The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers

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Abstract

Statistical analysis of a systematic series of geopolymers with varying alkali type (sodium and potassium) and Si/Al ratio after 7 and 28 days ageing has been used as a basis for observing the development of mechanical properties with time. Minimal change in the compressive strength of specimens was generally observed in specimens of different alkali or between 7 and 28 days of ageing. However, mixed-alkali specimens with high Si/Al ratio exhibited significant increases in strength, while pure alkali specimens displayed decreased strength. The development of Young’s modulus of geopolymers between 7 and 28 days was observed to be dependent on alkali, with the Young’s moduli of Na-specimens decreasing at low Si/Al ratio, but increasing at high Si/Al ratio, while K-specimens exhibited the opposite effect. Mixed-alkali specimens all exhibited nominal change in Young’s moduli, without any significant effect of Si/Al ratio being observed.

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1. Introduction

Geopolymeric materials are usually synthesised using activating solutions based on the alkalis of sodium and potassium. These two elements are able to form highly concentrated aqueous solutions and solvate large amounts of silicon and aluminium, both of which are critical for geopolymerisation. Geopolymeric materials synthesised with different alkali cations exhibit marked differences in Si/Al ordering [1,2], thermal stability [3–5] and setting properties [6]. To some extent, the effect of alkali cation on the mechanical properties of geopolymers has been observed [6–9]. Despite the apparent effects of alkali, there has been no systematic investigation to determine the extent to which alkali type will affect the development of the mechanical properties of geopolymers.

The molecular structure of geopolymers is described by $^{27}$Al and $^{29}$Si NMR spectroscopy as a matrix of alumina and silica tetrahedra joined at the corners with oxygen. Alkali cations are associated with aluminium, where the AlO$_4$ groups have a single negative charge due to aluminium(III) being in tetrahedral co-ordination. A study of the effect of alkali cations (sodium and potassium) on the molecular ordering of the geopolymer gel concluded that the concentration of silicon in the activating solution plays a large role in aiding the incorporation of aluminium into the matrix via solution phase speciation with silicon [1]. Similarly, the nature of the alkali cation also contributes to the level of reaction of the solid aluminosilicate source, as well as the level of aluminium incorporation [1]. Potassium was found to promote a greater degree of reaction of metakaolin, and a higher degree of aluminium incorporation compared to sodium and mixed-alkali (1:1) systems [1]. $^{29}$Si MAS-NMR has been used to determine the molecular structure of the geopolymer gel synthesised with different alkali cations [2]. It has been shown that geopolymers synthesised with potassium possess a lesser degree of Si/Al ordering than those of mixed-alkali (1:1) or sodium systems, respectively. The thermodynamic basis for the increased ordering of the gel with smaller cations has been described elsewhere [10]. The differences in molecular structure of geopolymeric gels based on different cations should result in some differences in the development of mechanical properties. However, the degree to which the small differences in structure described above will affect gel properties is unknown.
It is well known that the concentration of silicon in the activating solution of geopolymers has a significant effect on compressive strength [11]. The effect of the concentration of silicon in the alkali activating solution has been investigated on systems utilising both fly-ash [12,13] and metakaolin [11,14] as solid aluminosilicate sources. Furthermore, the relationship between geopolymer composition, microstructure and mechanical properties has recently been conducted by the study of geopolymers synthesised from metakaolin with composition Na(SiO2)·AlO2·5.5H2O, where 1.15 ≤ z ≤ 2.15 [14]. It was observed that there is a large increase in the compressive strength of geopolymers formed from metakaolin by addition of large quantities of silicon in a sodium-based alkali activating solution. The improvement in mechanical properties correlated with the increase in the volume of geopolymeric gel at a relatively constant nominal density, resulting in a more homogenous microstructure. The change in microstructure was linked to the chemical processes occurring in the solution phase during reaction. It is known that geopolymers based on different alkali cation exhibit structural differences [1,2,15]. Furthermore, differences in viscosity, lability and speciation in alkali silicate solutions with different cations may result in alteration of the processes occurring during reaction, which will manifest as differences in the development of microstructure and mechanical properties.

Though not explicitly stated in the study of mechanical properties, it has often been assumed or neglected that the properties of geopolymers are not strictly deterministic. Every material has inherent uncertainty in mechanical and chemical parameters, generally described by a distribution type or distribution variable, which form the basis of our understanding of the reliability of materials. It has been noted in the previous investigation of the mechanical properties of metakaolin-based geopolymers [14], that the error associated with the measurement of compressive strength was subject to variation with Si/Al ratio. However, the variation in mechanical strengths was not readily linked to either composition, or constant fraction of mechanical strength. The effect of composition on reliability and variance of mechanical properties has never been explicitly investigated in geopolymeric materials, and may provide another measure of material character from which to differentiate specimens of similar mean mechanical properties. In order to gauge the variance of mechanical properties, modest sample populations are required to provide meaningful mean and variance values. Therefore, the number of specimens of each composition prepared for analysis in the current work will allow for a degree of freedom sufficient for statistical analysis of sample populations by T- and F-tests, which are able to measure the significance of differences in both the mean mechanical strength and standard deviation of two sample populations.

The current work presents a systematic statistical study of the development of the mechanical properties of geopolymers between 7 and 28 days with composition (NaK)·(SiO2)·AlO2·5.5H2O, where 0 ≤ y ≤ 1 and 1.15 ≤ z ≤ 2.15, correlated to their microstructure, porosity and molecular structure. The statistical significance of 7-day mechanical properties is discussed in detail to serve as a basis of comparison with 28-day values. The effect of different alkali on the development of axial compressive strength, Young’s modulus, and microstructure will then be discussed. Differences in the development of mechanical properties are expected to manifest themselves as changes in gel structure, such as skeletal density, degree of reactivity, or changes in microstructure.

2. Experimental methods

2.1. Materials

Metakaolin was purchased under the brand name of Metastar 402 from Imerys Minerals, UK. The metakaolin contained a small quantity of a high temperature form of muscovite (PDF 46,0741) as impurity. The chemical composition of metakaolin determined by X-ray fluorescence (XRF) was 2.3-SiO2/Al2O3. The Brunauer–Emmett–Teller (BET) surface area [16] of the metakaolin, as determined by nitrogen adsorption on a Micromeritics ASAP2000 instrument, was 12.7 m²/g, and the mean particle size (d50) was 1.58 μm.

Sodium silicate solutions with composition SiO2/M2O = R = 0.0, 0.5, 1.0, 1.5 and 2.0, Na/[Na + K] = A = 0.00, 0.25, 0.50, 0.75 and 1.00, and H2O/Na2O = 11 were prepared by dissolving amorphous silica (Cabosil M5, 99.8% SiO2) in appropriate alkali hydroxide solutions until clear. Solutions were stored for a minimum of 24 h prior to use to allow equilibration. Alkali hydroxide solutions were prepared by dissolution of KOH and NaOH pellets (Merck, 99.5%) in Milli-Q water, with all containers kept sealed wherever possible to minimise contamination by atmospheric carbonation.

2.2. Geopolymer synthesis

Geopolymer samples were prepared by mechanically mixing stoichiometric amounts of metakaolin and alkaline silicate solution to give Al2O3/M2O = 1, forming a homogenous slurry. After 15 min of mechanical mixing the slurry was vibrated for a further 15 min to remove entrained air before being transferred to Teflon moulds and sealed from the atmosphere. Samples were cured in a laboratory oven at 40°C and ambient pressure for 20 h before being transferred from moulds into sealed storage vessels. The samples were then maintained at ambient temperature and pressure until testing. Specimens were synthesised with different Si/Al ratio by use of the five different concentrations of alkali activator solutions, R = 0.0, 0.5, 1.0, 1.5 and 2.0 with each of the five alkali ratios, A = 0.00, 0.25, 0.50, 0.75 and 1.00. This resulted in 25 different sample compositions with nominal chemical composition NaK·(SiO2)·AlO2·5.5H2O, where y was 0.00, 0.25, 0.50, 0.75 and 1.00 and z was 1.15, 1.40, 1.65, 1.90 and 2.15. For ease of discussion, the five alkali series will be referred to as Na, Na75, Na50, Na25 and K (i.e. no Na), representing each of the five alkali ratios, A = 1.00, 0.75, 0.50, 0.25 and 0.00, respectively.
2.3. Microstructural analysis

Microstructural analysis was performed using a Joel 2010 TEM. Specimens were polished using consecutively finer media, prior to final preparation using 1 μm diamond paste on cloth. Specimens (40 μm thick) were coated in gold and milled using a gallium ion beam (FEI xP200).

2.4. Compressive strength and density

Ultimate compressive strength and Young’s modulus were determined using an Instron Universal Testing Machine operated at a strain rate of 0.60 mm/min. Specimens were cylindrical, with an aspect ratio of 2 (25 mm in diameter; 50 mm in length). Specimen end surfaces were polished flat and parallel to avoid the requirement for capping. All values presented in the current work were an average of six samples, with error reported as standard deviation from mean. Nominal sample density was measured by averaging calculated density given by the weight of each of the six samples divided by their volume prior to compressive strength testing.

2.5. XRD analysis

XRD random powder diffractograms of geopolymer specimens were collected on a Philips PW 1800 diffractometer with Cu Kα radiation generated at 20 mA and 40 kV. Specimens were step scanned from 5 to 70° 2θ at 0.02° 2θ steps integrated at the rate of 4.0 s per step.

2.6. Statistical analysis

The significance of data may be determined by application of simple F- and T-tests, which test the hypothesis of two sample populations’ variance and mean being the same. If populations are shown to have unequal standard deviations using the F-test, then they need not be subjected to the T-test to determine if their mean strengths are equal. Eq. (1) represents the F-test, which is used to calculate the probability of the likelihood that two variances are the same.

\[
F = \frac{u_i^2}{u_j^2}
\]

where \(u_i\) is the larger of the two specimen population standard deviations being compared, and \(u_j\) is the lower. The more this ratio deviates from 1, the stronger the evidence for the hypothesis to be rejected, implying unequal population standard deviations. This F-value may be compared with \(F(\alpha)\), which is the critical value of the F-distribution with 2n – 2 degrees of freedom and a significance level of \(\alpha\). Here, \(n\) is 6, the number of samples of each composition, giving a degree of freedom (d.f.) of 10. The \(F(\alpha)\) values for different significance levels are shown in Table 1. If \(F > F_{\text{critical}}\) then the hypothesis that the groups of specimens have equal mean strengths is rejected.

Similarly, the T-test is used to determine if two population means are equal, and is defined by:

\[
T = \frac{\bar{u}_i - \bar{u}_j}{\sqrt{(u_i^2/n) + (u_j^2/n)}}
\]

where \(\bar{u}_i\) and \(\bar{u}_j\) are the mean strengths of two specimen populations. This T-value may be compared with \(T(\alpha)\), which is the critical value of the T-distribution, analogous to that of the F-distribution. The \(T(\alpha)\) values for different significance levels are shown in Table 1. If \(T > T_{\text{critical}}\) then the hypothesis that the groups of specimens have equal mean strengths is rejected.

3. Results and discussion

3.1. Effect of Si/Al ratio on compressive strength

Fig. 1 shows the compressive strengths of geopolymer specimens synthesised at five different Si/Al ratios from alkali solutions with five different alkali cation ratios. Some of these data incorporate values from a previous investigation [14]. It can be seen that the compressive strength of all alkali ratios (i.e. Na, Na75, Na50, Na25 and K) is increased as the Si/Al ratio increases from 1.15 to 1.90. A small decrease is observed in compressive strength in all series of specimens beyond Si/Al = 1.90. Specimens with different alkali composition exhibit similar compressive strengths at a given Si/Al ratio, suggesting that the difference in mechanical properties between specimens of different alkali mixture is in the order of 10–20%, which is typical for properties of chemically analogous glasses, where ionic diffusion is not involved [17]. Notably, K specimens were notionally stronger than Na specimens in the mid Si/Al region, where alkali effects have been observed previously [9]. However, this trend

![Fig. 1. Compressive strength of geopolymer specimens recorded at 7 days after preparation. Values for Na-specimens are taken from literature values [14].](image-url)
Table 2

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Values for pure sodium specimens are taken from literature values [14].

is not observed throughout the entire series, suggesting that the differences in the properties of different alkali materials are complex.

The standard deviation of the compressive strengths of the specimens in Fig. 1 are presented in Table 2, from which F- and T-tests were calculated. The F-value comparisons are not presented here, as only five of the 20 comparisons exhibited a confidence of >90% of having different standard deviations. Of these, each is also identified by T-test analysis below as exhibiting different mean compressive strengths. Fig. 2 shows the T-values for comparisons of the sample populations of geopolymer specimens of the equivalent alkali composition at different Si/Al ratio. It can be observed in Fig. 2 that 17 of the 20 population comparisons exhibit at least 95% confidence that their mean strength values are different. A confidence of at least 90% is associated with the specimen populations of sodium geopolymer with Si/Al ratios of 1.90 and 2.15 being different. The only population comparisons that do not exhibit a strong confidence of a difference in mean compressive strengths are those related to the three highest Si/Al ratio of the Na25 series. This will be explored later in this paper. It may otherwise be generalised that the compressive strength of geopolymers initially improves with increasing Si/Al ratio regardless of alkali composition, and that a decrease in compressive strength is observed above a Si/Al ratio of 1.90. Alkali composition does not appear to change the characteristic trends in compressive strength of geopolymers with an increase in Si/Al ratio.

3.2. Effect of Si/Al on Young’s modulus

The mean Young’s modulus of each geopolymer specimen investigated in the current work is presented in Fig. 3. It can be observed that the Young’s moduli of geopolymers increase for specimens with Si/Al ≤ 1.65, as observed for the mean compressive strengths in Fig. 1. However, beyond Si/Al ratio of 1.65, the Young’s moduli of geopolymers exhibit similar values, which has been observed previously for the sodium system [14]. There is a general trend in the decrease of Young’s modulus with increasing potassium content at low Si/Al ratio. However, at higher silica contents a maximum of Young’s modulus is recorded with mixed-alkali compositions (i.e. Si/Al ≥ 1.90).

The numerical values for the standard deviation of the Young’s moduli from which the T- and F-values were calculated are presented in Table 2. T-values, which present the greatest statistical differences between specimen populations comparing the Young’s moduli of geopolymer sample populations with different Si/Al ratio, are presented in Fig. 4. It can be seen that there is statistical certainty of at least 99.9% that geopolymer specimens with Si/Al ≤ 1.65 exhibit different Young’s moduli. The statistical certainty of the Young’s moduli is comparatively greater than the measured values of compressive strength in Fig. 2, implying that the Young’s modulus of the geopolymer specimens is more reliable than the compressive strength. The statistical significance of the Young’s moduli comparisons decreases for Si/Al > 1.65. The specimen populations with Si/Al ratios of 1.90 and 2.15 exhibit a weak correlation compared to Si/Al ≤ 1.65.
implying that there is a reduced likelihood of them being different, which is observed in the similarity of their values in Fig. 3. It is interesting that a clear maximum in compressive strength is observed in Fig. 1 with Si/Al ratio of 1.90, yet this is not necessarily so for Young’s modulus in Fig. 3 (i.e. Young’s modulus values for Si/Al > 1.65 are similar).

It has been shown previously that the relationship between the Si/Al ratio of Na-geopolymers and Young’s modulus is closely linked to the microstructure [14]. It can be observed in Fig. 4 that the statistical significance between sodium geopolymers only decreases to below 99.9% confidence when comparing Si/Al ≥ 1.65. The decrease in confidence that these values are different correlates with previous findings, that specimens with Si/Al ≥ 1.65 exhibit similar values for Young’s modulus. The comparisons of Young’s moduli for the potassium geopolymers exhibit a similar trend in decreasing statistical difference between the Young’s moduli of specimens with Si/Al > 1.65. However, the sample populations with mixed-alkali compositions (i.e. Na75, Na50, Na25) exhibit significant confidence that the Young’s moduli between the specimens with Si/Al ratios of 1.65 and 1.90 are different. This suggests that there is some interaction of mixed-alkali that changes the mechanical behaviour of these specimens. This will be discussed in the following sections. Despite the differences in behaviour at high Si/Al ratio, both measures display similar trends of rapid increase at low Si/Al ratio. Small differences are observed between the behaviour of the different alkali series, in particular the mixed-alkali specimens in the high Si/Al ratio region. At high Si/Al ratio, geopolymers in the current investigation appear to exhibit a small increase in compressive strength and Young’s modulus compared to the Na and K systems, which may be a result of mixed-alkali interactions.

3.3. Effect of alkali cation on compressive strength

It can be observed from Fig. 1 that the selection of different alkali compositions does have some effect on the compressive strength. At a Si/Al ratio of 1.15 there is general decrease in the compressive strength of geopolymers with a decrease in sodium content. In the compositional range of 1.40 ≤ Si/Al ≤ 1.90 there is a trend of the mixed-alkali compositions being generally stronger than either Na or K specimens. At the highest Si/Al ratio studied in the current investigation, there is no trend in alkali composition and strength that can be observed. By comparing the Na and K results presented in Fig. 1 it can be seen that the Na specimens are stronger at the Si/Al ratios of 1.15 and 2.15, but the K specimens exhibit a slightly higher compressive strength in the intermediate compositions. This suggests that the effect of alkali on compressive strength is varied across the Si/Al ratios investigated in the current work.

The results of the T-test comparisons at each of the five Si/Al ratios are presented in Fig. 5. Columns in Fig. 5 are marked with hatching, where the F-test identifies a significant difference between specimen populations based on standard deviation. At the Si/Al ratio of 1.15 (Fig. 5a), it is observed by the high T-values that any addition of potassium at this composition results in a definite change in mechanical properties of the specimens. While all specimens exhibit a strong confidence of having a different compressive strength to Na specimens, K specimens are less distinct from the mixed-alkali compositions. Small additions of potassium affect greatly the mechanical properties of these specimens. The large effect of potassium may be expected from the observation that potassium is preferentially incorporated into geopolymeric gels during formation [1] and that the compressive strength of potassium geopolymer is expected to be weaker at low Si/Al ratios due to lower levels of Al/Si ordering compared to sodium systems [10].

The compressive strength of K specimens with Si/Al ratio of 1.40 is greater than Na specimens (Fig. 1). The mixed-alkali specimens exhibit strengths in excess of the Na or K systems, which may be the result of a ‘mixed-alkali effect’ (MAE), with the maximum strength being observed in Na50 specimens. The low T-values in Fig. 5b imply there is a poor confidence in the suggestion that all but the Na specimens exhibit a different compressive strength to the potassium containing systems (i.e. Na75, Na50, Na25 and K). However, the F-test reveals that some mixed-alkali compositions exhibit different standard deviations to one another. Although the mean properties of the mixed-alkali specimens are similar, the variation in standard deviation suggests that alkali does have some effect on the structure, even if it is not reflected in the mean compressive strength.

It is more readily observed that there is an increase in the strengths of mixed-alkali specimens with Si/Al ratio of 1.65 (Fig. 1). Though consistently higher compressive strengths of mixed-alkali specimens can be observed in Fig. 1, the T-values (Fig. 5c) show that there is only a strong correlation suggesting that the Na specimens are significantly different to the mixed-alkali compositions. The T-values suggest there is some significance in the mixed-alkali specimens being stronger that the K specimens, the confidence of which is reduced from the Na75 and Na50 specimens to the Na25 specimens. The decrease in statistical confidence of differences in the mechanical behaviour of the mixed-alkali specimens compared to K specimens as the sodium content decreases (i.e. Na75 ≈ Na50 > Na25) implies that the MAE, which leads to the increase in observed strength, is somewhat reduced at high potassium content (i.e. Na75).
However, the low $T$-values of K specimen comparisons compared to the Na specimens comparisons imply that the MAE is greatly influenced by the inclusion of potassium. The very low $T$-values of the comparisons between mixed-alkali specimens imply their mechanical properties are very similar. This trend can also be observed to a lesser, but notable extent in the specimens with Si/Al ratio of 1.40 (Fig. 5b). The similar mechanical properties of all mixed-alkali specimens suggest that more than a simple mechanism of preferential incorporation of potassium is responsible for the differences in mechanical properties of these specimens. Molecular structure considerations would predict Na specimens being strongest, with a monotonic decrease with inclusion of potassium [2].

The Si/Al ratio of 1.90 consistently exhibits the highest compressive strength of specimens in this investigation, regardless of alkali composition (Fig. 1). The strengths of Na and K specimens appear similar at this composition, while the mixed-alkali specimens appear to exhibit higher compressive strengths, particularly those with proportionally higher sodium content (Fig. 1). However, the $T$-values in Fig. 5d are generally low, indicating that there is little statistical difference in the mean compressive properties of the specimens with Si/Al ratio of 1.90. This may be a result of $T$-values being heavily affected by the standard deviation of the sample populations. At Si/Al ratio of 1.90, the Na and K specimens exhibit a standard deviation in compressive strength two to four times that of the high sodium content mixed-alkali specimens (i.e. Na75, Na50). Only the specimens with the largest difference in mechanical properties, being the mixed-alkali specimens, exhibit a substantial confidence that their compressive strengths are different. However, the large variation in the standard deviation of these specimens in many of the comparisons exhibiting large $F$-values indicates that despite their similar mean strengths the specimens may indeed be different. These comparisons are marked on Fig. 5d with hatching.

The specimens with the highest Si/Al ratio cannot be separated by the $T$-test (Fig. 5e). The $F$-test reveals that the Na
and K specimens exhibit different standard deviations, suggesting that these two materials are different as also observed in specimens with Si/Al ratio of 1.90. All specimens with a Si/Al ratio of 2.15 have a compressive strength that can be statistically shown to be lower than specimens with Si/Al ratio of 1.90 (Fig. 2), yet also have the highest standard deviations of compressive strength (Table 2). The increase in standard deviation could be due to the effect of unreacted material, which has been discussed elsewhere [14]. The decrease in the magnitude of T-values in Fig. 5 as the Si/Al ratio increases may be expected from a combination of structural perspectives. The molecular structure of geopolymers is affected by alkali cations, particularly at low Si/Al ratio [1,2]. Potassium promotes a more disordered framework structure and a higher proportion of Al–O–Al linkages, which weakens the framework [1]. The effect of cation on the structure has also been observed to decrease as potassium in the specimen is replaced by sodium. The effect of alkali cations on the structure has also been shown to decrease as the Si/Al ratio increases, resulting in negligible difference in structure at the higher Si/Al ratio specimens investigated in the current work [1,10]. Therefore, the similarity in mechanical properties at high Si/Al ratio specimens, yet significantly higher strength of Na specimens at low Si/Al ratio may be understood by molecular structure considerations. The decrease in compressive strength of the highest Si/Al ratio specimens has been previously linked to the increase in unreacted material present in these specimens [1]. The general increase in standard deviation of the compressive strengths of specimens between Si/Al ratio of 1.90 and 2.15 observed in all series of alkali compositions, and the increase of unreacted material observed in these systems supports this reasoning. The high standard deviations in strength and the similar molecular structure clarify the resulting decrease of confidence in the difference of the compressive strength of the specimens as the Si/Al ratio increases. However, the increased strength of mixed-alkali specimens in the mid-Si/Al region cannot be understood by existing knowledge of geopolymer structure. The effect of alkali on the structure of polymeric materials appears to extend beyond simply molecular structure and Al/Si ordering considerations.

3.4. Effect of alkali cation on Young’s modulus

The trends observed in the Young’s moduli of geopolymers in Fig. 3 appear similar to those of compressive strength in Fig. 1. However, upon closer inspection there are some key differences. From Fig. 3 it can be observed that K specimens exhibit lower Young’s moduli than those of Na in the region 1.15 ≤ Si/Al ≤ 1.90, with K exhibiting a slightly greater value at the highest Si/Al ratio of 2.15. Values of Young’s moduli at a constant Si/Al ratio are generally within ±10%, suggesting that alkali effects are small as might be expected [18]. Similar trends are observed in the values of Young’s moduli of pure and mixed-alkali sodium and potassium glasses of analogous chemical composition [17–19]. However, the effect of Si/Al ratio on the Young’s moduli of geopolymeric materials in the current study is clearly not analogous to glasses. Therefore, the prima facie observation from a previous study that the Young’s modulus is more greatly determined by the microstructure than the chemical composition is supported [14]. A more detailed understanding of the trends on Young’s modulus can be observed from T-test values presented in Fig. 6. Results of the F-test do not add any additional information to the analysis of Young’s modulus and are not discussed.

The Young’s modulus values of geopolymers with a Si/Al ratio of 1.15 in Fig. 3 exhibit a mixed-alkali trend, typical of other aluminosilicates [18,19], with a minimum value observed at Na25. The Young’s modulus of Na is significantly higher than those of the other composition specimens. The significance of this difference is confirmed in Fig. 6a, where the comparisons between the Na and all other alkali compositions show greater than 99% confidence that this value is different to other compositions. The Na75 and Na50 specimens are observed to be different than the Na25 and K specimens with the highest potassium content. This trend contrasts with the compressive strength observations in Fig. 5, where all specimens with potassium exhibit similar strengths. Nonetheless, even small potassium concentrations significantly decrease the value of the Young’s modulus in geopolymers with Si/Al ratio of 1.15. This is consistent with the Young’s moduli of aluminosilicates increasing with field strength of the alkali cation [19].

Specimens with a Si/Al ratio of 1.40 exhibit a similar trend, whereby an increase in potassium content decreases the Young’s moduli of specimens (Fig. 3). However, Fig. 6b shows that the concentration of potassium required to effect a significant decrease in Young’s modulus is 50%. Furthermore, the magnitude of decrease is reduced in comparison to the specimens with Si/Al ratio of 1.15. The slight appearance of a negative MAE may still be observed (i.e. mixed-alkali composition exhibits lower value than the Na and K specimens), though this cannot be statistically confirmed as significant (Fig. 6b). At Si/Al ratio of 1.65, a monotonic decrease in Young’s modulus from Na to K specimens can be observed in Fig. 3. Similar to the specimens with Si/Al ratio of 1.40, the Na and Na75 specimens exhibit similar Young’s moduli, with the Na50, Na25 and K specimens observed to have similar, yet lower Young’s moduli. The significance of the correlation between the Na and Na75 specimens and the higher potassium content specimens is observed to reduce significantly between the Si/Al ratio of 1.40 and 1.65 (Fig. 6b and c). The decrease in the difference of the alkali effect in this compositional range suggests that the effect of different alkali on the Young’s modulus is reduced, but potassium content still significantly reduces the values recorded. This supports the understanding of geopolymer molecular structure and the preferential inclusion of potassium, as observed for compressive strength. Since the alkali acts in a charge balancing capacity with aluminium in geopolymers, it is not directly involved in the network structure. Therefore, as the Si/Al ratio increases, the affect of alkali on the properties is known to be reduced [2] and this is observed in the Young’s moduli in Fig. 3.

The values of the Young’s moduli at high Si/Al ratio exhibit similar values, as evidenced by their low T-values (Fig. 6d and e). The difficulty in observing differences between the Young’s moduli of specimens with high Si/Al ratio appears similar to that of compressive strengths discussed above, with increases
in standard deviation with Si/Al ratio being detrimental to the confidence of statistical analysis. At high Si/Al ratio the mixed-alkali specimens exhibit the highest Young’s moduli, with the K specimens exhibiting slightly higher values than the Na specimens, similar to compressive strength. These observations are not expected on purely compositional grounds [17] and may be a result of geopolymeric gel development at early ageing.

3.5. Mechanical properties of geopolymers at 28 days

It can be observed in the present investigation that the effect of alkali on the mechanical properties of a geopolymer is small but significant at 7 days after synthesis. However, it has been found previously that geopolymeric materials generally exhibit some change in compressive strength in the first month after synthesis [20]. The 28-day compressive strengths of geopolymers are presented in Fig. 7. The strength of geopolymers increases for 1.15 ≤ Si/Al ≤ 1.90. A large decrease in compressive strength between Si/Al ratio of 1.90 and 2.15 is observed for the Na, Na75 and K specimens, while only a nominal decrease in strength is observed for Na50 and Na25 specimens. Despite the differences at Si/Al ratio of 2.15, the general trend in strength at 28 days is remarkably similar to 7-day strength (Fig. 1).

A comparison of the compressive strength of the Na, Na50 and K specimens at 7 and 28 days is presented in Fig. 8. The largest changes in strength occur with increases in the mixed-alkali specimens with high Si/Al ratio, and decreases in the high Si/Al ratio Na and K specimens. With the exception of the Na specimen with Si/Al ratio of 1.40, both the Na and K systems exhibit a trend of strength that is stable or increases at
low Si/Al ratio, and increasingly declines with increase of Si/Al ratio, suggesting that the pure alkali gel is somehow increasingly unstable at high Si/Al ratio. In contrast the mixed-alkali specimens exhibit remarkably stable compressive strength in all but the lowest Si/Al ratio, and a large increase in strength at Si/Al ratio of 2.15.

Although the high Si/Al ratio K specimens exhibit reduced strengths, it appears from the exceptional strengths of high potassium content specimens (i.e. Na50 and Na25) in Fig. 7 that significant proportions of potassium in the structure are favourable for mechanical strength development over time. Neither the reduction in compressive strength of pure alkali specimens nor the increase in compressive strength of mixed-alkali specimens at high Si/Al ratio can be understood from the current literature.

Although it is well established that there are structural changes occurring in geopolymeric gels within the first month that alter their mechanical properties, it is clear from Fig. 8 that these changes are also subject to alteration by alkali composition.

The Young’s moduli values of geopolymers at 28 days are provided in Fig. 9. The Young’s moduli of each alkali series are observed to follow the general trend as that of the specimens after 7 days, where the Young’s modulus increases in the region 1.15 ≤ Si/Al ≤ 1.65 and is almost identical in the region 1.65 ≤ Si/Al ≤ 2.15. However, comparison of the 7-day and 28-day values provided in Fig. 10 shows that there are systematic changes to the Young’s modulus occurring as a result of ageing. The Young’s moduli of Na specimens are observed to decrease slightly at low Si/Al ratio, yet improve with increasing Si/Al ratio (~10%). In contrast, the K specimens exhibit an improved Young’s modulus at low Si/Al ratio (~15%), but reduces significantly with an increase in Si/Al ratio. The Na50 specimens exhibit a nominal change of less than 5% reduction in Young’s modulus, which is constant for all Si/Al ratios. After 28 days of ageing, there are clear trends observed in the Young’s modulus of geopolymers. At low Si/Al ratio (1.15 ≤ Si/Al ≤ 1.40) there is a negative MAE observed in the Young’s modulus of geopolymers, with Na specimens exhibiting a higher value than K, and
between 7 and 28 days (Fig. 10). However, the Na50 specimen exhibits a minimum value. At higher Si/Al ratio (1.65 ≤ Si/Al ≤ 2.15) there is a similar MAE observed, with Na specimens again exhibiting a higher Young’s modulus than K. However, in the high Si/Al ratio region the MAE is positive (i.e. the mixed-alkali specimens exhibit greater values than the pure alkali systems) (Fig. 9). The magnitude of the MAE increases with Si/Al ratio in this region, and appears to be maximised at high sodium content at Si/Al ratios of 1.65 and 1.90, but at Na25 at Si/Al ratio of 2.15. The observance of a negative MAE at low Si/Al ratio and a positive MAE at high Si/Al ratio is not expected when compared with trends observed in other alkali aluminosilicate systems [17]. Given the clear separation of the two different MAE regions, the different behaviour may be linked to the two different microstructures observed in these specimens [14].

The molecular structure of K geopolymer is known to be less ordered than that of Na-specimens [2,10]. Fig. 11 shows XRD diffractograms of geopolymers with Si/Al ratio of 1.15 in the current work at 7, 28 and 90 days. The crystalline phases observed in these diffractograms are due to zeolite structures, which have been identified previously [21]. Na-specimens with a Si/Al ratio of 1.15 were observed to become more ordered (observance of crystalline phase) after only 7 days (Fig. 11a), which has been observed widely [21,22]. The crystalline phase development in the Na-specimen after just 7 days may contribute to the specimen’s high early Young’s modulus compared to other alkali compositions, that are observed to be amorphous to XRD (Fig. 11b and c). The K specimen exhibits a crystalline phase after 28 days (Fig. 11c), implying a slow process of reorganisation after synthesis, which may explain the large increase in Young’s modulus of Na-specimens at high Si/Al ratios is related to prolonged reaction of metakaolin and production of geopolymer gel for structural support. Therefore, the production of gel would be expected to be greatest in Na-specimens as the transformation is more rapid and there is a larger amount of material to transform. The relative increase in the strength of Na-specimens compared to K-specimens in Fig. 8 correlates with this reasoning. However, the overall decrease in the strength of the highest Si/Al ratio Na- and K-specimens remains poorly understood. On the basis of increased Young’s modulus of the Na-specimens and small decreases in values of the K-specimens, it is unlikely that the mechanism of Young’s modulus development and compressive strength deterioration between 7 and 28 days are related.

Some of the mechanical properties of geopolymers may be understood by applying the existing knowledge of the effects of alkali cation on the molecular structure of an aluminosilicate framework. However, the current understanding of geopolymerisation does not extend so far as to include aspects of alkali interactions, especially at high Si/Al ratio, that may account for the emergence of a positive MAE, which is observed to become more prominent over time and the deterioration of strength in pure alkali specimens. There has been limited study into the mechanical properties of mixed-alkali aluminosilicate materials, namely because the MAE is primarily concerned with processes that involve the transport of ions within a material structure [17]. Furthermore, most alkali aluminosilicate materials studies have been glasses, where compressive strength is not a commonly measured property. As such, there has been little investigation of the mechanism of mixed-alkali interactions in terms of mechanical properties.

Fig. 12 shows TEM micrographs of three regions of Na50 geopolymer with a Si/Al ratio of 2.15. All micrographs appear amorphous under selected area diffraction. It can be observed that there are two characteristically different regions of the microstructure that are not observed in the Na and K specimens shown elsewhere [14,23,24]. Typically homogenous regions, similar to those observed for pure alkali systems appear in the microstructure (Fig. 12a) while other regions of the microstructure appear to exhibit some type of phase-segregation (Fig. 12c) identified by differing contrast. Fig. 12b shows a transitional zone between the two characteristically different microstructures suggesting that the appearance of the microstructure is not related to specimen thickness or beam damage. Although

![Fig. 11. XRD Diffractograms of (a) Na, (b) Na50 and (c) K geopolymers at 7, 28 and 90 days, having a Si/Al ratio of 1.15.](image-url)
Fig. 12. TEM BF images of Na50 geopolymer with Si/Al ratio of 2.15, showing (a) homogeneous (b) transitional and (c) phase segregated regions of the microstructure.

these regions are amorphous under selected electron diffraction, chemical inhomogeneity in either Si/Al ratio or alkali composition may be responsible for the contrast observed in the micrographs (Fig. 12b and c). The contrast observed in the micrograph implies that alkali composition is likely to be the cause, as silicon and aluminium have similar atomic weights. The nano-segregation observed in the Na50 specimen could be responsible for the increased compressive strength of the mixed-alkali specimens between 7 and 28 days, as the level of unreacted material is known to decrease with increasing content of potassium and does not appear to be reflected in the compressive strengths in Figs. 1 and 7 [1]. There is currently not enough experimental evidence showing how the microstructure of geopolymers with different Si/Al ratio and alkali composition develop with time to propose a mechanism responsible for the simultaneous decrease in strength in pure alkali specimens of high Si/Al ratio, while a significant increase in the properties of mixed-alkali specimens is observed in the current work.

The effect of alkali on the development of mechanical properties of geopolymers is likely to be linked to numerous factors, including but not limited to changes in the level of unreacted material [1] and the distribution of porosity [14,15], though these have not been explicitly investigated in the literature. However, a difference in the microstructure of geopolymers on the nanometer length scale, as observed in Fig. 12, that may be the result of alkali driven phase separation has not yet been considered. Further in-depth investigation is required to identify the mechanism responsible for the increase in strength of the mixed-alkali specimens and the weakening of the pure alkali specimens of high Si/Al ratio during ageing. The evidence presented here shows that the strength, Young’s modulus and microstructure of geopolymeric materials are fundamentally altered by alkali composition, and that the effect of alkali on mechanical properties differs with time and Si/Al ratio. These effects must be considered in formulating an extended theoretical understanding of geopolymerisation incorporating gel formation, to supplement
the current structural understanding that is based on molecular structure and thermodynamics [1,2,25]. Previous investigation of the Na-system has concluded that a complex process of gel reorganisation and densification must occur during geopolymer synthesis, which results in the volume and density of gel produced during synthesis being greatly affected by the Si/Al ratio, or more specifically the concentration of soluble silicon in the activating solution. Given the differences in viscosity [26], speciation and chemical reactivity and lability [25,27,28] of alkali aluminosilicate solutions with different alkali cations, it is likely that these aspects of aluminosilicate chemistry and phase separation must be incorporated into any view of the geopolymerisation process before a full understanding of the trends observed in the current work may be accounted for. The effect of different alkali cations on the time-dependent transformation/crystallisation of low Si/Al ratio specimens shown here (Fig. 11) must be explored and included in mechanistic descriptions. Interpretation of crystallisation in geopolymers has been discussed recently [29], but greater experimental evidence is required, especially at high Si/Al ratio.

Geopolymerisation is a highly complex transient reaction system. All of the important chemical processes and physical properties of the material are greatly altered at different stages of reaction, including synthesis, early strength development and long-term ageing [13]. Although geopolymers reach close to maximum strength after only 7 days (Figs. 1 and 7), the changes in compressive strength, Young’s modulus and crystallinity of specimens in the current work suggest that the transient nature of geopolymerisation extends into longer time periods, and that the development is dependent on the combination of alkali and Si/Al ratio. The significant differences in the development of Young’s modulus with Si/Al ratio and cation between 7 and 28 days (Fig. 10), imply that the action of both the cation and Si/Al ratio are important in determining the long-term physical property development of geopolymers. As such, an understanding of the microstructure of each system is critical in determining how the solution chemistry is altered during synthesis and ageing, and how this will affect the mechanical properties of the material.

4. Conclusions

A systematic study of the effect of alkali composition and Si/Al ratio of geopolymeric materials synthesised from metakaolin has been performed. Statistical analysis of the compressive strengths and Young’s moduli of specimens in the current work was performed by T-test and F-test analysis in order to determine the significance of alkali and Si/Al ratio on the mean value and standard deviation of geopolymer compressive strengths and Young’s moduli. The results of the statistical analysis showed that the trends in compressive strength [11,14] and Young’s modulus [14] were observed in geopolymers of different alkali compositions. Comparison of specimens with different alkali composition indicated that the effect of alkali on the mechanical properties of geopolymers is small after 7 days. However, after 28 days the compressive strengths of mixed-alkali specimens with Si/Al ≥ 1.90 was observed to increase by up to 30%, compared to Na and K specimens, which were observed to decrease in strength. The Young’s moduli of specimens exhibited two distinctly different mixed-alkali effects after 28 days curing. In specimens with Si/Al ≤ 1.40 ratio the mixed-alkali specimens exhibited reduced values compared to Na and K specimens, whereas in specimens with Si/Al ≥ 1.65 the mixed-alkali specimens exhibited maximum Young’s moduli values. The change in the effects of alkali with Si/Al ratio may be related to the two different microstructures observed to form in the same specimens. The development of Young’s modulus between 7 and 28 days was observed to be dependent on alkali, with the Young’s modulus of sodium specimens decreasing at low Si/Al ratio, but increasing at high Si/Al ratio, and K specimens exhibiting the opposite effect. Mixed-alkali specimens all exhibited nominal change in Young’s moduli, without any significant effect of Si/Al ratio observed. The development of mechanical properties of geopolymers investigated in the current work highlights the importance for microstructural analysis of geopolymers of varied Si/Al ratio, and alkali content with time to determine the basis for the reduction in compressive strength of pure alkali specimens, and increase in compressive strength of mixed-alkali specimens of high Si/Al ratio between 7 and 28 days.

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