. Therefore, in this system condensation is likely to have occurred between aluminate and silicate species, producing poly(sialate) polymer structures. With increasing Si content, more silicate species are available for condensation and reaction between silicate species, resulting in oligomeric silicates, becomes dominant [6]. Further condensation between oligomeric silicates and aluminates results in a rigid 3D network of poly(sialate–siloxo) and poly(sialate–disiloxo) 3D rigid polymeric structures. However, as the rate of condensation between silicate species is slower than that between aluminate and silicate species, setting occurs later with increasing Si content. The geopolymers of poly(sialate–siloxo) and poly(sialate–disiloxo) structures are 3D networks, which are more rigid and stable than poly(sialate) structures and produce higher strengths. Therefore, even though Al plays a major role in regulating the setting time of geopolymer formation, the amount of Si present is responsible for higher later strength development of these systems.

While high SiO_2/Al_2O_3 mixtures in this study resulted in amorphous Na–Al–Si-containing polymer phases (geopolymer), the low SiO_2/Al_2O_3 mixtures tended to produce Na–Al–Si-containing grains. The low SiO_2/Al_2O_3 mixtures were also accompanied with low strengths. There was not enough evidence in this study to confirm any amorphous to crystalline transition associated with the initial SiO_2/Al_2O_3 ratio. However, an increased crystalline nature of products with increasing Al content on the initial mixtures ($SiO_2/Al_2O_3<2$), in alkali-activated metakaolin systems, has been noted previously [10]. It is also known that poly(sialate) geopolymer units are the backbone of products like bricks and ceramics [5,15]. Therefore, it is conceivable that the high Al compositions considered in this study may be more suitable in the development of ceramic-type materials rather than cement binder-based geopolymer products.

Metakaolin is highly reactive in an alkaline medium and near-100% reactivity was assumed in this study. The results presented clearly demonstrate how the properties of geopolymers can be drastically affected by a minor change in the amount of Si and Al available for the reaction. Depending on the composition and especially the reactivity of raw materials, the amount of Si and Al available for geopolymer formation can be very different. Therefore, a thorough understanding of the reactivity of raw materials in an alkaline medium is important when deciding the initial compositions in the synthesis of geopolymers to achieve the desired properties.

5. Conclusions

The following conclusions can be drawn from this study.

- The amount of Al available for geopolymer reaction during synthesis appears to have a dominant effect in controlling setting time; accordingly, increasing the SiO_2/Al_2O_3 ratio leads to longer setting times.
- Increasing SiO_2/Al_2O_3 molar ratios up to 3.4–3.8 is largely responsible for the high-strength gains observed at later stages.
- A corresponding increase in Al (low SiO_2/Al_2O_3) leads to products of low strengths, accompanied by microstructures with increased Na–Al–Si grains rather than amorphous Na–Al–Si-containing geopolymers.
- EDAX measurements revealed that the SiO_2/Al_2O_3 ratios of geopolymer phases are quite similar to those of starting mixtures, but they have a much lower Na content.
- The properties of a geopolymer can be significantly altered by relatively minor changes in Si and Al concentrations during synthesis.

References

[1] J. Davidovits, Mineral polymers and methods of making them, US Patent 4,349,386 (1982).
[2] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: a cement for the future, Cem. Concr. Res. 29 (1999) 1323–1329.
[3] J.G.S. Van Jaarsveld, J.S.J. Van Deventer, G.C. Lukey, The effect of composition and temperature on the properties of fly ash and kaolinite-based geopolymers, Chem. Eng. J. 89 (2002) 63–73.
[4] T. Bakharev, Geopolymer materials prepared using class F fly ash and elevated temperature curing, Cem. Concr. Res. 35 (2005) 1224–1232.
[5] J. Davidovits, Properties of geopolymer cements, Alkaline Cements and Concretes, Kiev, Ukraine, 1994, pp. 131–149.
[6] L. Weng, K. Sagoe-Crentsil, T. Brown, Speciation and hydrolysis kinetics of aluminates in inorganic polymer systems, presented to Geopolymer 2002 International Conference, 28–29 October, Melbourne, Australia.
[7] T.W. Swaddle, Silicate complexes of aluminium (III) in aqueous systems, Coord. Chem. Rev. 219–221 (2001) 665–686.
[8] M.R. Anseau, J.P. Leung, N. Sahai, T.W. Swaddle, Interactions of silicate ions with zinc (II) and aluminium (III) in alkali aqueous solution, Inorg. Chem. 44 (22) (2005) 8023–8032.
[9] M.R. North, T.W. Swaddle, Kinetics of silicate exchange in alakaline aluminosilicate solutions, Inorg. Chem. 39 (12) (2000) 2661–2665.
[10] R.A. Fletcher, K.J.D. MacKenzie, C.L. Nicholson, S. Shimada, The composition range of aluminosilicate polymers, J. Eur. Ceram. Soc. 25 (2005) 1471–1477.
[11] M. Rowles, B. O'Connor, Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by sodium silicate activation of metakaolinite, J. Mater. Chem. 13 (2003) 1161–1165.
[12] M. Stevenson, K. Sagoe-Crentsil, Relationship between composition, structure and strength of inorganic polymers: part 1 — metakaolin-derived inorganic polymers, J. Mater. Sci. 40 (2005) 2023–2036.
[13] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. Deventer, Understanding the relationship between geopolymer composition, microstructure and mechanical properties, Colloids Surf., A Physicochem. Eng. Asp. 269 (2005) 47–58.
[14] J.L. Provis, G.C. Lukey, J. Deventer, Do geopolymers actually contain nanocrystalline zeolites? A re-examination of existing results, Chem. Mater. 17 (2005) 3075–3085.
[15] M. Schmucker, K.J.D. MacKenzie, Microstructure of sodium polysiatate siloxo geopolymer, Ceram. Int. 31 (2005) 433–437.