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Medium-term phase stability of $Na_2O–Al_2O_3–SiO_2–H_2O$ geopolymer systems

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Abstract

The phase evolution and microstructural development of a series of geopolymer mixtures comprising SiO_2, Al_2O_3, Na_2O and H_2O prepared by alkali reaction of metakaolin, have been studied. The study also included the effects of cure duration and its impact on physical properties such as compressive strength. The characteristic molar ratios of the geopolymer mixtures were of the range SiO_2/Al_2O_3 [2.50–5.01] and Al_2O_3/Na_2O [0.60–1.70], respectively. The formulations were subjected to continuous curing at 40 °C for 7 months, and were analyzed periodically by XRD and SEM techniques.

Amorphous Na–Al–Si phase(s), observed at early ages, gradually transformed to crystalline phase(s) with prolonged curing. The initial SiO_2, Na_2O, and Al_2O_3 contents of mixtures appeared to be critical factors governing the observed amorphous → crystalline transformation. Well-developed crystalline zeolitic phases, including chabazite, faujasite, zeolite A and zeolite P, were identified in some of the mixtures investigated. In most cases, with prolonged curing, some correlation emerged relating compressive strength development with corresponding phase changes. In essence, the mixture formulations that developed crystalline phases after prolonged curing tended to produce low strengths. The relevance of these findings on the phase development of mild- to warm-temperature prolonged curing of geopolymer systems is discussed.

Keywords: Metakaolin geopolymers; Acceleration; Microstructure; Phase stability; Strength

1. Introduction

Inorganic polymerization of Al_2O_3- and SiO_2-containing materials in strong alkali environments often results in products generally referred to as “geopolymers” [1]. The basic process of geopolymerization can be, in many ways, similar to the formation of zeolites, as both processes involve the dissolution of solid reactants, hydrolysis of the dissolved species and condensation of the gel phase. Furthermore, because both starting materials as well as the conditions of synthesis are similar, some classes of geopolymers can be broadly regarded as similar to zeolites in chemical composition [2,3]. However, a key difference between zeolites and geopolymers is their respective relative levels of matrix phase crystallinity [2]. The geopolymer phase is typically “X-ray amorphous” in contrast to the well-developed crystalline structures of zeolites. The structural differences make these two classes of materials suitable for different applications [1,2]. From a thermodynamic viewpoint, geopolymer phases can be considered as metastable with respect to zeolites [4].

The presence of nanocrystalline particles, which have been identified as zeolitic structures, embedded in the geopolymer gel has been reported [5–7]. 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 $CaO–Al_2O_3–SiO_2$ 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 [8,9]. Similar changes may also be expected to occur in hydrated $Na_2O–Al_2O_3–SiO_2$ systems.

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It has been postulated that the degree of crystallization in geopolymer systems is largely related to the system formulation and conditions of synthesis [5]. In geopolymer or zeolite formation, a number of factors seem to control the chemistry and nature of the final product. For instance, higher temperatures (≥100 °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 [9–11]. It is believed that the reaction rate is substantially faster for geopolymer formation [2,11,12], which results in amorphous or semi-crystalline matrices compared to highly crystalline and more ordered zeolite structures. Traditionally, the zeolite synthesis route involves an "aging time" (time between mixing and curing at high temperature) [10], and that this period assists aluminate and silicate species to rearrange in some orderly manner in the gel phase.

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 Na_2O–Al_2O_3–SiO_2 systems [3–6,13–15]. In alkali-activated fly ash systems, the formation of zeolite P and chabazite has been shown to be favoured by the presence of Na^+ rather than K^+ ions [13,15]. Silica-rich fly ashes, activated by NaOH, are reported to result in zeolite Na-P1 and/or hydroxysodalite phases [14]. In some studies, it was shown that alkali silicate activators tend to produce less or smaller crystals than alkali hydroxide activators [5]. When exposed to deionised water, sea water, Na_2SO_4 or acidic (H_2SO_4) solutions, amorphous or semi-crystalline geopolymer phases have been shown to crystallize into a zeolite material belonging to the faujasite family [6]. As indicated previously, it is also well established that the amount of water required in the synthesis of zeolites is typically much higher than that of geopolymers [10].

This work is aimed at investigating the effect of some key variables on the stability of hydrated Na_2O–Al_2O_3–SiO_2 systems using alkali-activated metakaolin systems. The variables chosen in this study are the Na_2O, Al_2O_3 and SiO_2 contents in the initial mixtures. A relatively warm-temperature cure, i.e. 40 °C, was selected for continuous curing of samples. Chemical and microstructural development of various formulations with slight variations in initial Na_2O, Al_2O_3 and SiO_2 contents were investigated with respect to their physical properties, in particular compressive strength. To consider practical implications, laboratory investigations into thermodynamic stability, phase transformations and the establishment of long-term stable phase assemblages should be carried out at ambient conditions. However, it is assumed that the lower curing temperature of 40 °C adopted in this study, does not significantly alter the basic chemical processes.

2. Materials and experimental

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 Grade N sodium silicate (8.9 wt.% Na_2O, 28.7 wt.% SiO_2, 62.5 wt.% H_2O) from PQ Australia were used as alkaline activators.

As shown in Table 1, three series of mixtures were prepared, with each set incorporating different Na_2O, SiO_2 or Al_2O_3 contents. Relatively low water contents representative of geopolymer synthesis were adopted. The amount of water in the mixtures was kept constant, except for admixture Na-07, which required a slightly higher amount to achieve good workability. Mixture compositions were chosen to cover typical SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ranges for metakaolin geopolymers reported in the literature, and to represent step changes in molar ratios.

Samples were identified according to the variable (Si, Na or Al) being tested, i.e. samples Si-38, Si-30 and Si-25 (Si series) assessed the effect of Si at constant concentrations of Na_2O, Al_2O_3 and H_2O. Similarly, samples Al-06, Al-10 and Al-12 (Al series) assessed the effect of Al at constant concentrations of Na_2O, SiO_2 and H_2O. Finally, samples Na-07, Na-10 and Na-14 (Na series) assessed the effect of Na at constant Al_2O_3, SiO_2 (water could not be considered as a constant factor). These initial mixture compositions and also the compositions of Na-zeolites that are known to be stable at low temperature (up to 100 °C), are shown by the Na_2O–Al_2O_3–SiO_2–H_2O compositional diagram in Fig. 1 (the diagram is a projection on the Na_2O–Al_2O_3–SiO_2 face and therefore does not show water content).

The water content in each system included the total water content derived 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 moisture loss. Specimens were subsequently

Table 1
Mix formulations

Sample	Initial composition	SiO_2 (moles)	Al_2O_3 (moles)	Na_2O (moles)	SiO_2/Al_2O_3 (molar ratio)	Al_2O_3/Na_2O (molar ratio)	SiO_2/Na_2O (molar ratio)
Si-38	$1.0Na_2O·1.0Al_2O_3·3.8SiO_2·13.6H_2O$	3.81	1.0	1.0	3.81	1.00	3.80
Si-30	$1.0Na_2O·1.0Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	1.0	1.0	3.00	1.00	3.00
Si-25	$1.0Na_2O·1.0Al_2O_3·2.5SiO_2·13.6H_2O$	2.50	1.0	1.0	2.50	1.00	2.50
Al-06	$1.0Na_2O·0.6Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	0.6	1.0	5.01	0.60	3.00
Al-10	$1.0Na_2O·1.0Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	1.0	1.0	3.00	1.00	3.00
Al-12	$1.0Na_2O·1.2Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	1.2	1.0	2.50	1.20	3.00
Na-07	$0.7Na_2O·1.0Al_2O_3·3.0SiO_2·16.3H_2O$	3.00	1.0	0.7	3.00	1.70	4.28
Na-10	$1.0Na_2O·1.0Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	1.0	1.0	3.00	1.20	3.00
Na-14	$1.4Na_2O·1.0Al_2O_3·3.0SiO_2·13.6H_2O$	3.00	1.0	1.4	3.00	0.86	2.14

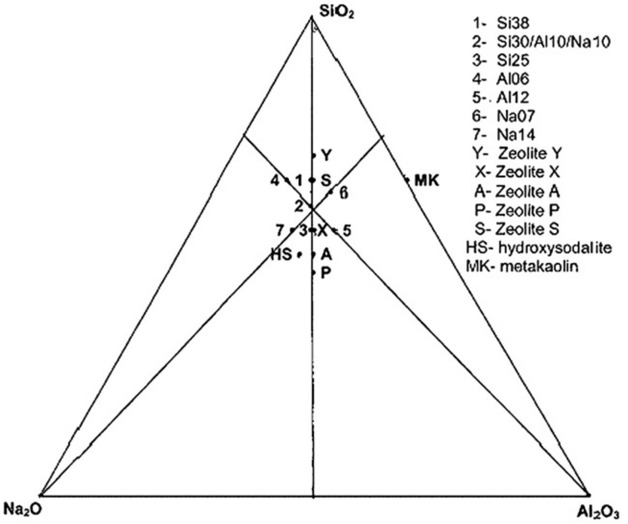

Fig. 1. Na_2O–SiO_2–Al_2O_3–H_2O compositional diagram showing initial mixture compositions and zeolite compositions.

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 placed in sealed polythene bags for rest of the curing period. Samples were tested for compressive strength, using Instron testing machine, at different curing times (3, 53 and 210 days). 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.

The development of microstructure and geopolymer phases was observed by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). Ground, powder samples were used in XRD analysis. Fracture samples, (dried under vacuum) coated with gold were used in the SEM study, and compositional analysis of phases was carried out using energy dispersive X-ray analysis (EDAX).

3. Results

3.1. Compressive strength development

Plots of compressive strength development with curing time of mixtures are shown in Fig. 2. There were clear differences in the strength development trends. At 3 days, mixtures Si-30 (or Al-10 or Na-10), Si-38 and Na-07 possessed higher strengths than the others, and their strength continued to increase with further curing up to 53 days, and remained almost constant thereafter. However, it should be noted that even though the patterns are similar, the magnitude of strength of these three mixtures with curing differs, following a decreasing order of Na-07 > Si-38 > Si-30.

Among the other compositions, Al-12, Na-14 and Si-25 initially attained very low strengths, which remained low throughout the curing period, except for Si-25, which showed a slight strength increase after 53 days. As can be seen in Fig. 2, the strength of mixture Al-06 was in the middle range at 3 days, but it decreased drastically with prolonged curing. Therefore, based on the strength development data, the mixtures can be categorized into two main groups: Na-07, Si-38 and Si-30 as the “high strength” group, and the rest of the mixtures as the “low strength” group.

To a certain extent, the pattern of strength development can also be analyzed according to the compositional variations of

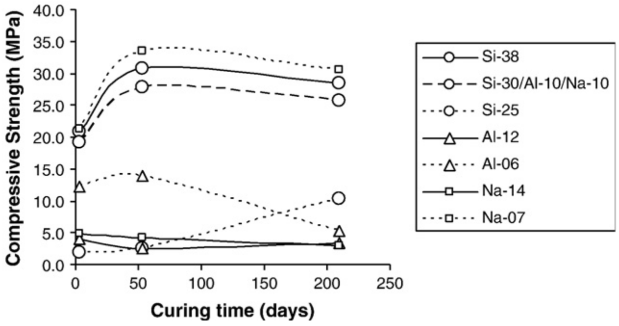

Fig. 2. Compressive strength development with curing time.

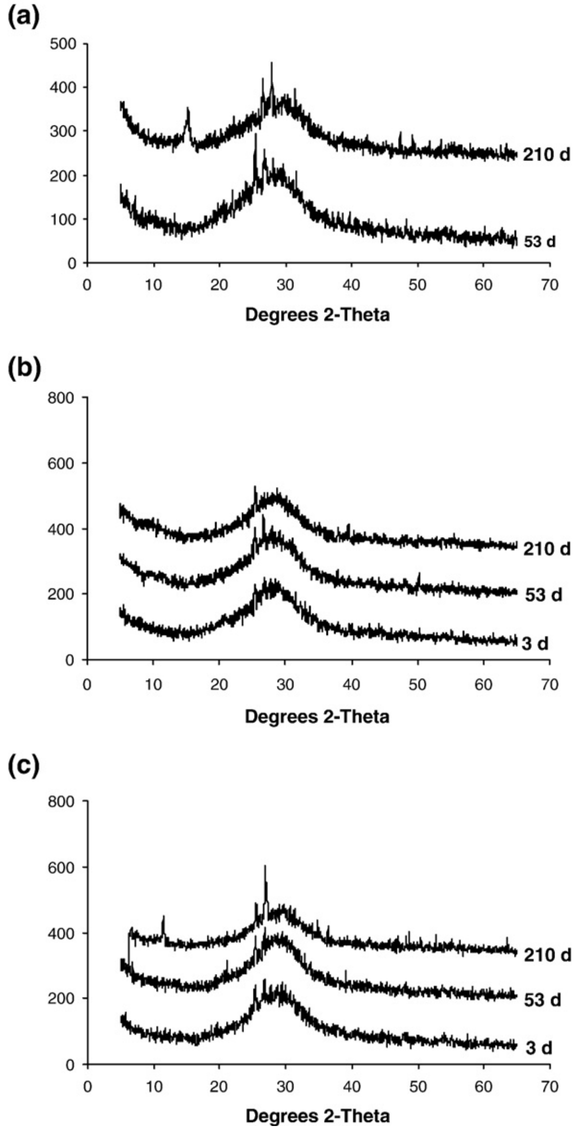

Fig. 3. XRD patterns of mixtures (a) Na-07, (b) Si-38 and (c) Si-30 at different curing intervals.

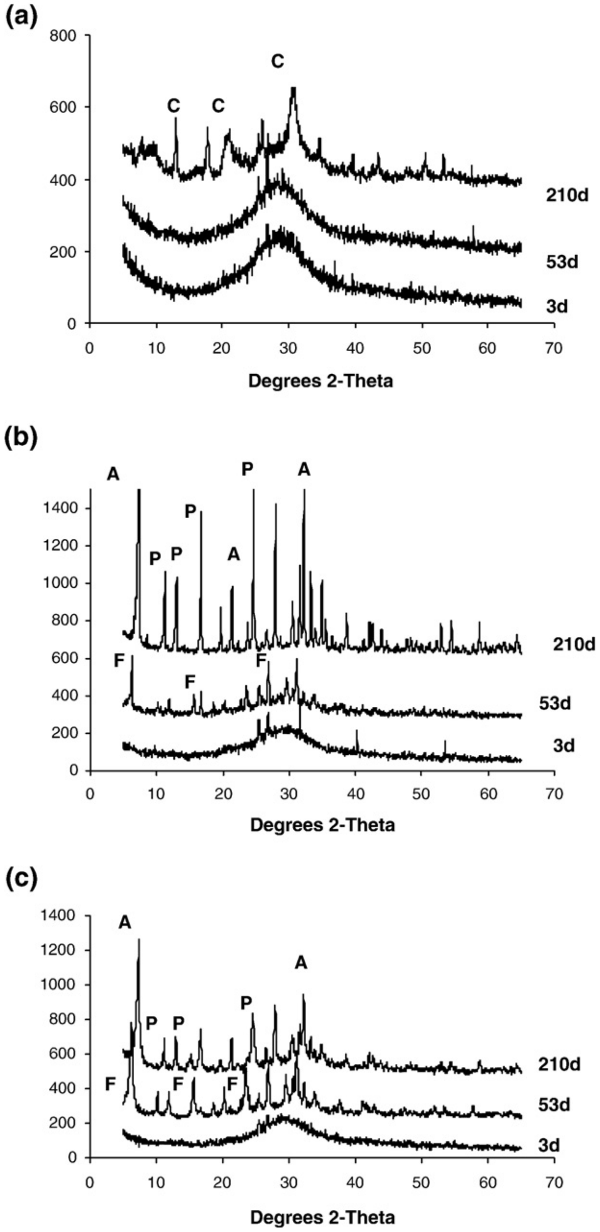

Fig. 4. XRD patterns of mixtures (a) Al-06, (b) Si-25 and (c) Na-14 at different curing intervals (A= zeolite A, P = zeolite P, F = faujasite, C = chabazite).

these mixtures. In the Si series, an increase in the initial SiO_2 content appeared to favour the observed strength characteristics, giving increasing strength order of Si-25 < Si-30 < Si-38. On the other hand, as shown by the Na series, higher initial Na_2O contents tended to decrease strength for all curing durations; in the decreasing order of Na-07 > Na-10 > Na-14. While it is difficult to draw a clear trend of strength variation in the Al series with curing, as both Al-06 and Al-12 possessed very low strengths at 210 days, the relative strengths decrease in the order of Al-10 > Al-06 > Al-12.

3.2. Solid phase development by XRD

The XRD patterns of mixtures Na-07, Si-38 and Si-30 at different curing intervals are shown in Fig. 3(a), (b) and (c) respectively. All three mixtures predominantly consisted of an amorphous phase corresponding to geopolymers with a broad band around 28° 2-theta. This phase dominated and seemed to be stable throughout the cure duration. However, it may be worthwhile noting that for mixture Si-30 (Fig. 3(c)), the height of this broad band was somewhat lower at 210 days when compared with that at 3 or 53 days.

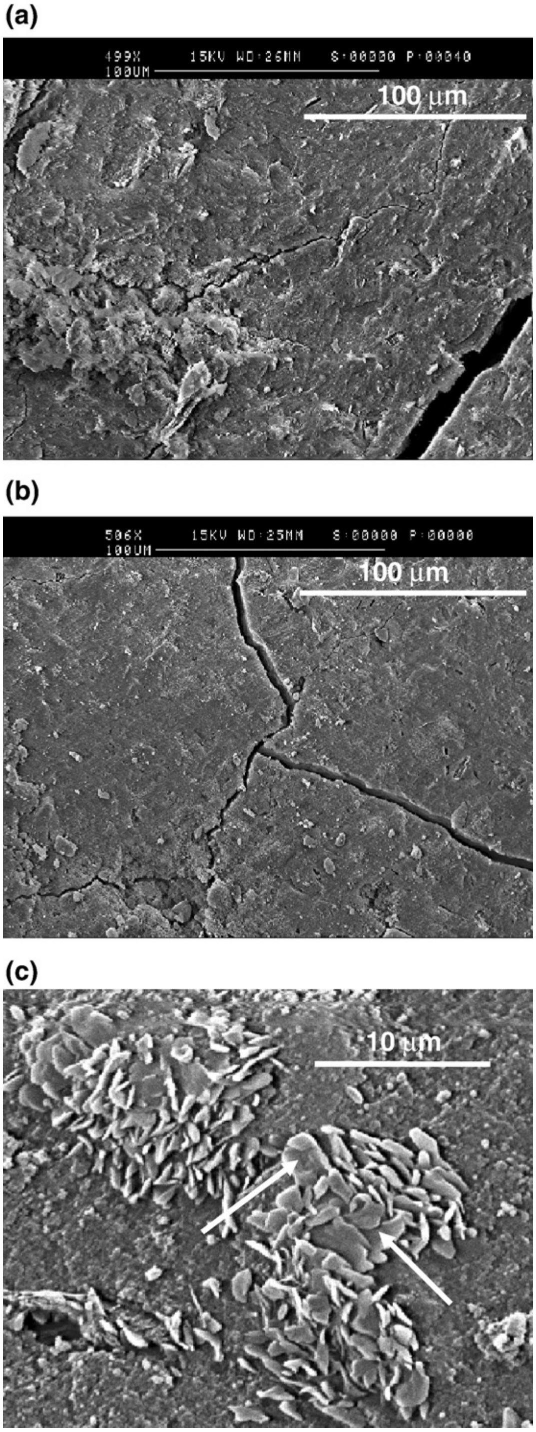

Fig. 5. SEMs of fracture surfaces of samples at 210 days curing: (a) Na-07, (b) Si-30; (c) higher magnification of Si-30 sample in Fig. 5(b) showing crystal growth embedded in the amorphous phase (arrows show the areas used for EDAX analysis).

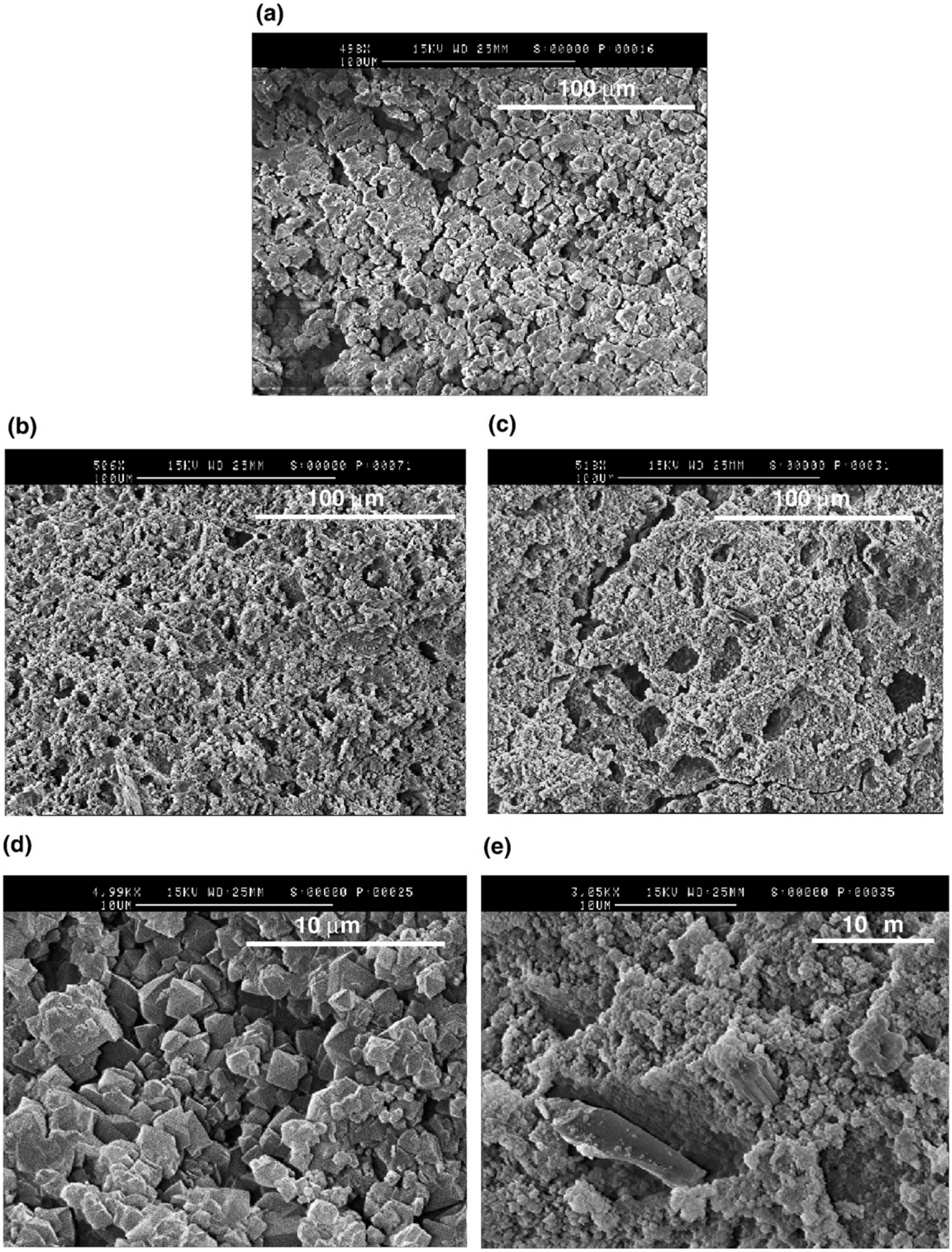

Fig. 6. SEMs of fracture surfaces of samples at 210 days curing: (a) Al-06; (b) Si-25; (c) Na-14; (d) higher magnification of Si-25 sample shown in Fig. 6(b) showing zeolite crystals; and (e) higher magnification of Na-14 sample shown in Fig. 6(c) showing zeolite crystals.

Fig. 4(a), (b) and (c) present the XRD patterns of mixtures Al-06, Si-25 and Na-14 respectively. Up to 53 days, mixture Al-06 was characterized by the presence of an amorphous phase, but clear transformation to crystalline phase(s) occurred with further curing. The crystalline phase present at 210 days was identified as a chabazite-like zeolite phase. The amorphous → crystalline phase transformation that occurred in this sample between 53 and 210 days corresponds with the observed strength reduction during this same period (see Fig. 2).

Mixtures Si-25 and Na-14 (Fig. 4(b) and (c)) seemed to produce very similar phase development patterns with prolonged curing. At 3 days, both samples were dominated by the presence of an amorphous phase with a broad peak around 28° 2-theta. At 53 days, a crystalline phase appeared with peaks corresponding to faujasite (zeolite X), which gradually transferred to another crystalline phase(s) by 210 days. These phases have been identified as zeolite A and zeolite P [16]. These crystalline phases seemed to be more developed in Si-25 than in Na-14. As far as strength is concerned, Si-25 showed some strength improvement at later stages, but the overall strength of both these samples fell under the "low strength" category. (The XRD patterns of mixture Al-12 at different curing intervals were very similar to those of Si-25 and Na-14, and are therefore not presented.)

From the data presented, a tentative relationship between phase transformation and strength characteristics can be loosely established. The systems that showed little or no evidence of amorphous → crystalline transformation (Si-38 and Na-07) had reasonably high strengths, which were maintained throughout the cure duration. Si-30 underwent a slight phase transformation and a corresponding decline in strength after prolonged curing. The rest of the mixtures that showed clear transformation of amorphous to crystalline phases possessed low strengths throughout the monitored curing regime.

3.3. Microstructure development

Microstructural observations by SEM were very much consistent with the phase transformations observed by XRD. At 210 days of curing, the microstructures of mixtures Na-07, Si-38 and Si-30 were characterized by dense and homogeneous phases (Fig. 5(a) and (b)), which accounted for their high strengths. However, a detailed examination (at higher magnification) of the amorphous-looking phases revealed that, especially in mixture Si-30, there were embedded pockets of crystalline growths (Fig. 5(c)). EDAX analysis showed that this crystalline phase contained Na, Al and Si at an Si:Al molar ratio of 1.75:1. XRD analysis did not clearly show the presence of crystalline phase(s) in the Si-30 sample, but EDAX analysis confirmed that after prolonged curing, the crystalline phase seen in mixture Si-30 was high in Si. It is worth recalling that all three mixtures were in the "high strength" category, but with magnitude of strength in the order of Na-07 > Si-38 > Si-30. Therefore, it is conceivable that the low strength associated with Si-30 was linked to the appearance of small pockets of crystalline phase(s) in this mixture with prolonged curing.

Fig. 6(a), (b) and (c) show SEM images of samples Al-06, Si-25 and Na-14, at 210 days curing, respectively. Compared with the dense, homogeneous microstructures previously described (Fig. 5(a) and (b)), these seemed to have porous microstructures, which possibly explains the observed low strengths in these samples. The EDAX analysis of crystalline grains present in Al-06 contain Na, Al and Si, with an Si:Al ratio of about 2.5, which may represent the partially developed chabazite-like crystal phase identified by XRD. The microstructures of Na-14 and Si-25 had a similar web-like appearance, but with Na-14 being slightly more porous. Fig. 6(d) and (e) show higher magnifications of the crystal phases of the Si-25 and Na-14 samples shown in Fig. 6(b) and (c) respectively. The Si-25 sample was dominated by well-developed cubic crystals (most likely zeolite P), but the crystalline phase(s) present in the Na-14 sample were not as developed. This was in agreement with XRD data, where it was shown that even though both Si-25 and Na-14 contained similar crystalline phase(s), such phases were more developed in Si-25 than in Na-14. This perhaps provides some explanation as to why somewhat higher strengths were observed in Si-25 compared to Na-14.

4. Discussion

The present study reasonably demonstrates how relatively small variations in initial molar concentrations of Na_2O, SiO_2 or Al_2O_3 in a geopolymer system can dramatically change its long-term properties, due to various phase transformations taking place within the system when subjected to prolonged warm-temperature curing conditions. Given the curing temperature used in the study, 40 °C, the findings can be relevant to the practical phase development of geopolymer systems under initial prolonged exposure to mild temperatures and high humidity levels.

Irrespective of initial molar ratios of ingredients in the range investigated, the reaction between Na_2O, SiO_2, Al_2O_3 and water always produced a precursor amorphous phase. The susceptibility of this amorphous phase towards crystallization, depends on various factors and, as also confirmed by this study, initial mix formulation remains a key parameter [3,13,14]. From the phase development observed in the Na series in this study, it is evident that increasing the initial Na_2O content tended to promote Na_2O–Al_2O_3–SiO_2–H_2O amorphous phase(s) that were vulnerable to crystallization. Accordingly, zeolitic phases were identified in the most alkaline mixture used in the series, i.e. Na-14.

According to the phase development patterns observed in the Si series reported here, decreasing the SiO_2 content in the initial mixture formulation favoured and also accelerated the amorphous → crystalline transformation. Well-developed zeolitic phases were detected in mixture Si-25 ($SiO_2/Al_2O_3 = 2.5$) even at 53 days of curing compared with Si-38, which has an SiO_2/Al_2O_3 molar ratio of 3.8. However, in the Al series, both mixtures with initial high (Al-12, $SiO_2/Al_2O_3 = 2.5$) and low (Al-06, $SiO_2/Al_2O_3 = 5.0$) Al_2O_3 contents respectively, showed susceptibility to crystallization. Thus, there appears to be a maximum SiO_2/Al_2O_3 ratio of around 3.8 at which a stable amorphous phase forms, with no tendency towards phase transformation, at least for the curing period and conditions investigated in the present study.

Due to the differences in initial phase compositions, starting materials and curing regimes, it is hard to compare the results of this study directly with those of conventionally treated systems (curing temperature 80 °C or more). However some similarities can be drawn; as shown in this study, the formation of zeolitic phases in higher alkaline mixtures has also been reported at higher curing temperatures (80 °C) with both fly ash and metakaolin based systems [3,10]. In addition, in agreement with current findings, metakaolin systems with SiO_2/Al_2O_3 molar ratios of around 3.8 (with $Na_2O/Al_2O_3 = 1$), cured at higher temperatures (80 °C) have been previously shown to produce geopolymer products with good properties [7,17]. There is also evidence for the development of crystalline phases in metakaolin geopolymer systems with low SiO_2/Al_2O_3 molar ratios (0.25), at 80 °C curing, resulting low-strength products [7,17].

Interestingly, the chemical compositions of the zeolites identified in this study fall within the area of the $Na_2O–Al_2O_3–SiO_2–H_2O$ compositional diagram investigated. It is known that zeolites A, X, P, R, S, Y and HS can all be synthesized at low temperatures (20–100 °C) using alkali-activated metakaolin systems [10]. Therefore, the formation and detection of these zeolitic phases in the mixtures studied is not surprising. Among these, zeolites X and A have shown to be metastable with respect to zeolite P [10,18]. The nucleation of secondary zeolite phases occurs as the result of the rearrangement and decomposition of the lattice of primary crystals. In the present study too, with time, the metastable faujasite-type zeolites formed in high Al_2O_3 or high Na_2O mixtures transformed to the more stable zeolite P phase.

In addition, both curing temperature and cure duration appear to have played a very important role in controlling the chemistry (mainly composition and crystallinity) of the final products. As the reactions were slow at 40 °C, it is possible that there was enough time for the orientation and localization of zeolite nuclei within the gel (amorphous phase). If this was the case, all systems studied should have formed crystals at some stage during curing. Perhaps the time period investigated in this study, i.e. 210 days, was insufficient to draw firm conclusions on this and is worth further investigation.

It is also apparent from the study that in the hydrated $Na_2O–Al_2O_3–SiO_2$ systems, in order to achieve a thermodynamically stable state, various phase transformations occurred. The initial mixture formulations and perhaps the curing temperature seemed to control these transformations. These phase changing phenomena, to a certain extent, can be compared with that occurring in hydrated $CaO–Al_2O_3–SiO_2$ (Portland and blended cement) systems. It has been shown that in $Ca(OH)_2$-activated fly ash or metakaolin systems, depending on the initial mixture contents, the $CaO–Al_2O_3–SiO_2–H_2O$ gels formed tend to produce zeolitic phases, such as gismondine, after prolonged curing [8,9]. This was especially attributed to systems with low initial CaO contents.

Strength development and phase transformation of the systems investigated in this study appeared to be broadly linked. Systems that favoured the formation of zeolitic products tended to possess lower strengths for the range of system chemistry and parameters investigated. It is possible that phase transformations are associated with volume changes. Therefore, the porosity and dimensional changes in the systems studied merit future investigations.

5. Conclusions

Following conclusions can be made from this study.

1. In $Na_2O–Al_2O_3–SiO_2–H_2O$ systems, amorphous → crystalline phase transformations are feasible at temperatures as low as 40 °C and high RH.
2. The initial molar contents of Na_2O, Al_2O_3 and SiO_2 were shown to play a key part in controlling the above phase transitions. In particular, SiO_2/Al_2O_3 molar ratios lower or higher than 3.8 and increasing the Na_2O content tended to favour this transformation. Zeolite phases belonging to the faujasite group, as well as zeolite X, A, P and chabazite types were identified in these mixtures.
3. Based on this study, a tentative link between phase transformation/stability and strength characteristics can be drawn. Systems that favoured the formation of zeolitic products tended to possess lower strengths.

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