

碱激发胶凝材料：早期成核、化学相演变和体系性能

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摘要：近些年，通过碱激发硅铝酸质材料形成聚合物水泥基材料的研究得到了广泛关注。由于在此聚合物胶凝体系中，硅铝质原料存在多样性，包括粉煤灰、矿渣、煅烧高岭石等，因此其原料化学性质在动力学和固相演变过程中起到非常重要的作用，并决定了最终产品的化学和物理性质。本文分析了原料化学组成对从溶解到最终水化产物性能的碱激发全过程的影响。并使用了包括 X 射线同步衍射分析在内的一系列分析技术对多种原料的无定形和沸石状结构进行了表征。研究了具有特定无定形 SiO₂/Al₂O₃ 比的钠铝硅酸盐沸石在 Al₂O₃-SiO₂-H₂O 凝胶中的结晶趋势，并基于可识别的三元相图中的组成结构，研究了钙离子和剩余阳离子种类的主要影响。讨论了不同体系的相组成和化学成分、物相转变、微观结构变化及其长期强度发展和耐化学性的关系。

关键词：混凝；耐久性；模拟；服役寿命；验证

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Alkali-activated binders: Early Age Nucleation Reactions, Chemical Phase Evolution and Their Implications on System Properties

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Abstract: Formation of polymeric cementitious binders *via* alkaline activation of aluminosilicates has gained significant attention within the manufacturing and building sectors in recent years. Given the diversity of aluminosilicate source materials employed in these systems, such as fly ash, blast furnace slag, calcined kaolinite, *etc.*, the chemistry of raw materials play a crucial role in both kinetics and stability of solid phase evolution which govern chemical and physical properties of resultant products. This paper analyses the effects on elemental composition of raw materials on the overall alkaline activation process; from dissolution to end-product properties. A range of analytical techniques including X-ray synchrotron analysis has been used to characterise amorphous and zeolitic domains from a range of raw materials. In particular, the tendency of aluminosilicate source materials with defined amorphous SiO₂/Al₂O₃ ratios to nucleate sodium aluminosilicate zeolitic phases originating from Na₂O-Al₂O₃-SiO₂-H₂O gel assemblages is investigated, alongside the dominant influence of Ca ions and residual cationic species based on identifiable compositional domains within ternary phase diagrams. Stable phase assemblages and optimal compositional ranges for different systems are discussed with respect to phase development, microstructural changes and their relationship to long term strength development and chemical resistance.

Key words: geopolymer; X-ray synchrotron; aluminosilicates; fly ash; metakaolin, zeolites

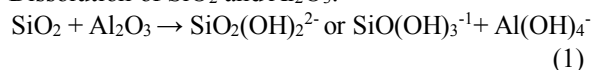
Originality: The need to gain clearer understanding of key factors governing fundamental reaction chemistry of Geopolymer systems alongside the inter-play between feedstock materials and basic engineering parameters such as binder setting characteristic continues to pose significant challenges to the development of practical and useable protocols for geopolymer concrete mix design. Accordingly, the present study investigates relative dependencies of type, chemical composition and reactivity of raw materials and how these factors alters the chemistry of the resulting geopolymers and, hence, end-product properties and durability. The range of analytical tools employed in the present study including high resolution Synchrotron XRD patterns, in agreement conventional XRD technique, disclose presence of nano-crystalline particles embedded in the amorphous matrix with possible long-term durability implications. The study further demonstrates that decreasing of SiO₂/Al₂O₃ ratio (or increasing Al₂O₃) favour higher strengths reaching a maximum ratio of SiO₂/Al₂O₃ ~3.50 and remains constant thereafter. There also exists optimum SiO₂/Al₂O₃ ratio (3.20-3.70) which yields mixes with longer setting time and higher strengths.

1 Introduction

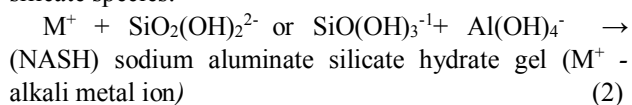
Alkali activated binder systems comprise of a group of inorganic polymers obtained by low-temperature alkali activation of alumina (Al_2O_3) and silica (SiO_2) containing materials. The binding mechanism involves the dissolution of Al and Si in the alkali medium, transportation (orientation) of dissolved species, followed by a polycondensation process, forming a polymeric network of silico-aluminate structures^[1]. 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^[2-3]. Depending on the Si/Al ratio (degree of polymerisation), the chemical and physical properties of the geopolymers can be varied. A low Si:Al ratio (*e.g.* 1, 2 or 3) initiates a 3D-Network which is very rigid. However, the polymeric character of geopolymers increases with increasing Si/Al ratio. The type, chemical composition and reactivity of the raw materials and the curing conditions play a major part in controlling the chemistry of the resulting geopolymers, and hence the properties.

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. The presence of $[\text{SiO}_2(\text{OH})_2]^{2-}$ ions is preferred to $[\text{SiO}(\text{OH})_3]^-$ in very high alkaline conditions. 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 (refer: Eqs. 1 and 2). These oligomeric silicates in turn condense with $\text{Al}(\text{OH})_4^-$, forming a rigid 3D network of polymer structures [poly(sialate-siloxo) and poly(sialate-disiloxo)].

Dissolution of SiO_2 and Al_2O_3 :



Orientation and polycondensation of aluminate and silicate species:



Apart from some differences in synthetic conditions, the basic process of geopolymer formation has many similarities to that of zeolites, another group of silico-aluminates. As the starting materials for the synthesis are more or less similar, some classes of geopolymers are often regarded as similar to zeolites in chemical composition^[4]. The key difference between zeolites and geopolymers is notionally linked to their respective relative levels of matrix phase crystallinity. The geopolymer phase is typically “X-ray amorphous” in

contrast to the well-developed crystalline structures of zeolites. From thermodynamic viewpoint, geopolymer phases are considered as metastable with respect to zeolites. This makes the synthesis of geopolymers quite challenging and, a thorough understanding of the underlying chemistry of these systems is a necessity. Defining the extent of crystallinity or the amorphous nature of the geopolymer phase is rather challenging as sometimes the crystalline morphologies can be present as nano-crystalline particles embedded in the amorphous matrix. Conventional XRD is a popular technique used to analyse well developed crystalline materials, but, it has some limitations in detecting initial crystal growths/nano-crystalline particles. One of the advanced techniques that can be considered in geopolymer phase analysis & identification is the Synchrotron. High intense radiation of Synchrotron light is found to have many useful properties and is currently used in a wide range of non-destructive, high-resolution, rapid, *in-situ*, real-time imaging and analysis techniques.

More broadly, the mechanism of geopolymerisation and the properties of resulting products are controlled by several factors. One of these is the nature and composition of the source materials. The variations of the alkaline activators are usually limited as they are derived from sodium/potassium silicates and/or hydroxides. However, the chemical and physical characteristics of aluminosilicate source material can vary widely because of source origin (geological history), thermal processing, particle size, total SiO_2 and Al_2O_3 content and reactive (amorphous) phase content. In addition, the presence of other elemental oxides (oxides of calcium, magnesium and iron *etc.*) as minor phases in the raw material also can play a vital role as they can provide network modifying cations to the geopolymerisation process^[5-6]. Current common sources of aluminosilicate materials investigated in geopolymer synthesis are metakaolin (calcined kaolinite), fly ash (a by-product of coal combustion process) and blast-furnace slag (a by-product of iron manufacturing process)^[7-11]. Metakaolin is considered a pure aluminosilicate source material that can be nearly 100% reactive in the alkaline medium resulting pure $\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ geopolymer phase. Conversely, the composition of fly ashes is generally variable depending on the composition of original coal. In general Class F fly ash also contains mainly alumina and silica phases, most of which are reactive in alkaline medium, and generally produce $\text{M}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ geopolymers. However, Class C fly ash (derived from lignite coal sources) and blast furnace slag contain, in addition to alumina and silica phases, considerable amounts CaO. Calcium oxide gives fly ash and slag pozzolanic properties and the presence of calcium in a cement system can change its setting characteristics. Therefore, when calcium is present in a

M₂O–SiO₂–Al₂O₃–H₂O system, some changes in the chemistry, especially with respect to setting and hardening processes, are to be expected [12]. This paper investigates the effects on elemental composition of raw materials on the overall alkaline activation process including dissolution and the formation of initial stage gel and final product. Several techniques such as conventional XRD, Synchrotron XRD, EDAX were used to characterise microstructural development of phases. Stable phase assemblages and optimal compositional ranges for different systems are investigated and discussed with respect to phase development, microstructural changes and their relationship to long term strength development.

2 Experimental

2.1 Raw Materials

A variety of materials such as metakaolin, obtained by calcining kaolin (Commercial Minerals, Australia, 47.3% (mass fraction, the same below) SiO₂, 35.7 % Al₂O₃, 3.1 % other minerals) and class C fly ash (Mae Moh Power Station, Thailand) have been used as the main aluminosilicate sources. N-grade sodium silicate (8.9 % Na₂O, 28.7 % SiO₂, 62.5 % H₂O – from PQ Australia) and laboratory grade NaOH were used as the alkali sources. Rice husk ash (RHA), nano silica and nano alumina were also used as additional silica and alumina sources to obtain required elemental oxide ratios in the calcium based systems.

2.2 Process

2.2.1 Paste sample preparation for non-Ca systems: characterisation of amorphous and zeolitic domains

Seven mix formulations (numbered as 1–7), as shown in Table 1, with changing SiO₂, Al₂O₃ and Na₂O molar ratios have been used in this study. Relatively low water contents representative of geopolymer synthesis were adopted. The water content in each system included the total water content derived from NaOH, sodium silicate and extra added water. A low temperature (40 °C) continuous curing was adopted. At low temperatures, the reactions occur at a lower rate hence the development of new phases. Slow rate phase development would help gaining more information about the pattern of reactions. The domain of the mix formulations and compositions of Na-zeolites that are known to be stable at low temperature (up to 100°C) shown in the Na₂O–Al₂O₃–SiO₂–H₂O phase compositional diagram in Fig. 1.

In preparing the 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 moisture loss. Specimens were subsequently cured at 40 °C and 95% RH. Care was taken to minimize the time between sample preparation and curing for all mixtures. Specimens were removed from the moulds after 24 h and

Table 1 Mix Formulations for Non-Ca systems

Sample No.	Initial composition	Chemical composition/mol			Molar ratio of SiO ₂ to Al ₂ O ₃
		SiO ₂	Al ₂ O ₃	Na ₂ O	
1	1.0Na ₂ O.1.0Al ₂ O ₃ .3.8SiO ₂ .13.6H ₂ O	3.81	1.0	1.0	3.81
p	1.0Na ₂ O.1.0Al ₂ O ₃ .3.4SiO ₂ .13.6H ₂ O	3.40	1.0	1.0	3.40
2	1.0Na ₂ O.1.0Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	1.0	1.0	3.00
3	1.0Na ₂ O.1.0Al ₂ O ₃ .2.5SiO ₂ .13.6H ₂ O	2.50	1.0	1.0	2.50
4	1.0Na ₂ O.0.6Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	0.6	1.0	5.01
q	1.0Na ₂ O.0.7Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	0.7	1.0	4.28
r	1.0Na ₂ O.0.8Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	0.8	1.0	3.76
5	1.0Na ₂ O.1.2Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	1.2	1.0	2.50
6	0.7Na ₂ O.1.0Al ₂ O ₃ .3.0SiO ₂ .16.3H ₂ O	3.00	1.0	0.7	3.00
7	1.4Na ₂ O.1.0Al ₂ O ₃ .3.0SiO ₂ .13.6H ₂ O	3.00	1.0	1.4	3.00

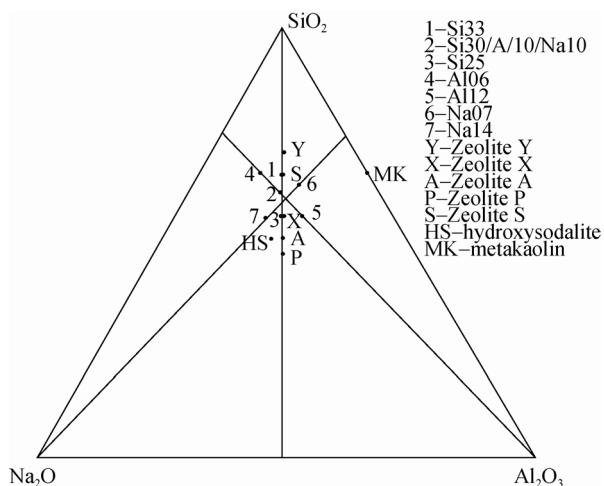


Fig. 1 Na₂O-SiO₂-Al₂O₃-H₂O compositional diagram showing mix formulations

placed in sealed polythene bags and continued to cure at 40 °C and 95% RH. Samples were tested for compressive strength, at different curing times up to 210 days. The average value of three measurements was considered as the reported strength of the compact. Portions of these samples were used in solid phase analysis. The development of microstructure and geopolymer phases was observed by scanning electron microscopy (SEM) and conventional X-ray diffractometry (XRD). Ground, powder samples were used in XRD analysis. Fracture

samples, (dried under vacuum) coated with gold was used in the SEM study, and compositional analysis of phases was carried out using energy dispersive X-ray analysis (EDAX). A separate set of mixtures of the all mix formulations shown in Table 1, including p, q, r formulations, were prepared for setting time measurements. Setting time trials were also performed at 40 °C, using standard Vicat needle apparatus. The details of the procedures are available in Refs.[13-14].

2.2.2 X-ray synchrotron analysis

A set of samples with the same compositions as in Table 1 were prepared and cured at 80 °C for 24 h. Ground portions of these samples were analysed using Synchrotron XRD technique.

2.3 Sample preparation for Ca based systems

A mix formulation of Na₂O·1.17Al₂O₃·4.80 SiO₂·11.45H₂O with SiO₂/Al₂O₃ ratio ~ 4 was used as the control mix. Series of mixes with changing SiO₂/Al₂O₃ ratios, as shown in Table 2, were prepared using eithernano-silica, nano-alumina or RHA. Samples were prepared as indicated in section 2.2.2 and cured at 60 °C for 24 h. Analysis of samples was also carried out as indicated in section 2.2.2. The detailed procedures are available in Ref.[12]. A separate set of mixtures of the same mix formulation were prepared for setting time measurements. Setting time trials were performed at room temperature, i.e., 22 °C, using standard Vicat needle apparatus.

Table 2 Mix formulations of Ca based systems

Mix Design	Added SiO ₂ or Al ₂ O ₃ /mol	Molar composition	Mole ratio of SiO ₂ to Al ₂ O ₃
1	Control mix	Na ₂ O.1.17Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	4.00
2	0.14SiO ₂ (nano-SiO ₂)	Na ₂ O.1.17Al ₂ O ₃ .4.94 SiO ₂ .11.45H ₂ O	4.22
3	0.18SiO ₂ (nano-SiO ₂)	Na ₂ O.1.17Al ₂ O ₃ .4.98 SiO ₂ .11.45H ₂ O	4.26
4	0.25SiO ₂ (nano-SiO ₂)	Na ₂ O.1.17Al ₂ O ₃ .5.05 SiO ₂ .11.45H ₂ O	4.32
5	0.14SiO ₂ (RHA)	Na ₂ O.1.17Al ₂ O ₃ .4.94 SiO ₂ .11.45H ₂ O	4.22
6	0.18SiO ₂ (RHA)	Na ₂ O.1.17Al ₂ O ₃ .4.98 SiO ₂ .11.45H ₂ O	4.26
7	0.25SiO ₂ (RHA)	Na ₂ O.1.17Al ₂ O ₃ .5.05 SiO ₂ .11.45H ₂ O	4.32
8	0.50 SiO ₂ (RHA)	Na ₂ O.1.17Al ₂ O ₃ .5.30 SiO ₂ .11.45H ₂ O	4.53
9	0.80 SiO ₂ (RHA)	Na ₂ O.1.17Al ₂ O ₃ .5.60 SiO ₂ .11.45H ₂ O	4.79
10	0.20 Al ₂ O ₃	Na ₂ O.1.37Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	3.50
11	0.30 Al ₂ O ₃	Na ₂ O.1.47Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	3.27
12	0.33 Al ₂ O ₃	Na ₂ O.1.50Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	3.20
13	0.50 Al ₂ O ₃	Na ₂ O.1.67Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	2.87
14	0.70 Al ₂ O ₃	Na ₂ O.1.87Al ₂ O ₃ .4.80 SiO ₂ .11.45H ₂ O	2.57

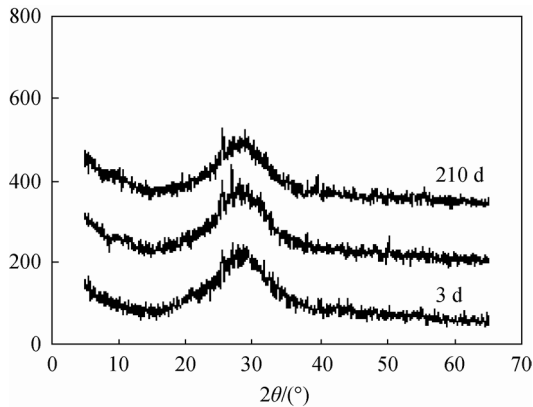
3 Results and discussion

3.1 Amorphous and zeolitic domains in non calcium Na₂O-Al₂O₃-SiO₂-H₂O geopolymer systems

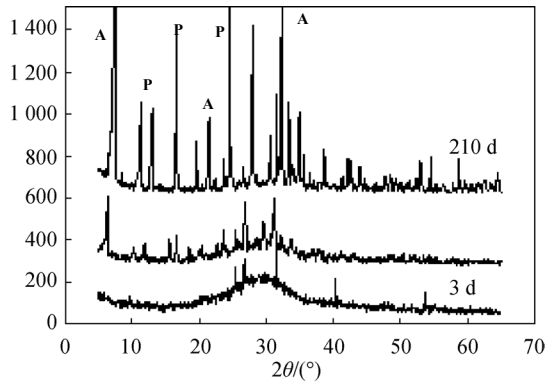
XRD results obtained in this study for the metakaolin

based samples (Mixes 1 & 3) cured continuously at 40 °C for different curing times are shown in Fig. 2 (Mixes 1 and 3 had same Na₂O, H₂O content but different SiO₂ and Al₂O₃ contents with SiO₂/Al₂O₃ ratios of 3.8 and 2.5 respectively). At 3 days, the XRD patterns of these samples look alike with both showing the presence of a

broad peak around $2\theta=28^\circ$ corresponding to the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ gel (geopolymer) phase. The XRD pattern seemed to be stable throughout the cure duration for the Mix 1. In contrast there is a considerable change of the phase development with time in Mix 3. Crystalline phases start to appear in Mix 3 with the curing time and, at 210 days, the microstructure is dominated by the presence of zeolitic phases such as zeolite A, zeolite P and faujasite. From these results it is apparent that low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (≈ 2.5) tend to develop zeolitic phases in these systems. The amorphous phase seems to be stable throughout curing for higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (≈ 4).



(a) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 3.8, Mix 1



(b) $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 2.5, Mix 3
(A = zeolite A, P = zeolite P)

Fig. 2 Phase development with curing, by conventional XRD techniques, of alkali activated metakaolin mixtures [14]

The presence of nanocrystalline particles, which have been identified as zeolitic structures, embedded in the geopolymer gel has been reported [7-8,15]. Considering the similarities in chemistry and synthesis routes of geopolymers and zeolites, these findings are not totally surprising. However, for a geopolymer product, the establishment of synthesis conditions that can lead to crystal formation is important for assessing the potential impact on the final properties (both chemical and physical). In hydrated $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems (Portland and

pozzolanic cements), for example, the formation of zeolitic phases from corresponding gel phases has been shown to have significantly altered the immobilization potential of these cements towards various waste metals [16-17]. Similar changes may also be expected to occur in hydrated $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems.

It has been postulated that the degree of crystallization in geopolymer systems is largely related to the system formulation and conditions of synthesis [18]. In geopolymer or zeolite formation, a number of factors seem to control the chemistry and nature of the final product. For instance, higher temperatures ($\geq 100^\circ\text{C}$) and pressures are generally considered prerequisites of zeolite formation. Nevertheless, some zeolite types can be synthesized at lower temperatures, or even under ambient conditions [17,19-20]. The concentration and type of alkaline activators, water content, and SiO_2 and Al_2O_3 contents of the source materials, and exposure environments, are also reported to have an influence on the formation of crystalline zeolitic phases in hydrated $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ systems [4,21-24]. The role of $\text{SiO}_2/\text{Al}_2\text{O}_3$ content on zeolitic phase development, especially the type and form of zeolitic phase, in geopolymer systems is reported elsewhere [14,25].

3.2 Synchrotron X-ray analysis

Figure 3 shows the Synchrotron XRD patterns for mixes 1, 2 and 3. The pattern of mix 3 is in agreement with that of obtained using conventional XRD and shows a number of crystalline phase developments. However, the pattern of mix 1 does not depict a total amorphous look as was shown with conventional XRD. Instead mix 3 pattern contains some crystalline peaks, perhaps the nano-crystalline phases embedded in the gel, which were not detectable by conventional XRD. This is an important finding as it demonstrates that commonly used geopolymer composition with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as 4 are may not likely be entirely 100% amorphous. This in turn begs the question about long term stability of such geopolymer phases and its subsequent structural implications. A detailed analysis of synchrotron XRD results of the samples investigated in this paper will be available in a separate publication.

3.3 Strength and microstructure development: non-calcium $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ systems

Figure 4 shows the typical pattern of observed somewhat linear relationship between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and setting time for investigated alkali activated metakaolin systems. The influence of several factors, especially $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, on the setting and hardening characteristics of ordinary geopolymer systems (systems without calcium) has been well reported [7,13-14]. The changes in setting characteristics have been explained in terms of available SiO_2 and Al_2O_3 content in the original compositions. Setting is typically associated with the sodium aluminate silicate hydrate gel (NASH) formation. When the system is high in SiO_2 more silicate species are available for condensation and reaction between silicate

species, resulting oligomeric silicates, becomes dominant. And further condensation between oligomeric silicates and aluminates result in a rigid 3D net works. The rate of condensation between silicate species is slow and, this normally leads to longer setting times. Correspondingly,

when the system has excess Al_2O_3 , increased aluminate ($Al(OH)_4^-$) species become available for the reaction leading to a faster rate of condensation between $Al(OH)_4^-$ and silicate species and shorter setting times [13].

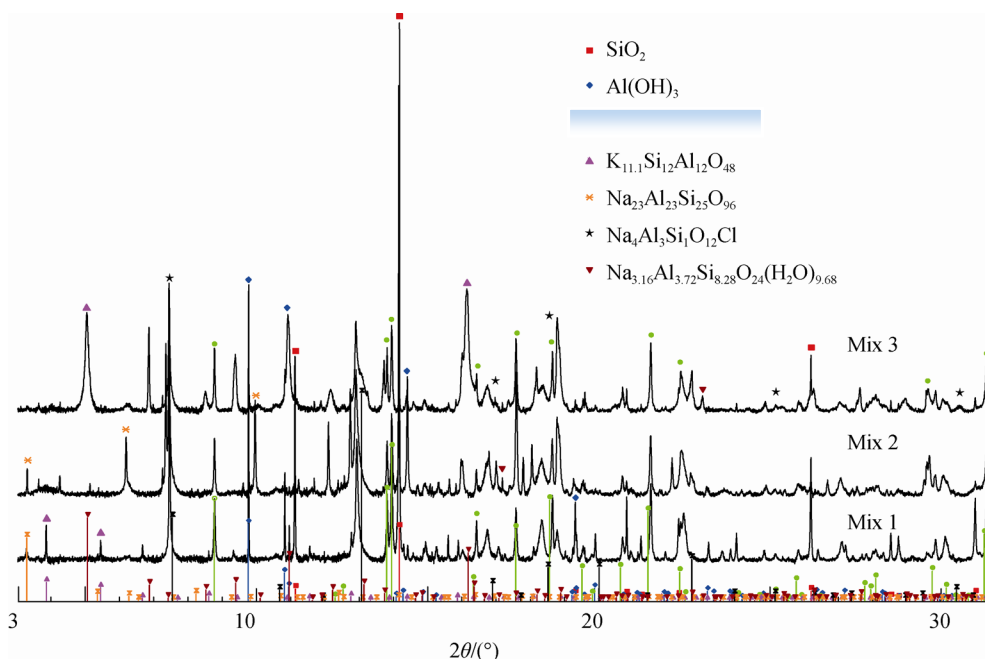


Fig. 3 Synchrotron XRD analysis of alkali activated metakaolin mixtures

Increasing SiO_2/Al_2O_3 ratio also increases the strength but only up to about $SiO_2/Al_2O_3 = 4$ and strength decreases thereafter. SiO_2/Al_2O_3 ratios around 3.50 – 4.00 has been accepted as the most suitable for optimal strength characteristics for calcium free geopolymer systems. Strength decrease, especially for the systems with SiO_2/Al_2O_3 ratio < 3, has been attributed to the development of crystalline zeolitic phases in high Al_2O_3 systems. Figure 5 shows the scanning electron micrographs of mix 1 and 3. The system of SiO_2/Al_2O_3 ratio ~ 4 (Mix 1, Fig.5(a)) is characterised by a dense homogeneous phase which accounted for its high strengths. Compared to this, the system with lower SiO_2/Al_2O_3 ratio, 2.5 (Mix 3, Fig. 5(b)) seemed to have porous microstructures, which possibly explains the observed low strengths in these samples. By EDAX analysis

metakaolin system [13] it has been confirmed the crystalline grains present are as partially developed chabazite-like crystals [14].

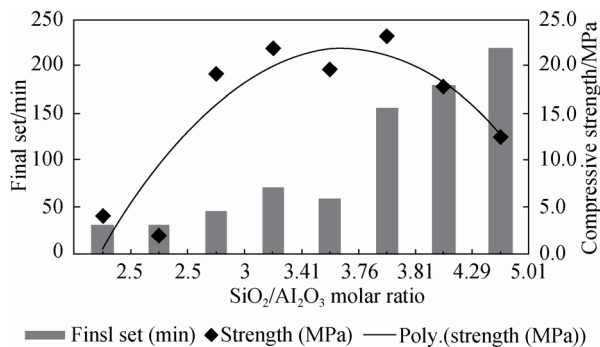
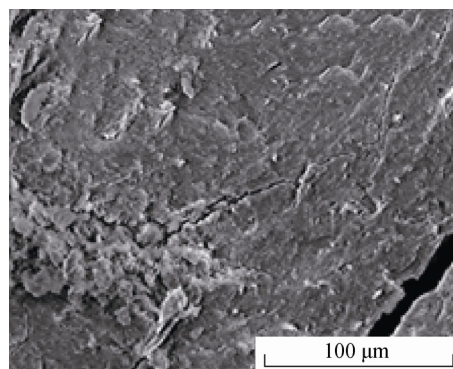
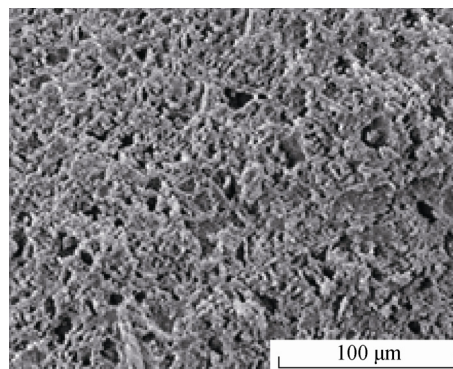


Fig. 4 Final setting times and compressive strength with respect to SiO_2/Al_2O_3 ratio of alkali activated



(a) SiO_2/Al_2O_3 ratio 3.8



(b) SiO_2/Al_2O_3 ratio = 2.5

Fig. 5 SEM micrographs of fracture surfaces of alkali activated metakaolin systems^[14]

3.4 Solid phase evolution: calcium based (CaO)Na₂O–Al₂O₃–SiO₂–H₂O geopolymer systems

The role of SiO₂/Al₂O₃ ratio on the setting and hardening properties of geopolymers, of the mix compositions provided in Table 2, made with high calcium fly ash has been previously published^[12]. It has been found that the two systems, with and without calcium, appear to act differently in many ways. Combined final setting times and compressive strength with respect to SiO₂/Al₂O₃ molar ratio of alkali activated high calcium fly ash based systems are shown in Fig. 6. It is evident that setting time characteristics and strength development do not follow the same trend. Decreasing of the SiO₂/Al₂O₃ ratio (or increasing Al₂O₃) favours higher strengths reaching a maximum at around SiO₂/Al₂O₃ ratio 3.50 and remains constant thereafter. There is an optimum SiO₂/Al₂O₃ ratio (3.20–3.70) which leads to products with longest setting time with reasonably high strengths.

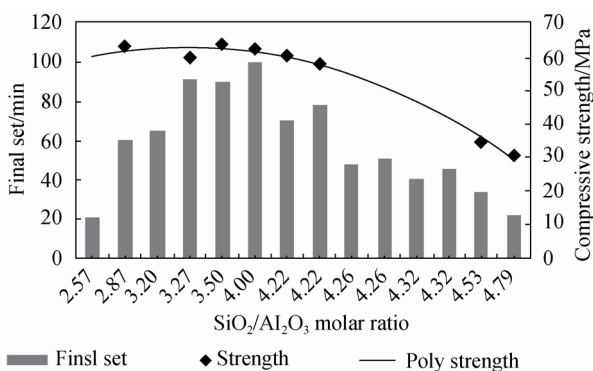


Fig. 6 Final setting times and compressive strength with respect to SiO₂/Al₂O₃ ratio of alkali activated high calcium fly ash system^[12]

The main concern with calcium containing system is its rapid setting property and hence low workability. Calcium sources are generally used to accelerate the setting of low calcium fly ash-based geopolymers^[26] and metakaolin based geopolymer systems^[27-28]. The setting is believed to be due to the formation of CSH phase. The coexistence of CSH phase with the geopolymeric gel has been shown to improve the mechanical properties of the final product^[26]. The role of calcium sources such as Ground granulated blast furnace slag (GGBFS), cement, wollastonite (CaSiO₃) and Ca(OH)₂ on mechanical properties of metakaolin geopolymer is reported elsewhere^[28]. Specifically, the effects of different calcium silicate sources on geopolymerisation seems to be highly dependent on the crystallinity and thermal history of the calcium silicate sources, as well as the alkalinity of the

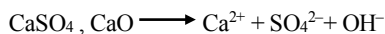
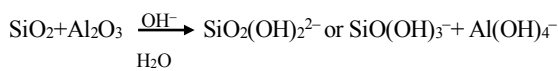
alkaline activator.

The key difference in high calcium based systems is the availability of Ca²⁺ ions arising from dissolution of CaSO₄ and CaO phases. Hence, during the setting process, and considering the Na₂O–SiO₂–Al₂O₃–CaO–H₂O system as a whole, the dissolution-precipitation reactions and hence the stable equilibrium phase assemblages involving these oxides have been shown to mainly depend on the pH of the medium and oxide concentration^[29]. The initial reaction pathway is typically governed by the CSH, CASH or NASH gel formation process. It has been shown that at high pH (>12) and with certain amount of CaO, Al₂O₃ and SiO₂, the presence of calcium degrades NASH in favour of CASH or (NC)ASH formation.

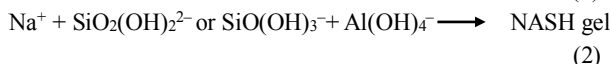
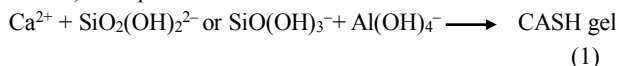
Fast dissolution of highly active Al₂O₃ and SiO₂ sources in high pH medium provides high initial concentrations of silicate (SiO₂(OH)₂²⁻ or SiO(OH)₃⁻) and aluminate (Al(OH)₄⁻) to react with Ca²⁺ forming CASH phase resulting shorter setting times. Therefore, increase in both SiO₂ and Al₂O₃ tend to decrease the setting time giving an optimum SiO₂/Al₂O₃ ratio for the longest setting time. The reaction between Ca²⁺ and aluminate, silicate species continues until all the available Ca²⁺ ions are exhausted and, with time, concentration of Ca²⁺ becomes the limiting factor for this reaction. The pH of the system also decreases with time, due to the consumption of OH⁻ during hydrolysis to further form silicate and aluminate species. The low pH and limited Ca²⁺ environment facilitate the polymerization reaction between silicate and aluminate species producing NASH gel.

Possible dissolution-precipitation reactions occurring during setting and hardening processes of high calcium based systems are proposed as follows;

1) Dissolution of SiO₂, Al₂O₃ and calcium sources (CaSO₄ & CaO).



2) Precipitation reactions



As CASH gel is stable at high pH (>12) environments and reaction 1 is dominant in the setting process whereas reaction 2 becomes feasible at lower pH (9–12) where NASH is stable. Therefore reaction 2 becomes secondary in these systems with mainly responsible for strength development.

4 Conclusions

1) XRD traces reveal initiation of crystalline phases at 210 days with the microstructure dominated by the presence of zeolitic phases such as zeolite A, zeolite P and faujasite. It is apparent that low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios (≈ 2.5) tend to develop zeolitic phases

2) Synchrotron XRD patterns, in agreement conventional XRD, reveal a number of crystalline phase developments. Most importantly, Synchrotron XRD analysis was able to detect nano-crystalline phases embedded in the gel that were not detectable by conventional XRD analysis.

3) In calcium based systems, at high pH (>12) and with limited amounts of CaO , Al_2O_3 and SiO_2 , the presence of calcium degrades NASH in favour of CASH or (NC)ASH formation. The reaction is characterised by dissolution of highly active Al_2O_3 and SiO_2 sources providing high initial concentrations of silicate ($\text{SiO}_2(\text{OH})_2^{2-}$ or $\text{SiO}(\text{OH})_3^-$) and aluminate ($\text{Al}(\text{OH})_4^-$) to react with Ca^{+2} forming CASH phase resulting shorter setting times. Therefore, increase in both SiO_2 and Al_2O_3 tend to decrease the setting time giving an optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the longest setting time.

4) In both, non – calcium and calcium based, systems the strength development is linked to the formation of NASH phase.

5) For non-calcium systems, decreasing of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (or increasing Al_2O_3) favours higher strengths reaching a maximum at around $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 3.50 and remains constant thereafter. There is an optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (3.20–3.70) which leads to products with longest setting time with reasonably high strengths. A similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ appears to be giving best performed systems for calcium based systems.

6) The general acceptance of the amorphous nature, hence the long term stability, of the geopolymer phases associated with optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios needs further investigation.

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