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Structure and mechanical properties of aluminosilicate geopolymer composites with Portland cement and its constituent minerals

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ABSTRACT

The compressive strengths and structures of composites of aluminosilicate geopolymer with the synthetic cement minerals C_3S, β-C_2S, C_3A and commercial OPC were investigated. All the composites showed lower strengths than the geopolymer and OPC paste alone. X-ray diffraction, ^{29}Si and ^{27}Al MAS NMR and SEM/EDS observations indicate that hydration of the cement minerals and OPC is hindered in the presence of geopolymer, even though sufficient water was present in the mix for hydration to occur. In the absence of SEM evidence for the formation of an impervious layer around the cement mineral grains, the poor strength development is suggested to be due to the retarded development of C–S–H because of the preferential removal from the system of available Si because geopolymer formation is more rapid than the hydration of the cement minerals. This possibility is supported by experiments in which the rate of geopolymer formation is retarded by the substitution of potassium for sodium, by the reduction of the alkali content of the geopolymer paste or by the addition of borate. In all these cases the strength of the OPC–geopolymer composite was increased, particularly by the combination of the borate additive with the potassium geopolymer, producing an OPC–geopolymer composite stronger than hydrated OPC paste alone.

1. Introduction

Ordinary Portland cement (OPC) is the highest volume engineering material in use today, but its production contributes 5% of anthropogenic carbon dioxide emissions [1]. Geopolymer cements have been proposed as more ecologically friendly alternatives [2] since their production does not involve limestone calcination. Geopolymers are a class of aluminosilicates formed by reaction of alkali silicate solution with dehydroxylated clay under highly alkaline conditions [3,4]. Their defining characteristics are that they cure and set under ambient conditions to a material with an X-ray amorphous three-dimensional network of aluminate and silicate units with charge-balancing alkali cations [4]. Aluminosilicate geopolymers gain strength more rapidly than OPC and their ultimate strength can be higher [5]. However, questions surrounding the long-term strengths of geopolymer cements, which are reported to correlate inversely with their development of zeolitic phases [6] have hindered their widespread adoption as an OPC replacement.

One possible method for offsetting the ecological disadvantage of OPC against the unknown long-term durability of aluminosilicate geopolymer cement could be to blend these in varying proportions, thereby reducing the amount of OPC and its environmental impact, while retaining its possible durability contribution.

The success of this approach requires knowledge of the interaction chemistry between the aluminosilicate and calcium silicate based systems. The strength of OPC cement paste is derived from its formation of calcium silicate hydrate (C–S–H) gel when hydrated. Where these systems also contain available aluminium, it is known that this element can be incorporated into the C–S–H gel structure, forming C–A–S–H [7], but phase separation between aluminosilicate geopolymers and these aluminium-containing C–A–S–H gels has been reported [7]. At very high alkalinity ($pH > 12$) Na-containing N–A–S–H gels are reported to be the major phase formed in cementitious systems containing C–S–H [8]. A ^{43}Ca MAS NMR study of aluminosilicate geopolymers containing various calcium compounds suggests that $Ca(OH)_2$ and nano-structured $CaSiO_3$ enters into the geopolymer network, possibly with Ca acting as the charge-balancing cation, whereas $CaCO_3$ and $Ca_3(PO_4)_2$ may simply be present as fillers [9]. A study of the effect of a number of calcium-containing minerals on the compressive strength of aluminosilicate geopolymers [10] showed that little dissolution of Ca occurs from natural calcium silicate minerals, resulting in little formation of C–S–H gel, and reduced strength. At high alkalinity, the strength was essentially independent of the calcium source mineral [10].

Since commercial OPC is a mixture of several silicate and aluminate minerals, with the complicating presence of gypsum added to prevent flash setting, its interaction chemistry with aluminosilicate geopolymers is likely to be complex. For this reason, the aim of the present study was to attempt to disentangle the various competing reactions by investigating the interaction of the individual cement

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minerals with a standard aluminosilicate geopolymer and to compare these with the behaviour of a commercial OPC–geopolymer mixture.

The principal hydraulically-active minerals in OPC are tricalcium silicate (C_3S or Ca_3SiO_5), β-dicalcium silicate (β-C_2S or Ca_2SiO_4) and tricalcium aluminate (C_3A or $Ca_3Al_2O_6$). C_3A reacts quickly with water for early setting, while the slower C_3S and β-C_2S hydration reactions form C–S–H gel, providing ultimate strength [11]. The interaction of these individual minerals with aluminosilicate geoplymer was studied and contrasted with OPC using XRD and solid state ^{27}Al and ^{29}Si MAS NMR and their microstructures were determined by SEM/EDS. The compressive strengths of their composites with the aluminosilicate geopolymer were determined, and chemical considerations of possible reasons for their poor structural performance suggested the possibility that geopolymer formation might interfere with the formation of C–S–H by competition for silicon in the system. Following this reasoning, the addition of borate to the system to retard geopolymer formation was found to produce significant strength improvement.

2. Experimental procedure

2.1. Materials

The sodium aluminosilicate geopolymer matrix was prepared from New Zealand halloysite clay (Imerys Premium Grade) dehydroxylated at 600 °C for 12 h, sodium silicate solution (FERNZ, Grade D, 14.7 wt.% Na_2O, 29.4 wt.% SiO_2) and NaOH pellets (BDH reagent grade). The chemical analysis of the halloysite is presented in Table 1.

The individual cement minerals were prepared by solid state synthesis. C_3S and β-C_2S were synthesised by ball milling mixtures of silicic acid and $CaCO_3$ of the appropriate stoichiometry, pressing into pellets and firing for 24 h in platinum dishes at 1350 °C (for C_3S) and 1450 °C (for β-C_2S). The β-polymorph of C_2S was stabilised by quenching the pellets from furnace temperature into a stainless steel canister of liquid nitrogen. C_3A was synthesised from Al_2O_3 and $CaCO_3$ in the appropriate proportions, ball milled, filtered, dried, pressed into pellets and fired at 1365 °C for 720 min. X-ray powder diffraction confirmed that all the synthesised products were crystalline, fully reacted and essentially monophasic.

The OPC was a commercial type GP cement (Golden Bay Cement Co.) conforming to NZS 3122:1995. Its mineralogical composition, which includes 4% gypsum setting retarder, is shown in Table 1.

2.2. Preparation of the composites

The geopolymer matrix was prepared by mixing together dehydroxylated halloysite, sodium silicate and a solution of NaOH in water, such that the composition corresponded to the molar ratios $SiO_2/Al_2O_3 = 3.32$, $Na_2O/SiO_2 = 0.25$ and $H_2O/Na_2O = 9.94$. Composites of this geopolymer with the individual cement minerals or OPC were prepared by thoroughly mixing the uncured geopolymer with 50 mass % of cement mineral, such that the mass of solid in the cement paste was equal to the mass of sodium silicate and halloysite in the geopolymer paste. In addition to the standard geopolymer formulation used in most of the experiments, a few composites were prepared using formulations in which the geopolymer setting time was retarded in three ways, namely, (i) reducing the alkalinity by omitting the NaOH, (ii) substituting KOH and potassium silicate for the sodium compounds, and (iii) adding 10 wt.% $Na_2B_4O_7$, which is known to retard the setting of flyash-based geopolymers. The composition of the potassium geopolymers was $SiO_2/Al_2O_3 = 3.05$, $K_2O/SiO_2 = 0.31$ and $H_2O/K_2O = 10.81$, to permit reasonable comparability with the sodium geopolymer used here.

After mixing, the geopolymer/cement blends were poured into cylindrical 30 mm diameter × 25 mm lubricated nylon molds, vibrated for 10 min, sealed with plastic film and cured at 60 °C for 24 h. This curing temperature is within the range commonly used to prepare aluminosilicate geopolymers. After demolding the samples were stored in sealed plastic bags until compressive testing.

For comparison, hydrated pastes of OPC and the individual cement minerals were prepared in a water/solid mass ratio of 0.5 and a reference sodium geopolymer was also prepared as above. Several potassium geopolymers of comparable composition $SiO_2/Al_2O_3 = 3.05$, $K_2O/SiO_2 = 0.31$ and $H_2O/K_2O = 10.81$ were also synthesised for comparison with the sodium composites.

Table 1
Mineralogical composition of Golden Bay Type GP OPC and Imerys Premium grade halloysite.

Mineral		Formula		wt.%	
OPC composition					
C_3S		Ca_3SiO_5		68	
C_2S		Ca_2SiO_4		14	
C_3A		$Ca_3Al_2O_6$		7	
C_4AF		$Ca_4Al_2Fe_2O_{10}$		7	
Gypsum		$CaSO_4.2H_2O$		4	
Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	LOI
Halloysite clay composition					
wt.%	50.4	35.5	0.25	0.05	13.8

Analysis also includes traces of CaO, MgO, K_2O and Na_2O.

2.3. Characterisation methods

2.3.1. X-ray powder diffraction

The cured samples were powdered and their X-ray diffractograms were recorded using a Philips PW1729 computer-controlled goniometer with a graphite monochromator and Co Kα radiation over the 2θ range from 4.025° to 79.975°. The XRD traces were compared with the ICDD Powder Diffraction Files.

2.3.2. ^{29}Si and ^{27}Al solid state MAS NMR

The ^{29}Si MAS NMR spectra of the powdered samples were acquired at 11.7 T using a Bruker Avance III 500 spectrometer operating at a frequency of 99.29 MHz and a 5 mm Doty MAS probe with a zirconia rotor spun at ~6 kHz. The excitation pulse was 7 μs with a recycle time of 30 s. The number of scans ranged from 32 to 87 and the spectra are referenced with respect to tetramethyl silane (TMS).

The ^{27}Al MAS NMR spectra were also acquired at 11.7 T at an operating frequency of 130.24 MHz and a 4 mm Doty MAS probe with a silicon nitride rotor spun at 10–12 kHz. The excitation pulse length was1 μs and the recycle time was 1 s. The number of scans ranged from 325 to 2840 and the spectra are referenced with respect to $Al(H_2O)_6^{3+}$.

2.3.3. SEM/EDS

Samples for SEM were prepared by cutting with a diamond saw and polishing with silicon carbide discs. The prepared samples were stored under vacuum for a week, then attached to aluminium stubs, coated with 12 nm thick gold and examined using a JEOL JSM-6500F scanning electron microscope with an acceleration voltage of 15.0 kV. Elemental analysis was performed using an EX23000BU energy dispersive X-ray analyser.

2.3.4. Compressive strength

Compressive strength measurements were made on 5–9 replicate samples after 28 days, consistent with conventional concrete testing convention. The samples were prepared by machining the top and bottom surfaces of the cylinders to be flat and parallel. The strength measurements were made using an Instron 25 t TTKM universal testing machine at a crosshead speed of 1 mm min^{-1}.

3. Results

3.1. Compressive strength

The 28 day compressive strength results are shown in Fig. 1. The hydrated β-C_2S and C_3A pastes and their geopolymer composites were too soft to be measured.

The sodium geopolymer matrix material displays the high compressive strength typical of geopolymers prepared from high purity ingredients. The strength of the OPC paste is in the typical range for cement mortar at 28 days [11], but the strength of the composite of these two materials is considerably lower than either of the components although this composite showed improved strength when the NaOH was omitted from the geopolymer synthesis (Fig. 1). Hydrated C_3S paste also shows low compressive strength, but unlike the behaviour of OPC, the strength of C_3S is increased when combined with geopolymer; this strength is still very much lower than that of the pure geopolymer however. Substitution of potassium for sodium in the geopolymer–OPC composite results in a significant improvement in strength (Fig. 1), but, by contrast with the sodium geopolymer–OPC composite, the omission of KOH from the synthesis mixture results in a strength decrease. The addition of sodium tetraborate to the composites of OPC with both sodium and potassium geopolymers increased their strength, especially in the case of the potassium composite, the strength of which exceeds the strength of the OPC component (Fig. 1). Possible explanations for these results were sought by an examination of the phases present, their atomic structure and the microstructure of the hydrated phases and composites.

3.2. XRD phase analysis

Fig. 2 shows the XRD diffractometer traces of unhydrated and hydrated OPC and cement minerals, pure sodium geopolymer (Fig. 2a) and its composites with the individual cement minerals and OPC. The XRD trace of sodium geopolymer (Fig. 2a) consists of a typical broad amorphous hump centred at $2\theta = 20–40°$ [4] with superimposed peaks of crystalline quartz impurity from the original clay.

The principal cement mineral present in the XRD trace of unhydrated OPC (Fig. 2b) is C_3S. Upon hydration, $Ca(OH)_2$ (portlandite) appears as the major crystalline phase (Fig. 2c). This compound is a crystalline co-product of C–S–H formation; the latter, being a gel, is X-ray amorphous. Portlandite is not present in the composite of sodium geopolymer and OPC (Fig. 2d), but this may be due to the additional presence of silica and alumina in the system which could form C–A–S–H or N–C–A–S–H with the available Ca; significantly, however, the persistence of unhydrated C_3S in the geopolymer–OPC composite (Fig. 2d) indicates a lack of hydration. The XRD trace of unhydrated C_3S (Fig. 2e) is similar to OPC; upon hydration, some crystalline portlandite appears (Fig. 2f), but the geopolymer–C_3S composite shows only C_3S (Fig. 2g), indicating that the presence of the geopolymer significantly retards the hydraulic behaviour of the system. The XRD traces for unhydrated and hydrated β-C_2S and the sodium geopolymer composite with this phase are all very similar, typically as in Fig. 2h, suggesting a lack of hydraulic activity in this mineral under the present reaction conditions.

The hydration behaviour of pure C_3A is different to that of the C_3A in OPC, due to the presence of gypsum in the latter. When pure C_3A (Fig. 2i) is hydrated, the product is the garnet mineral katoite (Fig. 2j), which in OPC further reacts with the sulphate additive [12]. By contrast, the sodium geopolymer–C_3A composite shows no evidence of the formation of katoite (Fig. 2k).

3.3. Solid state MAS NMR

Fig. 3 shows the ^{29}Si NMR spectra of the unhydrated and hydrated silicate minerals and OPC, and their composites with sodium geopolymer. The broad silicon resonance centred at -84 ppm in the geopolymer spectrum (Fig. 3a) is typical of the range of tetrahedral silicon environments in aluminosilicate geopolymers [6,16,17].

The spectrum of unhydrated C_3S (Fig. 3b) shows a major resonance at -73.3 ppm with a shoulder at -69.2 ppm, in agreement with other reported spectra of C_3S [13–15] in which several other small narrow peaks have also been fitted, corresponding to minor differences in the monomeric silicate units of the C_3S structure [15]. On hydration, two new resonances appear at -78.8 ppm and -83.5 ppm in the C_3S spectrum, in addition to unreacted C_3S (Fig. 3c). The new peaks correspond to the hydration product C–S–H, the resonance at -78.8 ppm corresponding to the Q^1 units and that at -83.5 ppm to the Q^2 units [16,17].

The ^{29}Si spectrum of β-C_2S (Fig. 3d) shows the typical single resonance at -71.2 ppm as previously reported for this phase [13]; on hydration, this spectrum is unchanged, reflecting its characteristic lack of hydraulic reactivity.

The ^{29}Si spectrum of OPC (Fig. 3e) is dominated by a single broadened resonance at -71.1 ppm, arising from the combination of the two silicate minerals. The broadening and spinning side bands in this spectrum arise from the presence of paramagnetic impurities, principally iron, which are not present in the pure minerals. On hydration of the OPC, the expected formation of C–S–H gel from the C_3S component is reflected by the appearance of the broad feature at about -79 ppm, with a shoulder at about -82 ppm (Fig. 3f). At this

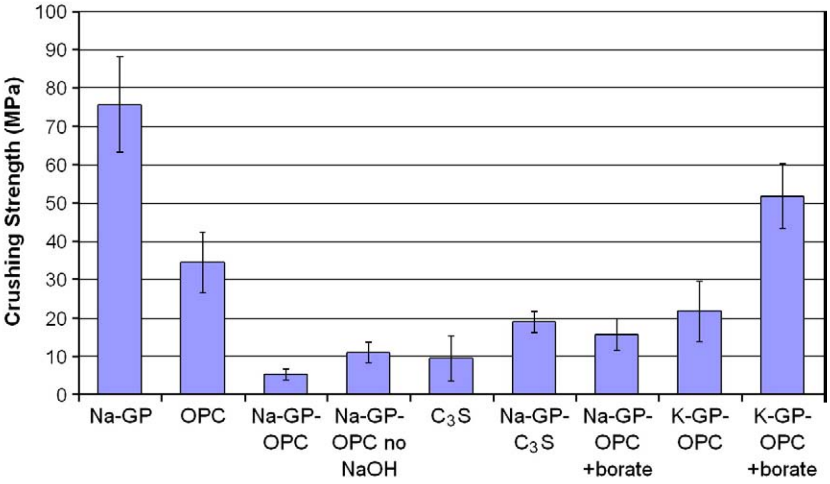

Fig. 1. Twenty-eight day compressive strength results. Error bars represent one standard deviation.

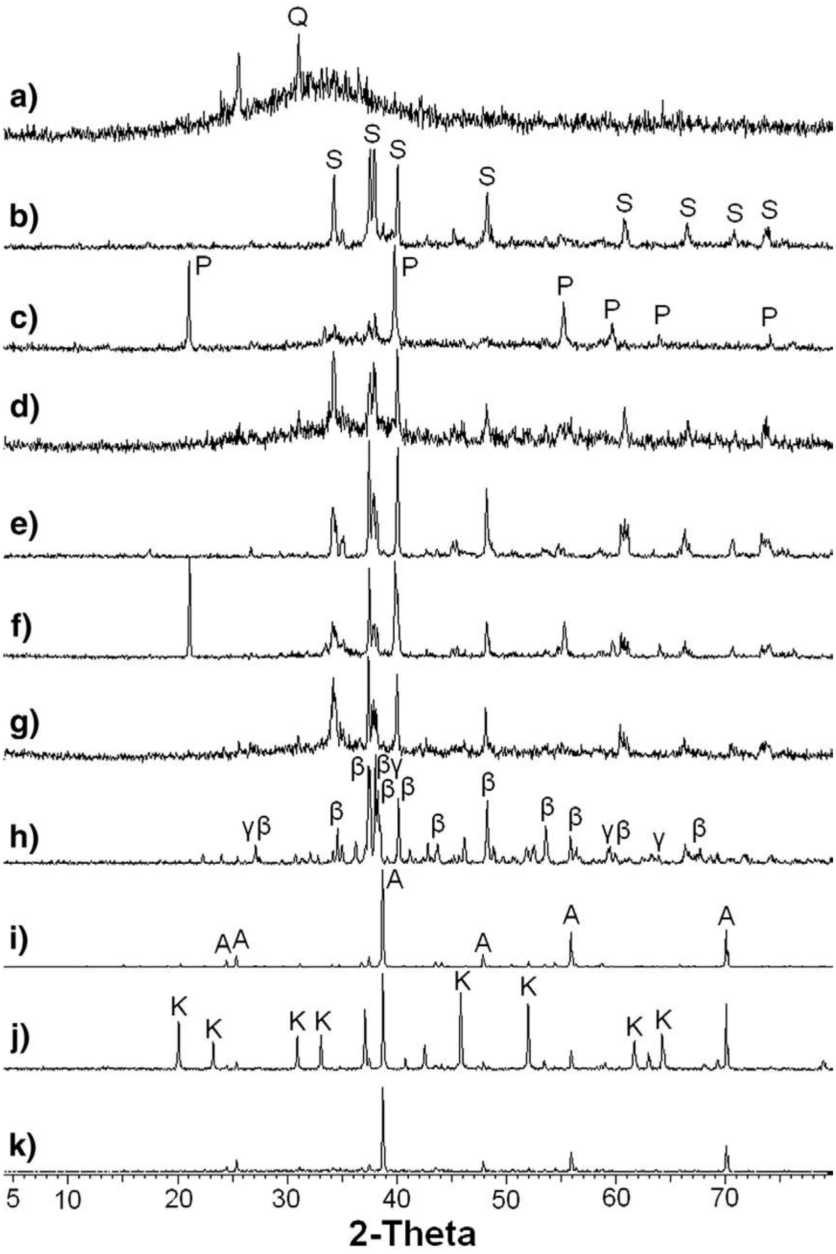

Fig. 2. XRD powder diffractograms. a) Geopolymer, b) unhydrated OPC, c) hydrated OPC, d) OPC–geopolymer composite, e) unhydrated C_3S, f) hydrated C_3S, g) C_3S–geopolymer composite, h) unhydrated β-C_2S, i) unhydrated C_3A, j) hydrated C_3A, and k) C_3A–geopolymer composite. Key: Q = quartz PDF #00-046-1045. S = C_3S PDF #00-049-0442. P = portlandite PDF #00-044-1481. β = β-C_2S PDF #00-033-0302. γ = γ-C_2S PDF #00-024-0034. A = C_3A PDF #00-038-1429. K = katoite PDF #00-024-0217.

stage of hydration, the C–S–H formed in OPC is dominated by the Q^1 silicon dimeric units [18].

The combination of C_3S or OPC with geopolymer results in a combination of the ^{29}Si spectra of the two components (Fig. 3g, h); the double peaks of the C–S–H hydration product may be masked by the broad geopolymer resonance, causing its slight downfield shift; however, the presence of C–S–H in these composites is not indicated by the other techniques used in this study, in particular, the XRD evidence of the retarding effect of geopolymer on the hydration of both C_3S and OPC.

Fig. 4 shows the ^{27}Al MAS NMR spectra of unhydrated and hydrated C_3A and OPC and their composites with geopolymer. The geopolymer spectrum itself (Fig. 4a) shows a broad tetrahedrally-coordinated Al resonance at 58.7 ppm typical of a well-cured material [19]. By contrast, the spectrum of unhydrated C_3A (Fig. 4b) is dominated by two quadrupolar lineshapes corresponding to the two distorted tetrahedral sites in this compound; this spectrum is similar to those previously reported [20,21] which were simulated to two quadrupolar sites with isotropic chemical shifts of 79.5 and 78.3 ppm [21]. Upon hydration, these tetrahedral features are replaced by a single octahedral resonance at 11.9 ppm (Fig. 4c), consistent with the single site in the cubic hydrogarnet structure of the expected hydrated phase C_3AH_6 for which chemical shifts of 10–13 ppm have previously been reported [22,23]. The hydrogarnet class of compounds includes katoite, identified by XRD in the hydrated C_3A sample.

Unhydrated OPC powder (Fig. 4d) contains a featureless tetrahedral Al resonance with some evidence of asymmetry towards lower field. Hydration produces, in addition to residual OPC, new weak tetrahedral peaks at 73.1 and 67.4 ppm arising from aluminium substitution into C–S–H gel (Fig. 4e); although these features are very poorly resolved, they probably correspond respectively to the bridging and non-bridging sites distinguished in C–A–S–H by triple-

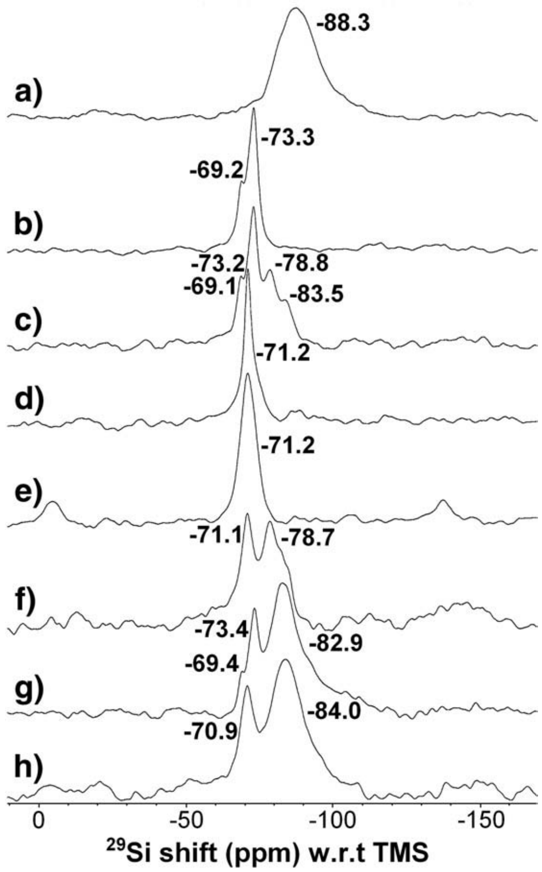

Fig. 3. 11.7 T ^{29}Si MAS NMR spectra. a) Geopolymer, b) unhydrated C_3S, c) hydrated C_3S, d) β-C_2S, e) unhydrated OPC, f) hydrated OPC, g) C_3S–geopolymer composite, and h) OPC–geopolymer composite.

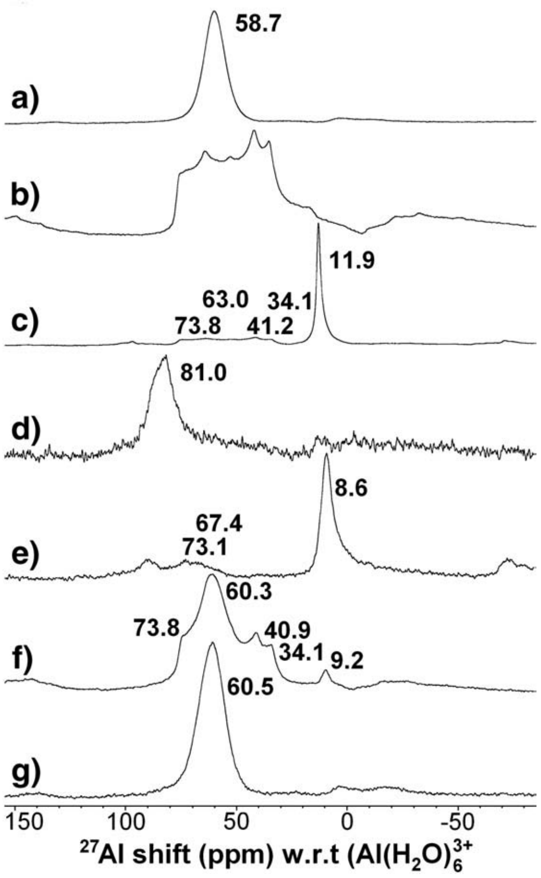

Fig. 4. 11.7 T ^{27}Al MAS NMR spectra. a) Geopolymer, b) unhydrated C_3A, c) hydrated C_3A, d) unhydrated OPC, e) hydrated OPC, f) C_3A–geopolymer composite, and g) OPC–geopolymer composite.

quantum MAS NMR [22]. The major resonance at 8.6 ppm in this spectrum is in the reported position for octahedral aluminium in C–A–S–H [22] but may also contain a contribution from the presence of the reported octahedral peak at 13 ppm from the hydrated aluminosulfate mineral ettringite, $Ca_6Al_2O_6(SO_4)_3.32H_2O$ [23] formed by reaction with the gypsum added to OPC as a setting retarder [24].

The ^{27}Al spectrum of the C_3A–geopolymer composite (Fig. 4f) contains the tetrahedral geopolymer resonance at 60.5 ppm superimposed on the quadrupolar features of unreacted C_3A. Of greater significance, however, is the octahedral peak at 9.2 ppm, suggesting the presence of a hydrated hydrogarnet phase.

The OPC–geopolymer composite (Fig. 4g) is dominated by the tetrahedral geopolymer resonance at 60.5 ppm, with no evidence of either hydrated or unhydrated aluminate cement phases (the small octahedral peak at 3 ppm probably arises from a small amount of unreacted halloysite). This result probably reflects the much greater aluminium content of the geopolymer compared with the aluminate phases in the OPC.

3.4. SEM EDS

Fig. 5 shows a scanning electron micrograph of a typical area of an OPC–sodium geopolymer composite, together with EDS elemental maps of the same region. The dense feature at the right hand side of the micrograph has a high silicon and aluminium content and very low calcium content, suggesting that it is a geopolymer region. An alternative possibility, that this is a relict of unreacted metahalloysite, is ruled out by the ^{27}Al NMR spectra, which show no evidence of this reactant in any of these samples. The calcium is concentrated in the regions around this area, which also contain little silicon. The fact that calcium and silicon do not seem to coexist suggests that there is no C–S–H present in this region; there is an indication of a correlation between calcium and oxygen, but since the XRD traces show no traces of crystalline portlandite or calcium carbonate, the calcium may be present as an amorphous calcium hydroxide.

The SEM micrographs show no evidence of an impermeable layer or concentration gradient between the cement mineral grains and the geopolymer matrix that might provide an explanation for the retardation of C_3S hydration in the presence of the geopolymer; the only demarcation between the grains and the matrix is the infrequent occurrence of a drying crack.

4. Discussion

Apart from the potassium geopolymer–OPC composite containing borate, all the other samples investigated here show lower crushing strengths than OPC or sodium geopolymer itself, suggesting that they lack an essential component that provides strength. In hydrated OPC and the calcium silicate cement minerals, the strength arises from the formation of C–S–H gel, the formation of which may be retarded by the presence of the geopolymer. This possibility is supported by the combination of experimental results reported here; (i) NMR provides no compelling evidence for the presence of C–S–H in the composite samples, (ii) XRD indicates the significant presence of unhydrated C_3S in the composites, whereas in the absence of geopolymer this is completely consumed under the reaction conditions, and (iii) EDS maps show the occurrence of calcium and silicon in separate regions (although geopolymer is present in the composite samples, it occurs in discrete regions rather than a continuous phase that would give strength to the whole sample). Although none of these strands of

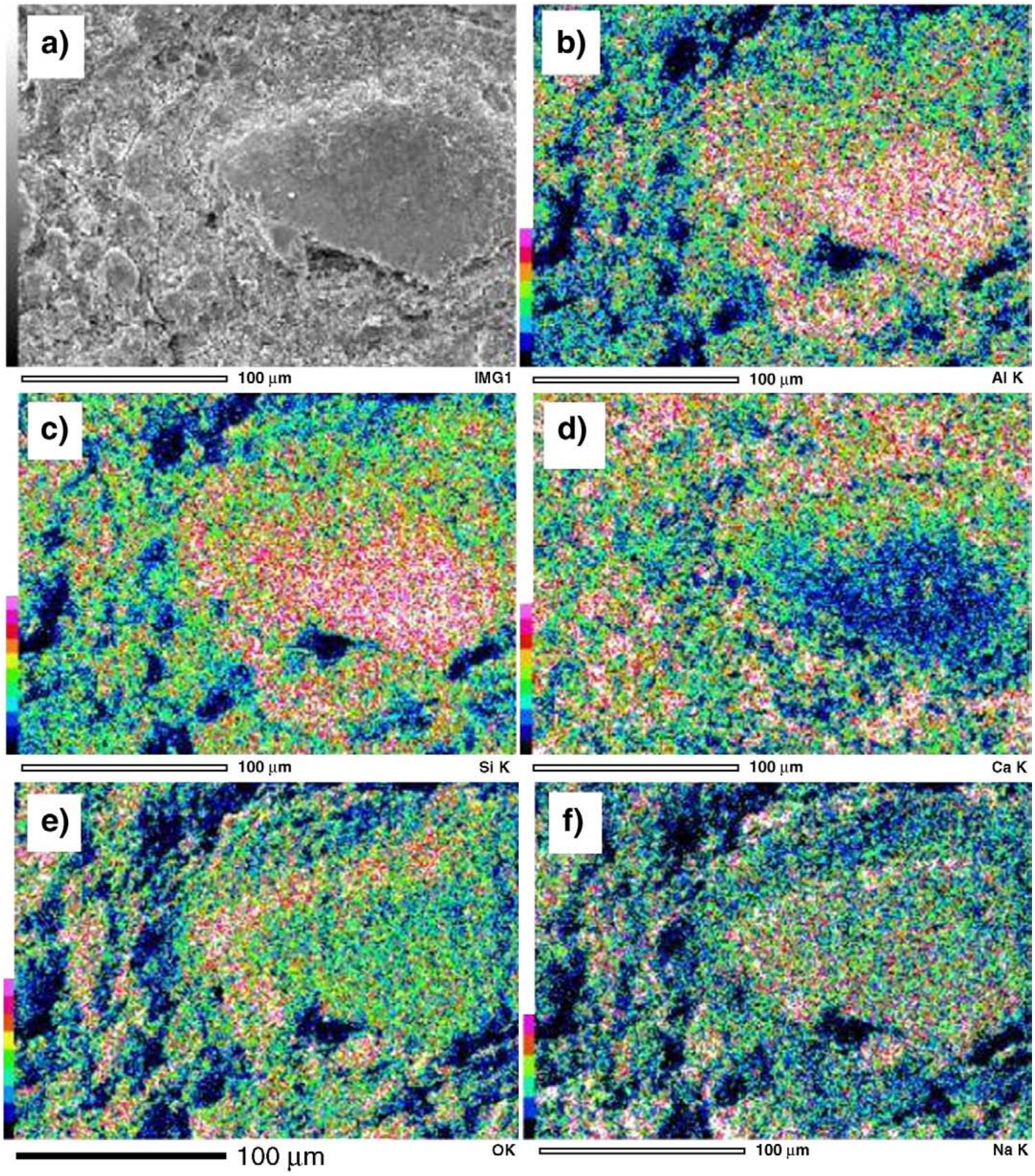

Fig. 5. EDS element maps of a typical area of an OPC–geopolymer composite. a) SEI image, b) Al distribution, c) Si distribution, d) Ca distribution, e) O distribution, and f) Na distribution.

evidence in itself provides definitive proof that the observed strength degradation of these composites is due to the suppression of C–S–H formation, taken together they more strongly support the hypothesis that C–S–H is implicated.

If this is the case, C–S–H formation may be suppressed by preferential reactions of calcium or silicon with the geopolymer, making those elements less available for C–S–H formation. In the highly alkaline environment of geopolymer formation, the most likely calcium reaction would be its precipitation as hydroxide, but portlandite is absent from the XRD traces. C–S–H has been reported to form in other highly alkaline environments, including the reaction of $Ca(OH)_2$ with metakaolin activated with NaOH [25] and in Portland cement activated with 18 M KOH solution [26].

The preferential removal of silicon is therefore a more likely explanation. Aluminosilicate geopolymer formation can be complete at 60 °C within 5 h of mixing the components [25]. Furthermore, geopolymer formation is reported to occur more quickly in the presence of calcium [27]. C–S–H formation is a slower reaction, and under alkaline conditions, the precipitation of calcium silicate products may not begin until after 5 h [28]. In highly alkaline environments calcium species dissolve more slowly, while silica dissolves more rapidly [28]. Thus, the present synthesis conditions would tend to accelerate the faster geopolymerisation reaction and retard the slower C–S–H forming reaction, allowing the geopolymer to consume the available silica before calcium precipitation began.

The hydration products of the constituent aluminium minerals of OPC are also interfered with by geopolymer formation. The octahedrally-coordinated aluminium species in hydrated OPC are not present in the composites and even the normally rapidly-hydrating C_3A shows little NMR evidence of significant hydration. These results suggest that either the hydration products undergo further reaction or that geopolymer formation interferes with the hydration reaction. The hydration of C_3A alone occurred within 10 min of mixing, the samples becoming very hot and solidifying during this time. The C_3A–geopolymer composite did not set or attain the same temperature as quickly, despite sufficient water being available in the mixture. The ^{27}Al MAS NMR spectra confirm that rapid C_3A hydration does not occur in the composite, probably because the high pH and availability of dissolved silicates preferentially facilitated geopolymer formation.

Possibly the best direct indication that the weakness of the products is caused by rapid geopolymer formation preventing C–S–H formation is provided by the strength results (Section 3.1) indicating that the strengths of the samples are significantly improved where steps were taken to retard the rate of geopolymer formation. Substitution of potassium for sodium in the geopolymer formulation is reported to result in higher final strength [29], and the potassium compounds polymerise more slowly than their sodium analogues. This is reflected in the significantly improved strength of the potassium geopolymer–OPC composite compared with its sodium counterpart (Fig. 1), although the OPC–potassium geopolymer composite is not as strong as either the OPC paste or geopolymer alone.

Lowering the alkalinity by omitting the NaOH from the sodium geopolymer–OPC composites results in only a small increase in strength (Fig. 1). At lower alkalinity in the absence of geopolymer, the hydration of OPC (or C_3S) to form C–S–H is facilitated. Under the same conditions, geopolymer formation accompanied by the preferential removal of silicate will be retarded and the combined effect should be an increase in strength. The ^{29}Si NMR spectrum of the sample synthesised without NaOH (not shown) retains the features of the corresponding higher-alkali compound, but is broader than reduced alkali geopolymer–OPC composite, due to the presence of a shoulder at -82 ppm that may arise from the Q^1 units of C–S–H.

The most significant increase in the strength of the composites is achieved by the addition of 10 wt.% of sodium tetraborate to the geopolymer formulation; this increases the strength of both the Na–geopolymer–OPC composite, and especially the K–geopolymer–OPC composite (Fig. 1) which is stronger than the OPC paste itself. The presence of significant calcium content in New Zealand flyash has been reported to cause flash setting in geopolymers prepared from this raw material, but the addition of borax retards the setting rate, by the incorporation of borate units into the tetrahedral geopolymer network, as evidenced by ^{11}B MAS NMR [27]. Borate is also known to retard the setting of OPC by interfering with its hydration reactions, but the differences between these retardation mechanisms in OPC and geopolymer are presently poorly understood. Although the strengths of the borax-containing composites are increased, their ^{29}Si NMR spectra are identical to that of the original OPC–geopolymer composite.

Thus, the success of all three geopolymer retardation strategies in improving the strength of the geopolymer–OPC composites is consistent with the hypothesis that the strength of these materials is compromised if their ability to form significant amounts of C–S–H gel is hindered. To improve the mechanical performance of such composites, the reaction conditions should therefore be such as to facilitate the formation of C–S–H gel; the present results suggest that one of the most promising methods for achieving useful strength is the addition of boron compounds.

5. Conclusions

Composites containing equal masses of aluminosilicate geopolymer and the synthetic cement minerals C_3S, β-C_2S, C_3A and commercial OPC were prepared and their mechanical and structural characteristics determined, with the following results:

1. All the composites show lower strengths than the geopolymer and OPC paste alone, but the strength can be significantly increased by the substitution of potassium for sodium as the charge-balancing cation in the geopolymer, and particularly so by the addition of 10 wt.% borate. The latter is thought to act by retarding geopolymer formation, thereby facilitating the formation of C–S–H gel by the C_3S component of OPC.
2. X-ray diffraction, ^{29}Si and ^{27}Al MAS NMR data of the composites suggest a lack of hydraulic activity of the cement minerals and the absence of their strength-forming hydration products, especially C–S–H gel and $Ca(OH)_2$, even though sufficient water was present in the mix for hydration to occur. SEM/EDS also indicates an absence of phases containing both Ca and Si, but provides no evidence of an impervious region between the cement mineral grains and the geopolymer matrix which would explain the lack of hydration in the presence of the geopolymer.
3. The lack of C–S–H to provide strength in the geopolymer-containing composites may be due to the preferential removal from the system of Ca or, more probably, Si, because the formation of the geopolymer is more rapid than the hydration of the cement minerals. This is supported by experiments to retard the rate of geopolymer formation (substitution of potassium for sodium, reduction of the alkali content of the geopolymer paste or the addition of borate) which all increase the strength of the OPC–geopolymer composite. The addition of borate to the potassium geopolymer–OPC composite is particularly successful in this respect.

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