Cement & Concrete Composites 30 (2008) 979–985

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Carbonate mineral addition to metakaolin-based geopolymers

Christina K. Yip, John L. Provis *, Grant C. Lukey, Jannie S.J. van Deventer

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia

ARTICLE INFO

Article history:
Received 12 July 2007
Received in revised form 14 July 2008
Accepted 17 July 2008
Available online 25 July 2008

Keywords:
Geopolymer
Carbonates
Microstructure
Mechanical properties
Shrinkage

ABSTRACT

The effect of adding significant percentages of alkaline earth carbonate minerals (calcite and dolomite) to metakaolin-based geopolymers is investigated by compressive strength testing, X-ray diffractometry and electron microscopy, with the aim of better understanding the role played by calcium ions, carbonate ions and mineral surfaces in geopolymers. Addition of around 20% calcite or dolomite is seen to improve the compressive strength of the geopolymeric material, although does induce additional shrinkage during the first 90 days of aging. More than 20% mineral additive has a deleterious effect on strength due to significant disruption of the geopolymer gel network and the reduced reactive aluminosilicate content. No distinct calcium silicate hydrate phase formation is observed in any of the systems studied. Some dissolution of the mineral particles is observed, however this is not a major effect in most instances. The mineral particles interact with the geopolymer gel predominantly via surface binding, which appears to be somewhat stronger in the case of calcite than dolomite.

1. Introduction

Alkali-activated aluminosilicate binders (geopolymers) represent a group of cement-like materials that can be formed by reacting calcined clays (e.g. metakaolin) or industrial wastes (e.g. coal fly ash or metallurgical slags), with an alkaline solution [1–3]. Through careful mix formulation, it is now possible to utilize a range of starting materials in tailoring an environmentally friendly product that will satisfy commercial and industrial needs [4]. Further application of geopolymer technology, however, requires detailed research focused on the development and understanding of the chemical mechanisms of geopolymerization. Significant advances have been made in this area recently with the development of new experimental and theoretical tools for the analysis of geopolymers and geopolymerization [5–12]. An area of particular interest and importance is the role of contaminant (non-aluminosilicate) species within the geopolymer matrix, which is of significant importance if these materials are to be used in applications such as waste immobilization. The interaction of geopolymeric binder phases with mineral aggregates is also of importance in the development of geopolymer concretes.

Previous studies have shown that the addition of moderate amount of calcium-containing material to a geopolymer can have a significant effect on the geopolymer structure and properties [13–23]. Granizo et al. [14] and Yip and van Deventer [17] each suggested that the calcium added to a geopolymeric system may initiate the formation of calcium silicate hydrate (C–S–H) gel in some cases, reinforcing the geopolymeric structure as shown by an improvement in compressive strength. This coexistence has recently been confirmed in NaOH-activated metakaolin-slag blends [20] and in alkali-activated fly ash-ordinary Portland cement (OPC) blends [24]. Lee and van Deventer have also investigated the addition of various inorganic salts to fly ash-based geopolymers, and found that a small amount of very finely powdered $CaCO_3$ increased the rate of initial setting [22], as well as the rate of strength development and ultimate strength attained [23].

Calcium carbonate materials such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are abundant and generally inexpensive natural minerals. The possible use of these bulk calcium carbonate materials in improving the mechanical properties of geopolymers will therefore be of great interest. The current work therefore investigates the effect of the addition of larger quantities of calcite and dolomite on geopolymerization, geopolymer microstructure, and on the long-term strength development and shrinkage properties of geopolymer mortars.

2. Experimental procedure

2.1. Materials

Metakaolin, obtained from ECC International under the brand name MetaStar 402, was used as the primary aluminosilicate source. Natural calcite and dolomite were purchased from Clayworks, Australia. The oxide compositions of these materials (Table 1) were obtained by XRF analysis (Siemens SRS 3000). The calcite used has a minor dolomite impurity, as well as a very small amount of an aluminosilicate mineral tentatively identified by XRD

---

* Corresponding author. Tel.: +61 3 8344 8755; fax: +61 3 8344 4153.
E-mail address: jprovis@unimelb.edu.au (J.L. Provis).

0958-9465/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconcomp.2008.07.004

Table 1
Chemical composition of metakaolin, calcite and dolomite in mass%, as determined by XRF

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	LOI
Metakaolin	0.1	54.8	40.4	0.8	0.4	2.7	0.1	1.1
Calcite	53.5	1.5	0.3	0.2	1.7	0	0	42.8
Dolomite	33.4	2.5	0.7	0.3	17.1	0.1	0.1	45.8

LOI: loss on ignition at 1000 °C.

as amesite, $(Mg,Fe)_2Al(Si,Al)_2O_5(OH)_4$ (powder diffraction file #037-0429). The only identifiable crystalline impurity in the dolomite is a very small amount of calcite. Particle size analysis using a Coulter LS130 optical size analyzer showed that the mean particle sizes of metakaolin, calcite and dolomite were 1.895, 17.13 and 34.99 μm, respectively. Washed sand with average size of 2 mm was used as an aggregate in mortar samples for compressive strength testing, at a mass ratio of sand to (metakaolin + carbonate mineral) of 3.0. Sodium silicate (Vitrosol N48) was supplied by PQ Australia (28.7% SiO_2, 8.9% Na_2O and 62.4% H_2O by mass; density 1370 kg/m^3). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the work.

2.2. Synthesis

Geopolymers were prepared by first dry-mixing metakaolin with calcite or dolomite (and sand for compressive strength testing samples), then combining with alkaline activating solutions in a mechanical mixer. Sodium silicate activating solutions were prepared at three different molar SiO_2/Na_2O ratios: Ms = 2.0, 1.5 and 1.2, by addition of solid NaOH to the commercial sodium silicate solution. The solids to solution mass ratios used were 0.69, 0.65 and 0.61 for Ms = 2.0, 1.5 and 1.2, respectively. Samples were synthesized with 0%, 20%, 40%, 60%, 80% and 100% replacement of metakaolin by calcite and dolomite. All samples were allowed to cure at 40 °C for 24 h in sealed molds, then demolded and aged at 25 °C prior to testing at specified times.

2.3. Analytical methods

Compressive strength testing (ELE International Auto Test Compression Machine) was performed according to the Australian Standard AS1012.9-1999, using the average of three mortar cylinders 50 mm diameter and 100 mm in height, and with approximately 5% experimental uncertainty in all strength data. While this standard is applicable strictly to the testing of concretes, it has previously been found to give good results for mortars also [21]. Samples were tested 2, 7, 28, 90, 360 and 560 days after synthesis. The length, and therefore relative shrinkage, of each mortar sample was also measured at 90 and 560 days. X-ray diffraction (Philips PW1800, Cu K_α radiation) was conducted on paste specimens using a scanning rate of 2°/min from 5 to 70° 2θ. A Philips XL30 scanning electron microscope (SEM), operated at 20 keV, was used to analyze the surface morphology of each paste specimen and to conduct elemental composition analyses (energy dispersive spectroscopy, EDS). A Dynavac sputter coater was used to coat samples with carbon.

3. Results and discussion

3.1. Calcite–geopolymer interactions at high alkalinity

Table 2 presents the compressive strengths of calcite-containing binders synthesized using an alkaline activator with Ms = 1.2, the most alkaline of the three activator compositions tested. The general trends observed from Table 2 are: (1) the addition of a moderate amount of calcite (~20%) gives an increase in compressive strength; (2) the addition of a larger amount (>40%) of calcite to the system gives a significant decrease in strength; and (3) strength development was generally close to complete within 2 days, with no significant change after 7 days. The observation of an optimum in strength at 20% calcite addition may also be compared with the results of a recent investigation of calcium silicate mineral addition to geopolymers [21], which showed that 20% addition of reactive calcium sources provided an enhanced strength, but that 40% was detrimental.

Table 2
Compressive strengths of matrices synthesized using Ms = 1.2 and activator/solids mass ratio = 1.63

Calcite content (mass% of solids)	Compressive strength (MPa)					
	2d	7d	28d	90d	360d	560d
0	35.4	36.2	38.4	38.6	37.5	38.2
20	42.1	44.4	45.4	46.1	46.8	48.5
40	23.3	23.7	24.1	24.2	26.0	25.8
60	14.1	15.0	15.8	16.3	14.9	14.4
80	8.0	11.8	12.1	12.3	11.3	11.4
100	<5.0	9.1	9.3	10.2	9.7	10.3

It is important to note that even though the compressive strength of the system with 100% of the metakaolin replaced by calcite (i.e., simply consisting of calcite + sodium silicate) is comparatively low (~10 MPa), the strength is consistent even after 560 days. It therefore appears that calcite is not chemically inert in the alkaline activated system. The binder in this sample is essentially a gelled and dried waterglass (sodium silicate) solution, containing a small amount of calcium and carbonate that have dissolved from the calcite surfaces under the prevailing alkaline conditions. It has previously been observed that the addition of a small amount of calcium causes gelation of silica sols [25], and it is likely that a similar effect is taking place here in the setting of these samples. This process is clearly slower than ‘true’ (aluminosilicate) geopolymerization, as shown by the fact that negligible strength is developed after 2 days. However, the fact that the strength was maintained up to 560 days suggests that a relatively stable binder phase was formed.

Fig. 1 shows the compressive strength and relative shrinkage of each calcite-containing sample with Ms = 1.2, at 90 and 560 days. It is seen that, in general, there is very little change in either of these properties from 90 to 560 days; each sample shrinks by up to 1% during this period, and the strength data for each sample at 90 and 560 days are almost unchanged. It is also seen that the extent of shrinkage increases monotonically with calcite addition, and that strength peaks at 20% calcite but decreases substantially beyond this. The shrinkage values shown in this plot are very much larger than would be acceptable in a mortar for construction use, however the aim of this study was not to design a commercially useable product but rather to use high-shrinkage mixes as a means of amplifying specific effects also observed in more ‘real’ systems. Metakaolin-based geopolymers, with a high water demand and high-Al gel phase, will in general show a higher degree of shrinkage than a fly ash-based mix, but are more straightforward to analyze for specific effects and so are the system studied here.

After 560 days, the high-calcite (>60%) samples are also observed to have voids on the surface with a diameters of up to 2 mm, and the concentration of these voids increased with increasing calcite addition. It is likely that these voids are related in some way to the shrinkage of the samples, although their exact cause is not yet clear. There also appears to be some correlation between strength and resistance to shrinkage. Of interest, though, is the fact that the degree of shrinkage is approximately linear with calcite addition, while strength approaches an asymptote at ~10 MPa

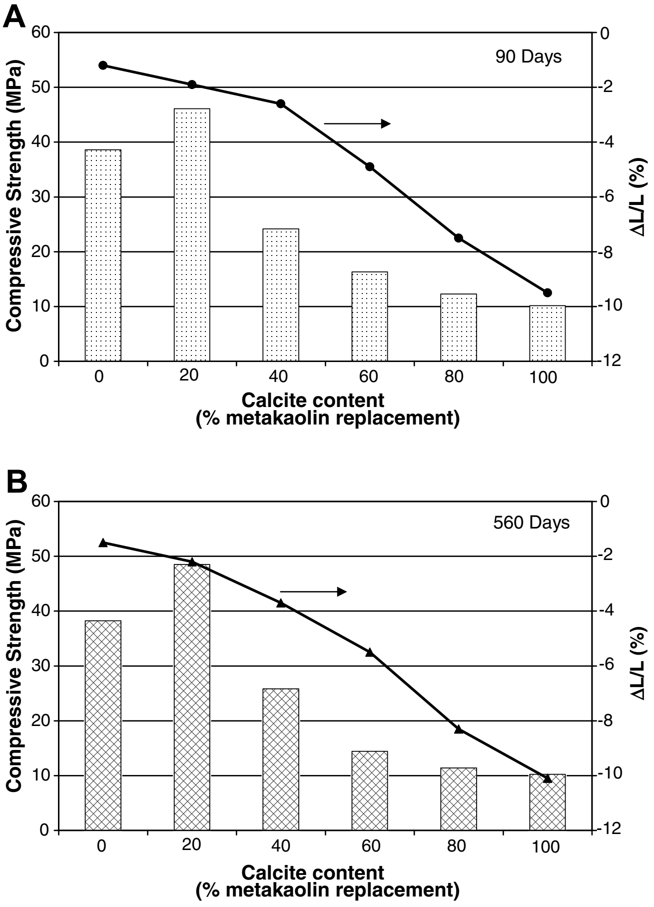

Fig. 1. Compressive strengths (columns) and relative shrinkage (points) of samples with Ms = 1.2 and varying calcite contents, at (A) 90 and (B) 560 days.

for 100% metakaolin replacement by calcite. This suggests that shrinkage is not the only factor that contributes to the reduction in mechanical strength as calcite addition increases.

Fig. 2 shows XRD diffractograms of the matrices synthesized using Ms = 1.2 and up to 60% calcite after 7 days. The sharp peaks in the metakaolin diffractogram are attributed to a partially reactive muscovite impurity [21]. These diffractograms show that there is still a significant amount of undissolved calcite present in each matrix. Furthermore, it is apparent that, as would be expected, the amount of unreacted calcite increases with increasing amount of calcite added to the system. Previous studies [13,26] showed that when metakaolin is activated by a sodium silicate solution, an amorphous alkaline aluminosilicate network (a geopolymer) is the dominant product formed. The presence of this geopolymer phase is often identified through the observation of a broad hump centered at around 28–30° 2θ [27]. The calculation of difference diffractograms (Fig. 3), as was done previously for calcium silicate mineral addition to geopolymers [21], shows that calcite dissolution is significant in systems with $\geqslant$40% calcite, but appears to be relatively limited in the 20% calcite sample. This indicates that surface binding of the calcite particles is the primary means by which the strength increase occurs in this sample, as the extent of calcium release into solution appears to be limited.

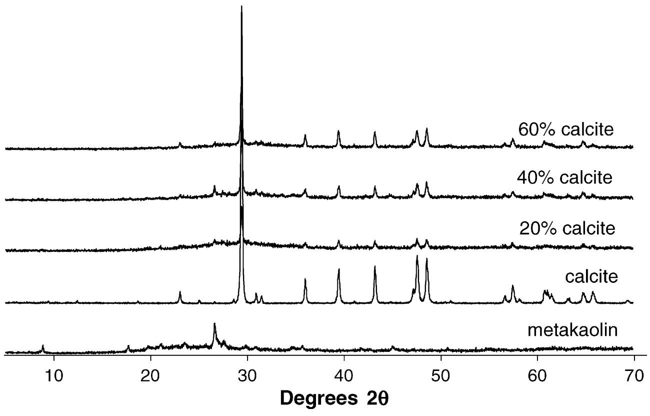

Fig. 2. X-ray diffractograms of source materials, and of geopolymers with various quantities of calcite (as marked) and Ms = 1.2, after 7 days.

The XRD results presented in Fig. 2 also suggest that despite the presence of carbonate ions associated with the dissolution of calcite, the calcium ions do not appear to take an active part in the synthesis of a geopolymeric binder. This is in agreement with previous findings [17,21] from when calcium silicate and calcium sulfate were added to a metakaolin-based geopolymeric system. However, the XRD data do not give strong indications of exactly how calcium ions originating from calcite will participate in geopolymerization. Given that there are no new crystalline phases identified in the final product, it is likely that calcium will either: (1) become part of the amorphous product at the end of the reaction (e.g. react with silicate in forming amorphous C–S–H [17], or be incorporated into the geopolymer gel) or (2) form crystalline precipitates (e.g. $Ca(OH)_2$, which may further react with CO_3^{2-} to form $CaCO_3$ again) at a concentration below the detection limits of XRD. Although the compressive strengths of geopolymers containing a moderate amount of calcite increase with time, XRD shows that no significant new crystalline phases are formed during up to 360 days' aging (data not shown). It should also be noted that the amount of calcite detected at 360 days is similar to the amount at 7 days.

Fig. 4 shows an SEM image of the 20% calcite, Ms = 1.2 sample. In contrast to the metakaolin plus ground granulated blast furnace slag (GGBFS) [21], cement [21], or calcium sulfate hemihydrate [13] systems studied previously, this sample displays no formation of a distinct C–S–H gel phase. It is important to note that the absence of a C–S–H phase was also observed for systems containing crystalline calcium silicate minerals including wollastonite, prehnite and anorthite [13,21]. Different types of particles found in

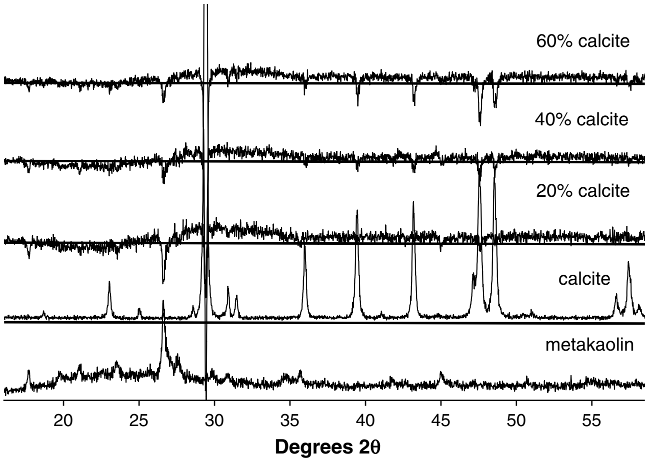

Fig. 3. Difference diffractograms, comparing XRD diffractograms of geopolymers containing different amounts of calcite with unreacted mixtures of calcite and metakaolin in the same proportions. All geopolymers have Ms = 1.2, and diffractograms were taken after 7 days of aging. The strong calcite (104) line at 29.7° 2θ is truncated vertically to enable other peaks to be seen.

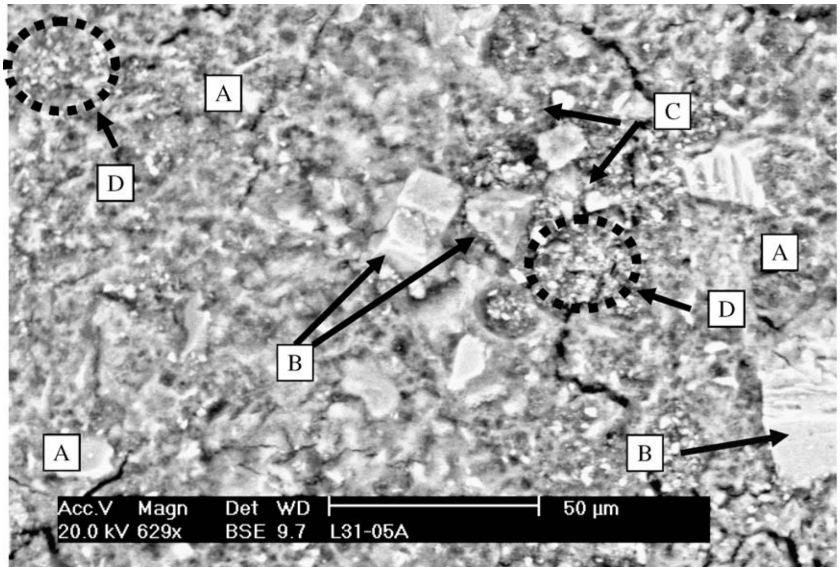

Fig. 4. SEM micrograph of a geopolymer with 20% calcite and Ms = 1.2 at 14 days. (A) geopolymeric gel; (B) raw calcite with traces of silica and alumina; (C) calcium precipitates including calcium hydroxide (<10 μm); (D) scattering of sodium aluminosilicate material with a high proportion of calcium (~2 μm).

the metakaolin-calcite geopolymer system were differentiated and identified using SEM-EDS analysis. Geopolymeric gel (marked in Fig. 4 with "A") was found to be the dominant component, however, a substantial number of calcium-containing particles were scattered throughout the geopolymeric gel. These particles include a large amount of unreacted calcite (particle "B" as indicated by rhombohedral morphology and EDS analysis), as was also observed in XRD. Other smaller calcium-containing particles (indicated by "C" and "D" in Fig. 4) were also found scattered throughout the geopolymeric gel ("A"). These particles are suggested to be products similar to calcium hydroxide ("C" with size <10 μm, Si and Al content each <1.0%) and some form of sodium aluminosilicate material with ~3% calcium ("D" with size ~2 μm) and similar Si and Al content to the geopolymer gel.

Despite the large variety of possible calcium-containing particles distributed throughout the geopolymeric gel, the calcium concentration of the gel itself was still found to be relatively low at around 1.5 mol%. This suggests that calcium leached from calcite did not play a significant part in geopolymerisation, i.e. forming a calcium-based geopolymeric gel (i.e. where Ca^{2+} acts as a charge-balancing cation to the Al^{3+} in 4-coordination). From a purely entropic standpoint, it is unlikely that Ca^{2+} is strictly excluded from the geopolymeric phase, however it appears to be present at low levels in this system.

Despite the low solubility of calcite in an alkaline activated system, calcite does participate in the reaction to some extent as evidenced by the consistent compressive strength of the 100% calcite sample. However, due to the slow release of calcium, calcite will play a more significant role as a surface-bound physical filler in improving the compressive strength of the binder where a significant amount of geopolymer gel is formed. The high shrinkage of the high-calcite samples (Fig. 1) corresponds well with this suggestion, as these samples will predominantly derive strength from the drying of the sodium silicate solution as it 'glues together' the poorly-reactive calcite particles, with some possible effect due to carbonation either from atmospheric sources or from ions released by dissolving calcite. The formation of geopolymer gel in the systems that do contain metakaolin reduces the shrinkage of these samples, however the calcite content is too high to enable formation of a genuinely continuous geopolymer gel, similar to the behavior observed when substituting 40% of the metakaolin with various calcium silicate minerals [21], which gives a reduced strength. The main contribution to the strength of the mortar synthesized using Ms = 1.2 is therefore attributed to the sodium aluminosilicate geopolymeric phase and its interaction with the calcite, which additionally acts as a physical filler/micro-aggregate.

3.2. Effect of activator composition

Figs. 5 and 6 show the compressive strength development of binders with different activating solutions (Ms = 1.2, 1.5 and 2.0), containing 20% and 40% calcite respectively. In this work, the SiO_2/Na_2O molar ratio is varied by changing the amount of sodium hydroxide used in the alkaline activator, meaning that the amount of silicate in the system remains constant. The compressive strength of the matrices increased with time in all cases, with the majority of strength gain achieved in <100 days. Also, and in agreement with other results reported recently for metakaolin geopolymers [17,28,29], the matrices synthesized using Ms = 1.5 exhibited a higher compressive strength than either Ms = 1.2 or Ms = 2.0.

Figs. 5 and 6 also show that the rate of strength development (as a proportion of final strength) decreases with increasing Ms ratio. This is more notable for the 40% calcite samples (Fig. 6) than for

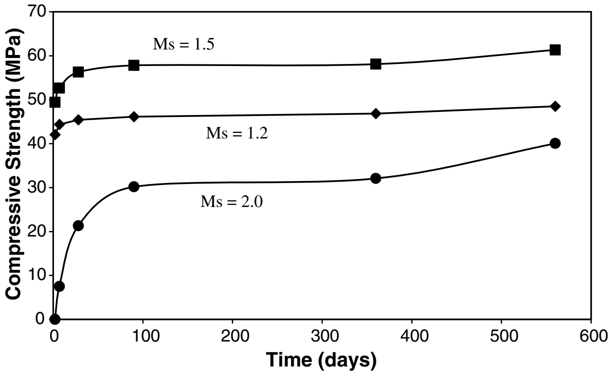

Fig. 5. Compressive strength development of geopolymers with 20% calcite and 80% metakaolin, using alkaline activators with Ms as marked.

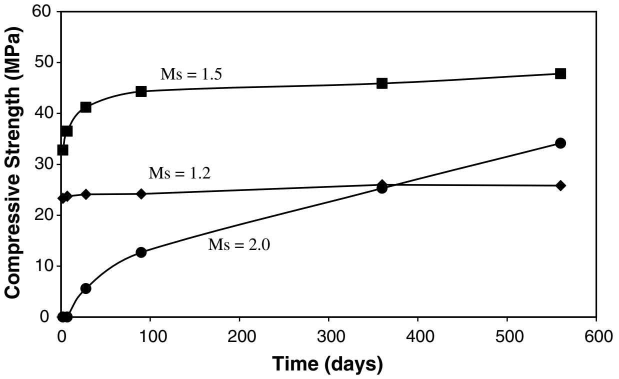

Fig. 6. Compressive strength development of geopolymers with 40% calcite and 60% metakaolin, using alkaline activators with Ms values as marked.

the 20% calcite samples (Fig. 5), and the final strengths of the 40% calcite samples are also lower as noted previously. These trends together show that the primary factor controlling strength development in these samples is the formation of geopolymer gel by dissolution/reprecipitation of aluminosilicate species derived from the metakaolin. Where too little metakaolin is present, strength development is poor because the gel network is highly disrupted by the relatively unreacted calcite particles. If too little alkali is present (Ms = 2.0), metakaolin dissolution is slow, giving a more gradual increase in strength. Where a lot of alkali is present (Ms = 1.2), dissolution and reprecipitation are relatively rapid, but the gel is not able to form an optimal structure for maximum strength because the system sets too rapidly. For Ms = 1.2 and 1.5, a high percentage of the final compressive strength of the binder was achieved at the early stage of synthesis (<7 days).

Fig. 7 provides a more detailed view of the correlation between geopolymer composition, strength, and shrinkage at 560 days. For binders containing the same amount of calcite but synthesized at different alkalinities, the degree of shrinkage follows the same trend as the compressive strength. For each of the three levels of calcite addition shown in this plot, there is an exact correlation between the samples showing the best dimensional stability and those with the highest strength. This does not indicate that shrinkage itself is specifically causing a reduction in geopolymer strength, as Fig. 1 shows that slight shrinkage is observed between 90 and 560 days but is accompanied in many cases by a small increase in strength. Rather, Fig. 7 shows that samples with a high degree of geopolymer gel formation display both high strength and good dimensional stability (low shrinkage). Samples with inadequate gel formation shrink as the poorly structured gel does not provide a continuous, highly-coordinated network throughout the sample, which correlates with a low strength.

3.3. Effects of dolomite

In order to obtain a better understanding on how the presence of calcium and carbonate ions impact geopolymerization, dolomite ($CaMg(CO_3)_2$) was used as a replacement for calcite in the system, to provide the potential for a supply of carbonate ions less specifically correlated with calcium release but from a similar chemical structure to that of calcite. Calcite and dolomite are very similar minerals; the calcite structure is composed of alternating layers of carbonate ions, CO_3^{2-}, and calcium ions, whereas in dolomite every second calcium layer is replaced by magnesium. The dolomite used here has a particle size roughly twice that of the calcite, which may also have some significance as discussed below.

Fig. 8 shows the compressive strength development of geopolymers with 20% replacement of metakaolin by dolomite. Similar to the case of calcite-substituted samples, the compressive strength of all samples increases with time and the highest compressive strength is achieved with Ms = 1.5. However, by comparing Figs. 5 and 8, the compressive strengths of dolomite-containing binders are found to be consistently lower than that of the calcite-containing binders at all alkaline conditions studied. The strength development of the dolomite-containing systems is also significantly slower, particularly in the Ms = 1.2 samples. No calcite-containing system with Ms = 1.2 and up to 40% calcite showed a significant increase in strength past 7 days, whereas the strength of the 20% dolomite system increases significantly up to 100 days. The decrease in strength in this sample from 360 to 560 days is within experimental uncertainty, and so may or may not be significant.

Similar to the metakaolin-calcite system, the XRD analysis (Fig. 9) of metakaolin-dolomite geopolymers reveals that a geopolymeric phase is the dominant product formed during alkali activation. This is again identified through the presence of an amorphous hump at around 20–35° 2θ, and is seen regardless of the alkalinity of the alkaline activator used. There also remains a significant amount of unreacted dolomite. Difference diffractograms (not shown) exhibit some slight reaction of dolomite, evidenced by diminution of the dolomite XRD peaks, and more notable at Ms = 1.2 than Ms = 2.0.

It may be suggested that the effectiveness of different minerals in improving the compressive strength of geopolymeric binders is due entirely to the physical hardness of the unreacted mineral particles as they act as a micro-aggregate in the system. However, based on this principle, the dolomite-containing binder would be expected to exhibit a higher compressive strength than that of a

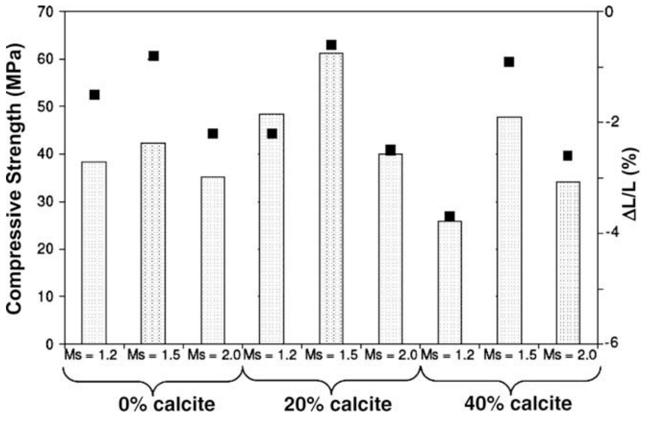

Fig. 7. The compressive strengths (columns) and relative shrinkage (points) of geopolymers with 0%, 20% and 40% calcite and different Ms values, after 560 days.

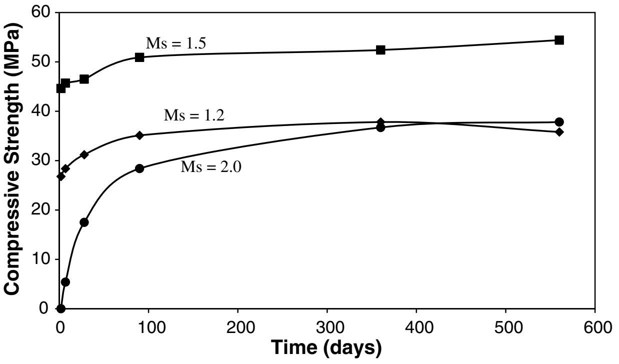

Fig. 8. Compressive strength development of geopolymers with 20% dolomite and 80% metakaolin, using alkaline activators with Ms values as marked.

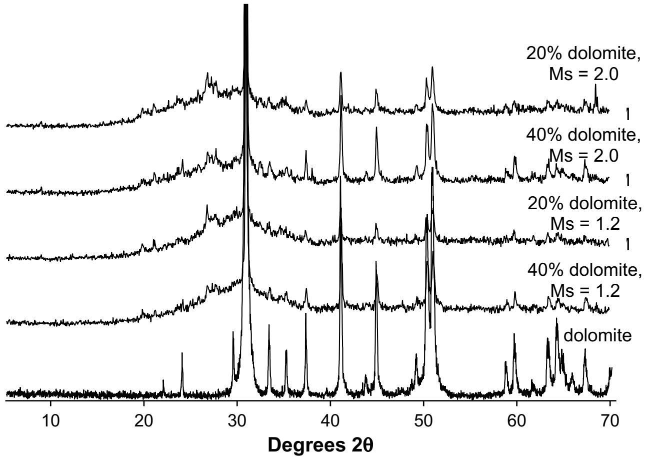

Fig. 9. X-ray diffractograms of geopolymers with 20% or 40% metakaolin replacement by dolomite at Ms = 1.2 and 2.0.

comparable calcite system for the same synthesis conditions, with the hardnesses of calcite and dolomite being 3 and 3.75 Mohs, respectively. This is clearly not the case, meaning that the micro-aggregate properties of the two materials are likely to be limited. The dolomite particles used were somewhat larger than the calcite particles, however their morphologies were not dramatically different. These differences are not likely to be sufficient to cause the significant differences between the two minerals in geopolymerization as observed by comparison of Figs. 5 and 8. The different sizes and therefore packing characteristics of the two minerals would be expected to become more significant at higher loadings, however will probably not have much effect at only 20% given that the fundamental particle sizes of both the metakaolin and the geopolymer gel are much smaller than either mineral. The consistently lower compressive strength achieved by dolomite-containing systems is therefore most likely attributed to either (1) a lower dissolved calcium level or (2) differences in surface properties of calcite and dolomite [30,31], which may affect the binding of the minerals to geopolymer gel.

It has previously been noted that it is possible for magnesium ions to replace some fraction of the calcium ions in calcium silicate hydrate gels, or in fact to form magnesium silicate hydrate gels [32,33]. However, the fact that no distinct C–S–H phase has been observed throughout this study indicates that this mechanism is unlikely to be significant here for magnesium. It is therefore possible that Mg^{2+} plays a similar role to Ca^{2+} in situations where it is found within the geopolymeric gel phase. Magnesium salts have been observed to have much less impact on geopolymerization kinetics than do their calcium counterparts, but do show some accelerating effect in geopolymeric setting which has been ascribed to nucleation effects [22]. It is not clear why this lesser effect should contribute to lower strength development in dolomite-containing systems than in the presence of calcite.

Previous work conducted by Lee and van Deventer [23] demonstrated that, in a fly ash-based geopolymeric system, ultimate strength increased without any apparent adverse effects when carbonate salts (K_2CO_3, $CaCO_3$ and $MgCO_3$) were added during synthesis. The current study has partially reinforced this observation, in that the presence of a small amount of carbonate material enhanced the long-term strength of a geopolymeric product, although at the cost of some additional shrinkage. It is most likely that some degree of surface binding of the geopolymer gel phase on the carbonate mineral particles is responsible for the increased strength of the 20% calcite and 20% dolomite samples over the pure metakaolin systems. Whether this is via a specific interaction involving bonds to carbonate sites or whether the alkaline earth cation layers are dominant is not clear, although the fact that calcite gives significantly stronger samples than dolomite indicates that the cation layers play at least some role.

4. Conclusions

The addition of a moderate amount (20% by mass) of calcite or dolomite was found to have a positive effect on the mechanical strength of a metakaolin-based geopolymeric binder. Excessive addition of calcite or dolomite to the geopolymeric gel (>20% by mass) was found to be detrimental, which is likely to be caused by a low degree of geopolymeric gel formation and connectivity. This is also responsible for the significant degree of shrinkage experienced in these systems. The highest-silica activating solution used (Ms = 2.0) showed a much slower rate of strength development than any other system tested, with strength still increasing notably at 560 days, while the more alkaline systems (Ms = 1.2 or 1.5) generally remained relatively constant after 2–7 days. Addition of calcite tends to lead to a stronger geopolymeric material than when dolomite is used. This is unlikely to be due to simple micro-aggregate effects, which suggests that the small amount of dissolution of the carbonate minerals that is observed is sufficient to release enough Ca^{2+} or Mg^{2+} to have a significant effect on the geopolymer gel structure. There are also potential differences induced by the different surface structures of the two minerals, which should be studied further in future investigations. Considering both this and the fact that no distinct C–S–H gel was observed, it appears probable that the alkaline earth cations are playing a limited structural role in the geopolymer gel. This is able to be observed in these systems because the concentration of these cations remains low enough to prevent phase separation to form a separate hydrated gel, with surface binding on the unreacted mineral particles contributing significantly to the increased strength of some of the carbonate-substituted samples.

Acknowledgements

The financial support received from the Australian Research Council (ARC), the Particulate Fluids Processing Centre (a Special Research Centre of the ARC), and the US Air Force Office of Scientific Research/Asian Office of Aerospace Research and Development (AOARD), under Contract AOARD 02-33, is greatly appreciated.

References

[1] Palomo A, Grutzeck MW, Blanco MT. Alkali-activated fly ashes – a cement for the future. Cement Concrete Res 1999;29(8):1323–9.
[2] Duxson P, Fernández-Jiménez A, Provis JL, Lukey GC, Palomo A, van Deventer JSJ. Geopolymer technology: the current state of the art. J Mater Sci 2007;42(9):2917–33.
[3] Davidovits J. Geopolymers – inorganic polymeric new materials. J Therm Anal 1991;37(8):1633–56.
[4] Duxson P, Provis JL, Lukey GC, van Deventer JSJ. The role of inorganic polymer technology in the development of 'Green concrete'. Cement Concrete Res 2007;37(12):1590–7.
[5] Granizo ML, Blanco MT. Alkaline activation of metakaolin – an isothermal conduction calorimetry study. J Therm Anal 1998;52(3):957–65.
[6] Rees CA, Provis JL, Lukey GC, van Deventer JSJ. Attenuated total reflectance Fourier transform infrared analysis of fly ash geopolymer gel ageing. Langmuir 2007;23(15):8170–9.
[7] Provis JL, van Deventer JSJ. Direct measurement of the kinetics of geopolymerisation by in-situ energy dispersive X-ray diffractometry. J Mater Sci 2007;42(9):2974–81.
[8] Palomo A, Alonso S, Fernández-Jiménez A, Sobrados I, Sanz J. Alkaline activation of fly ashes: NMR study of the reaction products. J Am Ceram Soc 2004;87(6):1141–5.
[9] Duxson P, Provis JL, Lukey GC, Separovic F, van Deventer JSJ. ^{29}Si NMR study of structural ordering in aluminosilicate geopolymer gels. Langmuir 2005;21(7):3028–36.
[10] Provis JL, van Deventer JSJ. Geopolymerisation kinetics. 2. Reaction kinetic modelling. Chem Eng Sci 2007;62(9):2318–29.

[11] Rahier H, van Mele B, Wastiels J. Low-temperature synthesized aluminosilicate glasses. 2. Rheological transformations during low-temperature cure and high-temperature properties of a model compound. J Mater Sci 1996;31(1):80–5.

[12] Wei S, Zhang Y-S, Wei L, Liu Z-Y. In situ monitoring of the hydration process of K-PS geopolymer cement with ESEM. Cement Concrete Res 2004;34(6):935–40.

[13] Yip CK. Ph. D. Thesis, University of Melbourne, Australia, 2004.

[14] Granizo ML, Alonso S, Blanco-Varela MT, Palomo A. Alkaline activation of metakaolin: effect of calcium hydroxide in the products of reaction. J Am Ceram Soc 2002;85(1):225–31.

[15] Alonso S, Palomo A. Calorimetric study of alkaline activation of calcium hydroxide-metakaolin solid mixtures. Cement Concrete Res 2001;31(1):25–30.

[16] Alonso S, Palomo A. Alkaline activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio. Mater Lett 2001;47(1-2):55–62.

[17] Yip CK, van Deventer JSJ. Microanalysis of calcium silicate hydrate gel formed within a geopolymeric binder. J Mater Sci 2003;38(18):3851–60.

[18] Yip CK, Lukey GC, van Deventer JSJ. The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. Cement Concrete Res 2005;35(9):1688–97.

[19] Dombrowski K, Buchwald A, Weil M. The influence of calcium content on the structure and thermal performance of fly ash based geopolymers. J Mater Sci 2007;42(9):3033–43.

[20] Buchwald A, Hilbig H, Kaps C. Alkali-activated metakaolin-slag blends – performance and structure in dependence on their composition. J Mater Sci 2007;42(9):3024–32.

[21] Yip CK, Lukey GC, Provis JL, van Deventer JSJ. Effect of calcium silicate sources on geopolymerisation. Cement Concrete Res 2008;38(4):554–64.

[22] Lee WKW, van Deventer JSJ. The effect of ionic contaminants on the early-age properties of alkali-activated fly ash-based cements. Cement Concrete Res 2002;32(4):577–84.

[23] Lee WKW, van Deventer JSJ. The effects of inorganic salt contamination on the strength and durability of geopolymers. Colloid Surf A 2002;211(2-3):115–26.

[24] Palomo A, Fernández-Jiménez A, Kovalchuk GY, Ordoñez LM, Naranjo MC. OPC-fly ash cementitious systems. Study of gel binders formed during alkaline hydration. J Mater Sci 2007;42(9):2958–66.

[25] Gaboriaud F, Nonat A, Chaumont D, Craievich A. Structural model of gelation processes of a sodium silicate sol destabilized by calcium ions: combination of SAXS and rheological measurements. J Non-Cryst Solids 2005;351(4):351–4.

[26] Palomo A, Glasser FP. Chemically-bonded cementitious materials based on metakaolin. Br Ceram Trans J 1992;91(4):107–12.

[27] Provis JL, Lukey GC, van Deventer JSJ. Do geopolymers actually contain nanocrystalline zeolites? – a reexamination of existing results. Chem Mater 2005;17(12):3075–85.

[28] Duxson P, Provis JL, Lukey GC, Mallicoat SW, Kriven WM, van Deventer JSJ. Understanding the relationship between geopolymer composition, microstructure and mechanical properties. Colloids Surf A 2005;269(1-3):47–58.

[29] Duxson P, Mallicoat SW, Lukey GC, Kriven WM, van Deventer JSJ. The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers. Colloids Surf A 2007;292(1):8–20.

[30] Wright K, Cygan RT, Slater B. Structure of the $(10\bar{1}4)$ surfaces of calcite, dolomite and magnesite under wet and dry conditions. Phys Chem Chem Phys 2000;3:839–44.

[31] Fenter P, Zhang Z, Park C, Sturchio NC, Hu XM, Higgins SR. Structure and reactivity of the dolomite (104)-water interface: New insights into the dolomite problem. Geochim Cosmochim Acta 2007;71(3):566–79.

[32] Glasser FP. Fundamental aspects of cement solidification and stabilisation. J Hazard Mater 1997;52(2-3):151–70.

[33] Brew DRM, Glasser FP. Synthesis and characterisation of magnesium silicate hydrate gels. Cement Concrete Res 2005;35(1):85–98.