



Influence of calcium compounds on the mechanical properties of fly ash geopolymer pastes

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ABSTRACT

The influence of calcium compounds (CaO and Ca(OH)₂) on the mechanical properties of fly ash based geopolymers has been studied. Calcium compounds were substituted in fly ash at 1, 2 and 3 wt%, respectively. Curing of the geopolymers was performed at ambient temperature (20 °C) and 70 °C. Addition of calcium compounds as a fly ash substitute improved mechanical properties for the ambient temperature cured samples while decreasing properties for the 70 °C cured samples. Seven days compressive strength of the ambient temperature cured samples increased from 11.8 (2.9) to 22.8 (3.8) MPa and 29.2 (1.1) MPa for 3% CaO and 3% Ca(OH)₂ additions, respectively.

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1. Introduction

Fly ash is usually described as the finely divided residue that results from the combustion of ground or powdered coal that is transported by flue gases from the combustion zone to the particle removal system [1]. Fly ash consists of fine oxide particles and compounds such as quartz, hematite, mullite and amorphous particles. The types and relative amounts of incombustible matter in the coal determine the chemical composition of fly ash. Fly ash arising from burning sub-bituminous coals is referred to as ASTM Class C fly ash or high-calcium fly ash as it typically contains more than 20% of CaO. On the other hand, fly ash from the bituminous and anthracite coals is referred as ASTM Class F fly ash or low-calcium fly ash [2]. A promising research outcome developed in last decade is low-calcium fly ash based geopolymer cement and concrete [2–5]. Its preparation includes activation in an alkaline medium and curing at moderate temperatures between 50 and 100 °C. Geopolymers prepared by using the low-calcium fly ash exhibit high compressive strength, excellent resistance to sulphate attack, good acid resistance, low creep, and minimal drying shrinkage [4]. For the geopolymers low-calcium ash is preferred as a source material rather than high-calcium fly ash as the presence of high amounts of calcium may interfere with the polymerisation process and alter the microstructure [6]. On the other hand, the addition of 4 wt% of high-calcium containing slag can greatly improve the compressive strength of fly ash based geopolymers [7].

Adding 3–5% quicklime to a fly ash/cement system has been performed and revealed that it accelerates the hardening process and increases the strength [8]. It has been reported that metakaolin and ground granulated blast furnace slag subjected to alkaline activation has both geopolymeric and C–S–H gels forming simultaneously [9,10]. Strength development of Portland cement involves the formation of C–S–H and calcium hydroxide and it is believed that the C–S–H component gives strength to the binder. On the other hand calcium hydroxide is highly unstable, which will further react with carbon dioxide in air to form calcium carbonate. The presence of the calcium hydroxide and subsequent carbonation is the main cause of concrete deterioration [10].

It is apparent that the addition of calcium to fly ash based geopolymer will affect the amount of alkaline liquid required and the final chemical and mineralogical composition. In fact one of the most important aspects of adding calcium to a geopolymer system is its ability to harden at ambient temperature. In this paper we examine and compare effects of calcium compounds on the physical properties of fly ash based geopolymer paste cured at ambient and elevated temperatures.

2. Experimental procedures

Collie fly ash from Western Australia was used as the geopolymer precursor, the chemical composition of this fly ash has been described elsewhere [12]. Sodium silicate D-51 (PQ Australia Pty Ltd.) and 14M sodium hydroxide solution were used as the activating solutions. The chemical composition of the sodium silicate solution by mass was Na₂O = 14.7%, SiO₂ = 29.4% and water = 55.9%. The bulk geopolymer composition had a Si:Al ratio

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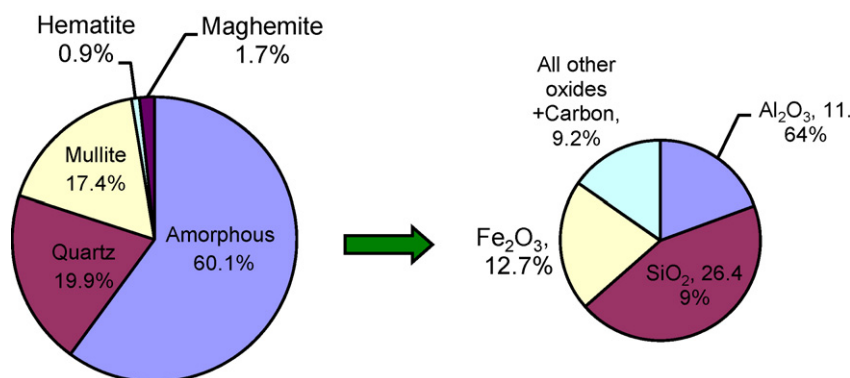


Fig. 1. Phase composition of the Collie fly ash (left) and chemical composition of the amorphous component (right) [12].

of 2.3 and a Na:Al ratio of 0.88. The geopolymer composition was adopted from Rangan and co-workers [2,4] although we specifically used the amorphous composition of the fly ash to determine the correct amount of activator. The method used to determine the amorphous component is described by Williams [13] and comprises subtracting the content of the crystalline component measured by quantitative XRD from the bulk composition measured by XRF. The phase composition of the fly ash and chemical composition of the amorphous phase are shown in Fig. 1.

Since we used only the content of the amorphous component of the fly ash to calculate the composition of the geopolymer, the alkali content was less than that used by Rangan and co-workers [2,4]. Analytical grade calcium oxide (CaO) and calcium hydroxide Ca(OH)₂ from Ajax Chemicals and Asia Pacific Speciality Chemicals Limited, respectively were used as calcium sources. All chemical reagents were used as supplied, thus without any pre-treatment. One, 2 and 3 wt% calcium oxide was substituted for fly ash in the geopolymer mixture. For calcium hydroxide 1.3, 2.6 and 3.9 wt% was added to maintain the same molar content of Ca²⁺ in both mixtures. The quoted molar values of Ca²⁺ represent an additional calcium component and ignores the 1.74 wt% calcium present in the fly ash. Samples with added calcium set faster as observed when using class C fly ash to manufacture geopolymers [14]. Therefore, in order to keep the pastes workable we added de-ionised water, but the weight ratio of Ca²⁺/H₂O was kept constant in both mixtures. The composition of different geopolymer pastes synthesised in this study is shown in Table 1.

The starting materials for the designated geopolymer composition were mixed in a Hobart mixer for 10 min. Samples were then placed in plastic moulds (25 mm diameter and 50 mm long) which were capped prior to curing at ambient temperature (20 °C) or 70 °C. After 24 h those samples cured at 70 °C were removed from the oven and de-moulded. Geopolymers with calcium were hard enough to de-mould after 1 day, while non calcium added samples were still soft. However, to maintain consistent experimental conditions all samples cured at ambient temperature were de-moulded after 3 days. Compressive strength of the samples was measured after 7 days using an Instron-5500R testing machine. The uncertainty in the measurement was taken as the standard deviation of the compressive strength of at least four samples.

The sectioned surface of the geopolymer pastes were carbon or gold coated prior to microstructure imaging with a Philips XL30 SEM (scanning electron microscope) and analysis of elemental composition with an energy dispersive X-ray spectrometer (EDS, Oxford Instruments). The XRD patterns were recorded on a Siemens D-500 with Bragg-Brentano geometry using a Cu K α source with a post sample K β filter. XRD patterns were collected from 10° to 120° 2 θ (step size 0.02° 2 θ and speed 0.4°/min). Zincite was used as an internal standard. For Rietveld analysis Rietica 1.7.7 software was

used. Densities and apparent porosities of the sectioned geopolymers were measured by the Archimedes principle using de-ionised water. However, because of possible leaching of Na ions into the water they should only be considered as relative values [12]. Values in brackets in either mechanical properties or porosities indicate the standard deviation of the measured values.

3. Results and discussion

3.1. Effect of calcium addition on the mechanical properties of the geopolymer

Fig. 2 shows the effect of the adding calcium on the compressive strength of geopolymer. Calcium compounds improved the mechanical strength of samples cured at ambient temperature while reducing the strength of samples cured at 70 °C suggesting the possibility of different hardening mechanisms. The data also indicates that the addition of Ca(OH)₂ is more beneficial than CaO in terms of compressive strength.

Sample density and apparent porosity are summarised in Table 2.

Samples cured at 70 °C exhibited lower density and higher apparent porosity relative to ambient temperature cured samples.

In ceramics mechanical strength usually increases with decreasing porosity and the same behaviour was also observed in metakaolin based geopolymer [15]. However, the opposite trend of decreasing compressive strength with decreasing apparent porosities has been observed in geopolymers made from calcined fly ash and was explained in terms of the incomplete geopolymerisation [12].

A possible reason for the higher porosity of the 70 °C cured samples may be linked with the water evaporation from the

Table 1
Composition of different geopolymer pastes synthesised in this study.

Mix designation	Solid mix composition (wt%)			Curing temperature (°C)
	Fly ash	CaO	Ca(OH) ₂	
W-20	100	–	–	20
W-70	100	–	–	70
C1-20	99	1	–	20
C2-20	98	2	–	20
C3-20	97	3	–	20
C1-70	99	1	–	70
C2-70	98	2	–	70
C3-70	97	3	–	70
CH1-20	98.7	–	1.3	20
CH2-20	97.4	–	2.6	20
CH3-20	96.1	–	3.9	20
CH1-70	98.7	–	1.3	70
CH2-70	97.4	–	2.6	70
CH3-70	96.1	–	3.9	70

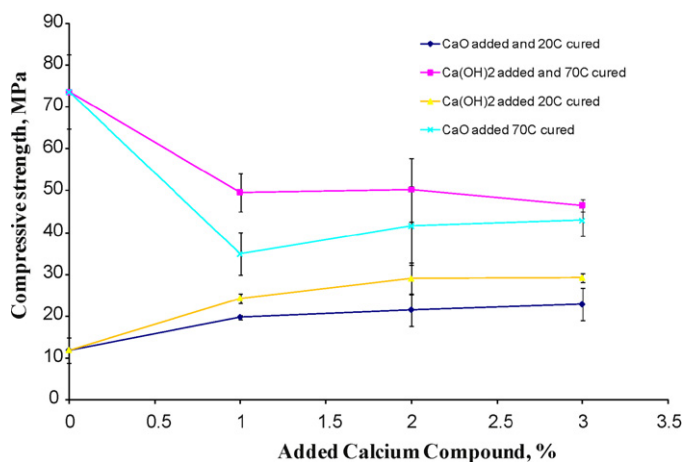


Fig. 2. Compressive strength versus wt% added calcium.

geopolymer matrix during the curing. Aluminosilicate network formation by the polycondensation and geopolymerisation reaction releases water, but most of it resides within the cavities of the geopolymer structure resulting in low shrinkage. However, curing at elevated temperatures not only accelerates dissolution of the aluminosilicate species and subsequently the polymerisation reaction but may also lead to evaporation of the water from the geopolymer matrix consequently leading to higher apparent porosity. Therefore, it is proposed that addition of a calcium compound for ambient temperature cured samples increases the geopolymerisation rate which is supported by higher compressive strength results and associated higher porosity values. This assumption of the higher water evaporation for elevated temperature cured samples has not been verified by measuring the residual water content in the plastic container after curing.

Fig. 3 shows compressing stress–strain curves for selected samples. With no added calcium the ambient temperature cured sample exhibited approximately 2.2% plastic deformation (strain). However, with calcium addition plastic deformation reduced to approximately 1.6% more like a brittle ceramic structure.

The higher compressive strength of samples with added calcium hydroxide cured at ambient temperature relative to samples with added calcium oxide suggests that the $\text{Ca}(\text{OH})_2$ is the reactive constituent in the geopolymer mixtures. It would appear incomplete hydration of the CaO in the alkaline medium to form $\text{Ca}(\text{OH})_2$ [16] results in about 20% lower compressive strength for samples with added CaO .

Fig. 4 shows an SEM micrograph of the fly ash based geopolymer (W-20) cured at ambient temperature. At higher magnification (Fig. 4b) it is apparent that there has been incomplete dissolution of

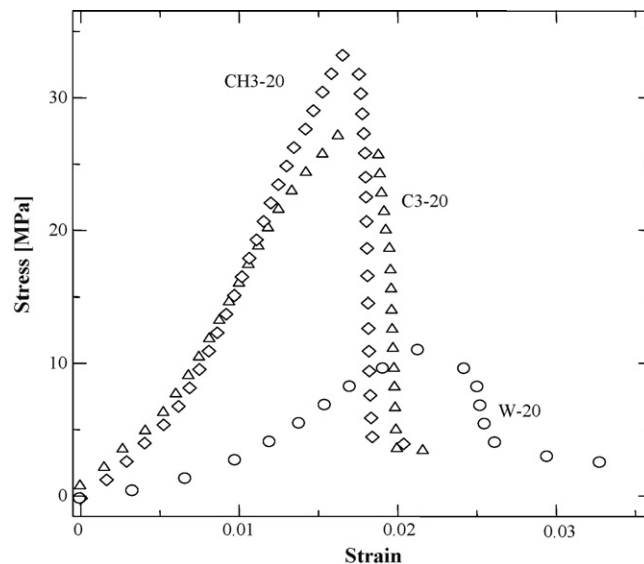


Fig. 3. Stress–strain curves for selected samples cured at ambient temperature.

the fly ash spheres indicating that low temperature curing of the geopolymer is not adequate for development of a structurally sound product. Efflorescence also appeared on the surface of this sample after de-moulding. It took several days for this sample to harden pointing to ongoing dissolution and development in strength over time in a manner similar to that occurring in concrete [17].

Fig. 5 shows an SEM micrograph of the CH3-20 sample (3 wt% $\text{Ca}(\text{OH})_2$, cured at ambient temperature). There is less amorphous gel and a smaller number of partially dissolved fly ash spheres. The microstructure of the geopolymer with added CaO shows a microstructure similar to the $\text{Ca}(\text{OH})_2$ sample (not shown).

Cracks observed in SEM micrographs are believed to be due to sample preparation.

Microstructural and X-ray mapping examination in the SEM did not reveal evidence of a C–S–H phase that may have contributed to increased compressive strength of the samples with added calcium. Moreover calcium was distributed homogeneously within the matrix. It is a common view that the pozzolanic reaction in fly ash–cement occurs slowly at low temperatures [18]. However, fast solidification rate and increased compressive strength of the samples with added calcium suggests that the pozzolanic reaction in fly ash–alkaline liquid occurs much faster. Simplified geopolymerisation reactions can be described as initial dissolution of the aluminium and silicon from fly ash followed by their polymerisation, gelation and hardening. Van Deventer and co-workers suggested that presence of calcium in solid waste materials will provide extra nucleation sites for precipitation of dissolved species and cause rapid hardening [19,20].

Fig. 6 shows micrographs of geopolymers with no added calcium and 1 and 3 wt% calcium cured at ambient temperature. From the micrographs it can be seen that addition of calcium causes a fine more homogeneous microstructure while for geopolymer with no added calcium there is evidence of partially reacted fly ash spheres. Increasing the calcium content caused a more compact and finer microstructure indicating that calcium is acting as a seeding or precipitating element. If this is the case then it is likely that calcium containing compounds were formed by interaction of the calcium hydroxide with dissolved aluminosilicates or sodium silicate solution. The probable reaction products would be calcium silicate hydrate (C–S–H) or calcium aluminosilicate either in amorphous or poorly ordered crystalline form which would be difficult to detect by XRD. There are several reports on the formation of the C–S–H phase within the geopolymer binder in the presence

Table 2
Density and apparent porosities.

Sample	Density (g/cm^3)	Apparent porosity (%)
W-20	2.08(0.01)	5.2(0.4)
W-70	1.85(0.02)	16.1(0.3)
C1-20	2.02(0.01)	9.2(0.1)
C1-70	1.89(0.01)	15.4(0.7)
C2-20	2.02(0.01)	8.4(0.3)
C2-70	1.82(0.01)	15.2(0.5)
C3-20	1.96(0.01)	10.4(0.3)
C3-70	1.79(0.01)	16.4(0.1)
CH1-20	2.00(0.03)	7.5(0.3)
CH1-70	1.84(0.01)	14.6(0.7)
CH2-20	1.99(0.01)	9.5(0.1)
CH2-70	1.78(0.02)	15.4(0.6)
CH3-20	1.97(0.0)	11.1(0.6)
CH3-70	1.76(0.03)	16.8(0.8)

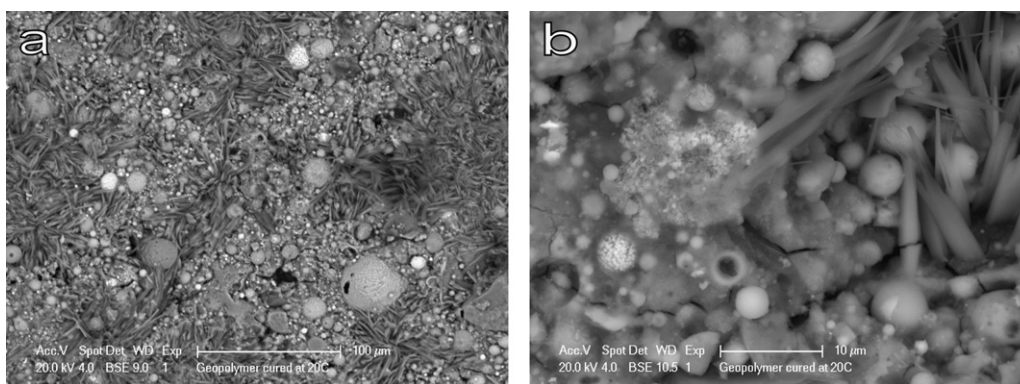


Fig. 4. SEM micrograph of fly ash based geopolymer cured at ambient temperature, (a) low, (b) high magnification.

of significant amounts of calcium [9–11], but also a report which describes the absence of the C–S–H phase in a geopolymeric system with addition of 50% of $\text{Ca}(\text{OH})_2$ [21]. Moreover, MacKenzie et al. suggested that $\text{Ca}(\text{OH})_2$ is incorporated into the geopolymer network [21]. In other words it is not clear what the exact mechanism is when calcium causes hardening of geopolymer. It obviously depends on many parameters including the aluminosilicate precursors, alkaline activator type and their concentrations and curing temperature.

The fine microstructure of the 3% CaO geopolymer (Fig. 6) indicates that the heterogeneous nucleation and crystallisation mechanism caused by the presence of the calcium salts suggested by Lee and van Deventer may be plausible [20]. Granizo et al. noted that the presence of $\text{Ca}(\text{OH})_2$ favoured the formation of products that gave rigidity to the geopolymer paste [22]. They concluded that formation of a C–S–H phase in favour of a network structure forming alkali material depends on the concentration of the alkaline liquid [22].

From published results it can also be concluded that noticeable amounts of crystalline or poorly crystalline C–S–H phase is usually formed at higher Ca concentrations. Present experiments exploited less than 5% CaO including the CaO present in the raw fly ash precursor which would be considered as a low Ca concentration. Therefore, it is likely that the partially precipitated compound may have a composition of calcium aluminosilicate or calcium silicate hydrate in amorphous form.

The hardening mechanism for samples with added calcium and cured at ambient temperature may be as follows: Since the amount of calcium hydroxide is not high it will readily react with sodium silicate or sodium hydroxide solution to precipitate amorphous or poorly ordered crystalline calcium silicate hydrate or calcium aluminosilicate hydrate phases causing a water defi-

ciency in the alkaline mixture which will raise its alkalinity. The higher alkalinity of the dissolution medium should allow higher dissolution of existing aluminosilicates and thus a greater rate of polycondensation–geopolymerisation. If hardening occurs with this mechanism then there will be contributions to mechanical strength from both the precipitated compound and the geopolymeric gel.

However, the question that arises is, if the addition of a calcium compound results in an improvement in mechanical properties for ambient temperature cured samples then why is the reverse effect observed for samples cured at elevated temperatures?

If heterogeneous nucleation–crystallisation occurs from the liquid phase and the geopolymeric gel formation the mechanical strength will not reduce with curing temperature.

Samples with added calcium shows finer microstructure than non-calcium added samples (Fig. 7). The microstructure of the calcium added sample cured at 70 °C resembles the microstructure of the sample with added calcium cured at 20 °C. This would suggest that the main factor contributing to a reduction of the mechanical properties is likely to be related to the structure of the geopolymeric gel rather than the heterogeneous nucleated compound.

We believe that there has been partial substitution of calcium into the aluminosilicate structure and this process occurs beneficially at elevated temperatures. Although elevated temperature curing will result in fast dissolution, the presence of the calcium possibly does not allow formation of the three-dimensional geopolymeric network and consequently reduces mechanical properties in comparison to samples with no added calcium. Such a mechanism also agrees with observations made by MacKenzie et al. who described the possible presence $\text{Ca}(\text{OH})_2$ in geopolymeric networks [21]. Unfortunately, MacKenzie et al. did not perform experiments to elucidate the influence of the Ca substi-

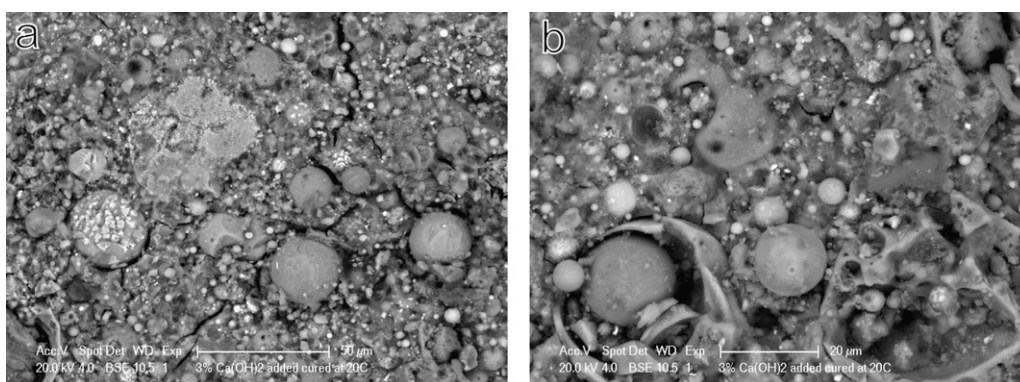


Fig. 5. SEM micrograph of fly ash based geopolymer with 3% $\text{Ca}(\text{OH})_2$ cured at ambient temperature, (a) low, (b) high magnification.

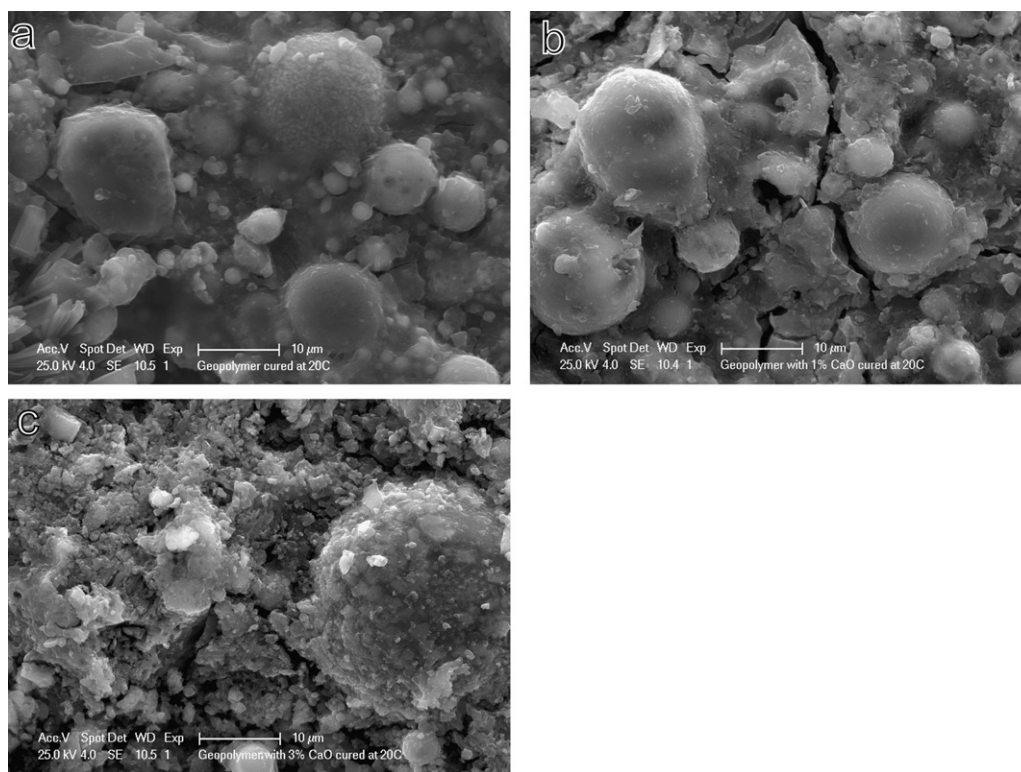


Fig. 6. (a) Microstructure of the non-calcium added and (b) 1% and (c) 3% CaO added geopolymers cured at ambient temperature.

tution in the geopolymeric network on compressive strength of the samples.

For the current experimental conditions there are possibly 2 concurrent hardening mechanisms taking place that include heterogeneous nucleation–crystallisation from the liquid phase and co-existence of the aluminosilicate geopolymeric phase. There is evidence that curing temperature has a strong influence on the hardening mechanisms. Since the hardening resulted from two concurrent mechanisms plus the amorphous nature of the heterogeneous nucleated compound, it is difficult to separate these mechanisms. However, it is obvious that at elevated temperature the curing aluminosilicate geopolymeric phase is the main contributor to hardening behaviour while at ambient temperature the two mechanisms may contribute equally. Buchwald et al. observed ongoing hardening in samples with 5–30 wt% $\text{Ca}(\text{OH})_2$ after curing at 40 °C at 28 and 111 days [23]. For the experiment described in this paper compressive strengths were measured after 7 days preventing direct comparison with the findings of Buchwald et al. [23] due to differences of experimental conditions. However, results of Buchwald et al. [23] indicate that ongoing hardening may occur in our samples.

3.2. Characterisation of efflorescence

All samples cured at ambient temperature exhibited efflorescence. However, no efflorescence was observed on samples cured at 70 °C. Efflorescence is believed to be one of the indications of insufficient geopolymerisation reaction or excess alkali [12]. In order to clarify the nature of the efflorescence some fragments of efflorescence were scratched off the surface of the C3-20 sample and analysed by SEM–EDS (Fig. 8). The efflorescence crystals were found to be composed of Na, O and P. The carbon peak in the spectrum comes from the substrate and is not present in the crystals. The appearance of the phosphorous was surprising because efflorescence is commonly described as sodium carbonate hydrate

($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) or sodium carbonate [12,24]. XRD patterns of the crystals are shown in Fig. 9 with clear evidence of the presence of the sodium phosphate hydrate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) in all ambient temperature cured samples with some minor unidentified peaks. The phosphate efflorescence is assumed to originate from the 1.3% P_2O_5 in the Collie fly ash. However, it is not clear if the phosphorous in the fly ash exists as a solid solution or a separate compound. It has been suggested that the phosphorous bearing compound apatite may be present in coal [25]. The product of apatite calcination is calcium phosphate. Calcium phosphate usually shows some solubility in ammonium citrate solution [26], which is usually assumed to be a weak alkaline medium [27]. Therefore, it is assumed that a strong alkaline medium such as sodium hydroxide or sodium silicate would readily dissolve calcium phosphate and enabling it to recrystallise as sodium phosphate efflorescence. It is apparent, that the composition of the efflorescence strongly depends on the chemical composition of the fly ash. We have previously observed sodium carbonate hydrate efflorescence in preliminary calcined Collie fly ash based geopolymer [12]. However, the present experiment indicates that the efflorescence is sodium phosphate. Therefore, it is proposed that the efflorescence depends not only on the chemical but also mineralogical composition and crystallinity of the fly ash. We have proposed that calcination of the fly ash leads to surface crystallisation of fly ash particles reducing its dissolution in alkaline liquid [12]. As a result we observed different efflorescence compounds in untreated and calcined fly ash based geopolymers.

One of the unique properties of geopolymers is their ability to immobilize hazardous heavy metals by incorporating them into the structure [16,28,29]. Davidovits has suggested that phosphates are able to form geopolymer structures such as poly(sialate-siloxo)/phosphate or phospho-siloxonate geopolymer [30]. But, phosphorous containing efflorescence indicates that in ambient temperature cured geopolymer, with excess alkaline medium phosphorous is not immobilized within the geopolymer structure and

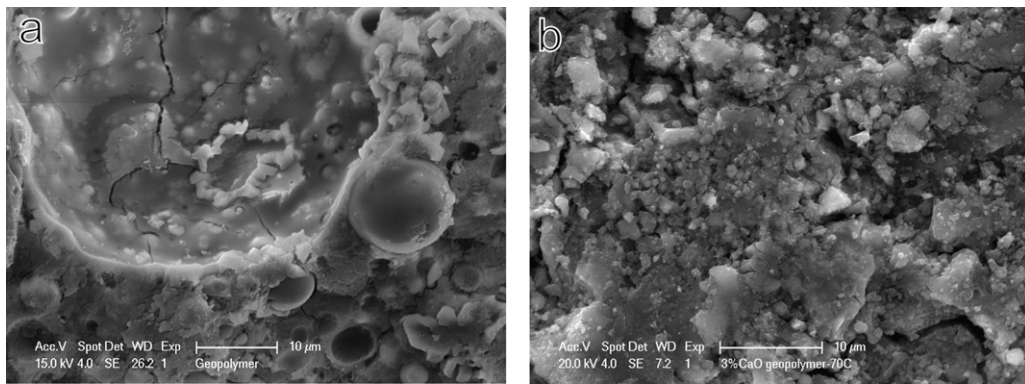


Fig. 7. Microstructure of geopolymer cured at 70 °C with (a) as supplied fly ash and (b) with addition of 3% CaO.

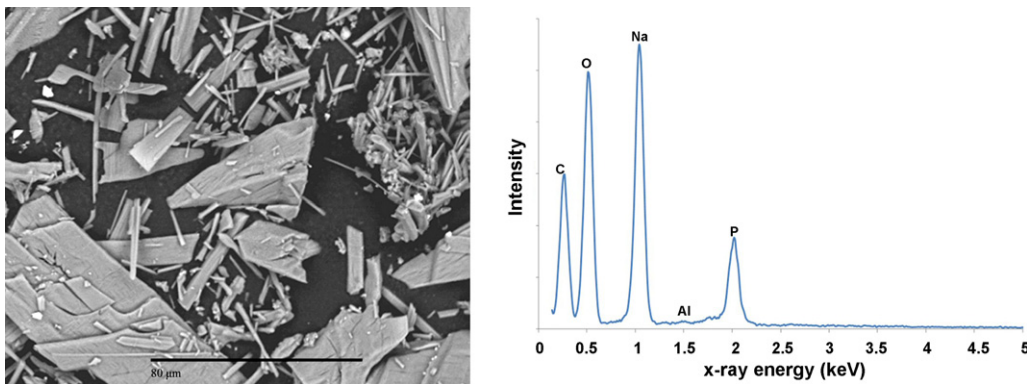


Fig. 8. SEM micrograph of efflorescence crystals and associated X-ray spectrum (back scattered electron image, 20 kV, sample is not coated).

moreover it will be expelled from the geopolymer as sodium phosphate.

Since, the geopolymers cured at elevated temperature exhibited no efflorescence we conclude that a greater level of geopolymerisation occurred leading to complete incorporation of the Na and P atoms into geopolymer structure.

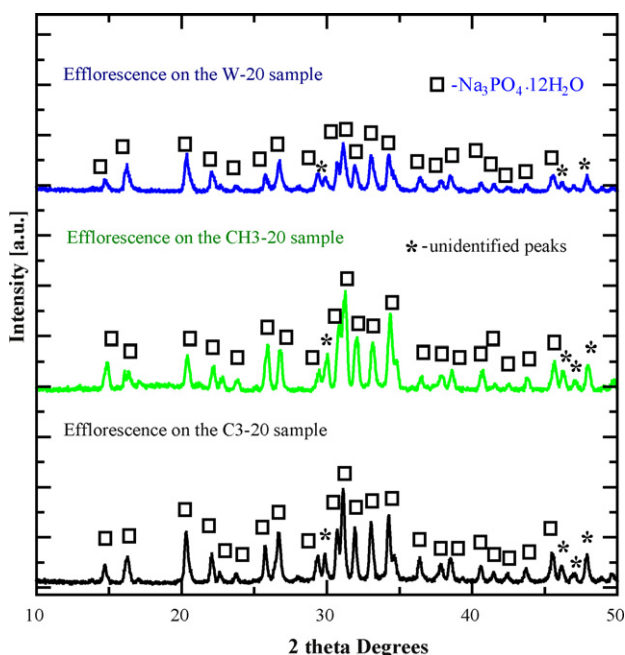


Fig. 9. XRD patterns of efflorescence from ambient temperature cured samples.

4. Conclusions

Addition of the calcium compounds CaO and Ca(OH)₂ improves mechanical properties of the fly ash based geopolymers cured at ambient temperature. Calcium hydroxide is considered to be a more beneficial additive than calcium oxide. Calcium compound addition is likely to result in precipitation of calcium silicate hydrate or calcium silicate aluminate hydrate phases and at the same time improve the dissolution of the fly ash in the alkaline medium and subsequently the geopolymerisation reaction. Calcium compound addition reduces mechanical properties of geopolymer cured at elevated temperatures. This can be explained by insufficient development of a three-dimensional geopolymeric aluminosilicate network caused by the presence of calcium in the aluminosilicate network. Ambient temperature cured samples exhibit efflorescence because of the presence of the excess alkaline solution caused by incomplete dissolution of the fly ash spheres and low dissolution rate. Efflorescence formed on the Collie fly ash based geopolymer is sodium phosphate hydrate and the composition of the efflorescence depends on the chemical and mineralogical composition of the fly ash.

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