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Characterisation of class F fly ash geopolymer pastes immersed in acid and alkaline solutions

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ABSTRACT

Acid and alkaline resistance of class F fly ash based geopolymer pastes has been investigated. As prepared geopolymers showed high solubility in both strong alkali and acid solutions. Calcination of the fly ash based geopolymers at 600 °C resulted in a decrease of amorphous component from 63.4 to 61.6 wt.%. However, the solubility of the Al, Si and Fe ions in 14 M NaOH and 18% HCl after 5 days immersion decreased from 1.3 to 16-fold in comparison to as prepared geopolymer samples. Calcination of the geopolymers also resulted in a 30% reduction in compressive strength. Acid and alkali resistance of the geopolymers investigated strongly depends on mineralogical composition change of the calcined geopolymer. Partial crystallisation of non-reacted fly ash particles in the geopolymer decreases its solubility in acid and alkali solutions.

1. Introduction

Geopolymers are a class of materials prepared by low temperature curing of alkali activated aluminosilicates. The chemical structure of geopolymers can be described as cross linked aluminium silicate networks with charge balancing alkaline cations and water in their internal pores and cavities. Thermal, mechanical and chemical properties of the geopolymers are strongly dependent on the starting materials from which they are prepared [1]. Typical starting materials include fly ash, slag and metakaolin.

Developed in the last decades of the 20th century, low calcium fly ash (class F) based geopolymers are attracting great interest due to their high compressive strength, low shrinkage and an excellent resistance to sulphate attack, good acid resistance and low creep [2,3]. It has been estimated that the price of fly-ash based geopolymer concrete is about 10–30% cheaper than that of ordinary Portland cement (OPC) concrete [2]. At the same time, other authors have concluded that the cost of the geopolymer concrete is slightly higher than that of the OPC concrete [4]. Investigations have shown that class F fly ash geopolymer can be used to manufacture structural elements such as concrete columns [3] and railway sleepers [5] and confirmed their applicability as structural members. Being able to withstand acid attack is important for structural materials where such attack may occur in the aggressive environment of sewers, mining, mineral processing, acid rain or acid ground-water [6,7]. It has been reported that class F fly ash based geopolymer is more durable against acid attack than OPC paste or mortar [6,8]. On the other hand concretes that are resistant to alkaline soil conditions are necessary in construction applications where high levels of sodium carbonate can increase the soil pH to 9 or higher [9]. It has also been reported that high concentration (8 M) NaOH causes structural damage to geopolymer [9]. It is expected that the acid and alkali resistant behaviour of fly ash based geopolymer depends on both the chemical and mineralogical composition of the fly ash and the extent of the geopolymerisation reaction.

Fly ash based geopolymers are a complex compound and usually contain non-reacted amorphous fly ash spheres beside the geopolymeric gel and mineral impurities. Solubility of the cations in acid or alkali environments will determine the structural integrity of the geopolymers. For instance, the iron compounds of fly ash (amorphous iron, hematite, magnetite and maghemite) do not significantly participate in the geopolymerisation reaction [10] and are vulnerable to acid attack which could leave pores after dissolution. Solubility of Al in acidic medium is high, while in alkali both Si and Al are expected to dissolve, though the solubility of Si is higher than Al. Therefore, un-reacted fly ash spheres (amorphous aluminosilicates) in geopolymer are susceptible to both alkali and acid attack. Thus the acid or alkaline resistance behaviour depends on the content and amount of amorphous materials in the geopolymers. Crystalline compounds are generally more resistant to chemical attack than their amorphous counterparts. Therefore, to make

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geopolymer materials more resistant to alkali or acid environments it is necessary to reduce or modify the non-reacted fly ash particles in geopolymer. Although, geopolymeric gel is itself amorphous its formation in a highly alkaline environment makes it more resistant than the non-reacted fly ash particles in terms of acid and alkali resistance.

Previously we have shown that calcination of fly ash at a moderate temperature (500 and 800 °C) caused surface crystallisation and consequently reduced its reactivity [11]. Such partial crystallisation of the surface of amorphous component within geopolymer pastes may also increase its acid and alkaline resistance. The aim of the present research is to elucidate acid and alkaline resistant behaviour of calcined geopolymer pastes.

2. Experimental procedure

2.1. Materials and testing procedure

Geopolymers were synthesised from Collie fly ash from Western Australia. A detailed description of the chemical and mineralogical composition of Collie fly ash and geopolymer preparation procedures are presented in previous papers [11,12]. The phase composition of Collie fly ash is presented in Table 1 while Table 2 shows the chemical composition of the fly ash and amorphous component.

The geopolymer formulation was based only on the amorphous aluminosilicate component of the fly ash. Geopolymer pastes were prepared by mixing fly ash with the alkaline liquids to achieve a composition Si:Al = 2.3, Na:Al = 0.88 and water:geopolymer solid = 0.19, which showed the highest compressive strength for geopolymers prepared from same fly ash [11]. The alkaline compounds were 14 M NaOH and D-grade sodium silicate solution (Na_2O – 14.7%, SiO_2 – 29.4%, H_2O – 55.9%, density 1.50–1.53 g/cm^3) from PQ Australia Pty Ltd. The solutions were mixed for 1 min using a Hobart mixer. The fly ash was then added and mixed for 10 min and placed in cylindrical plastic moulds with 25 mm diameter and 52 mm height. Samples were then cured at 70 °C for 1 day, demoulded and cut with a diamond saw to a height of 50 mm for compressive strength testing.

For a surface crystallisation of non-reacted fly ash spheres, the geopolymer pastes were calcined at 600 and 1000 °C for 6 h with a heating and cooling rate of 2.5 °C/min. Photographs of as prepared (A), 600 °C (B) and 1000 °C (C) calcined geopolymer samples are shown in Fig. 1. After exposure to 1000 °C sample colour changed to a deep red and was found to have large cracks. Both the colour change and cracking are believed to be due to oxidation of amorphous iron present in the fly ash as well as expansion of the quartz [13]. For samples calcined at 600 °C the colour change was not so obvious and cracking was minor. The severe cracking present in samples calcined at 1000 °C was considered to be unacceptable so no further experiments were undertaken on these samples.

For acid and alkaline resistance measurements, samples were separately immersed in 18% HCl and 14 M NaOH solutions within 1 week of calcination. The concentrations of the acid and alkali used in the current experiments are much higher than those reported in previous experiments [6,9]. Structural elements with the ability to withstand strong acids and/or strong alkali would be in great demand in many industrial applications. Acid resistance trials were performed in a glass beaker filled with 500 ml of acid and four cylindrical samples of 25 mm diameter and 52 mm height (about 25 cm^3 volume each sample and approximately 5:1 liquid:geopolymer volume ratio). Leaching was performed at ambient temperature with the solution agitated by a magnetic stirrer. After 1–5 days samples were removed from the beaker and dried at ambient temperature for 24 h. Alkali resistance trials were performed in the same manner with 500 ml sodium hydroxide in a Teflon beaker. The ratio of acid or alkali volume to geopolymer sample volume was the same for all batches. Once samples were immersed in acid or alkali no further adjustment to pH was made for the duration of the test.

Table 1
Phase composition of Collie fly ash.

Component	(wt.%)
Amorphous component	55.6 ± 0.7
Quartz (low)	24.7 ± 0.7
Mullite	13.7 ± 0.2
Maghemite (C)	3.1 ± 0.2
Hematite	1.3 ± 0.1
Magnetite	1.7 ± 0.1

Table 2
Chemical composition of fly ash and its amorphous component.

	Fly ash (wt.%)	Amorphous component (wt.%)
SiO_2	51.50	22.78
Al_2O_3	23.63	13.94
Fe_2O_3	15.30	9.95
LOI	1.78	
CaO	1.74	
TiO_2	1.32	
P_2O_5	1.31	
MgO	1.20	8.95
K_2O	0.84	
Na_2O	0.38	
SO_3	0.28	
MnO	0.13	

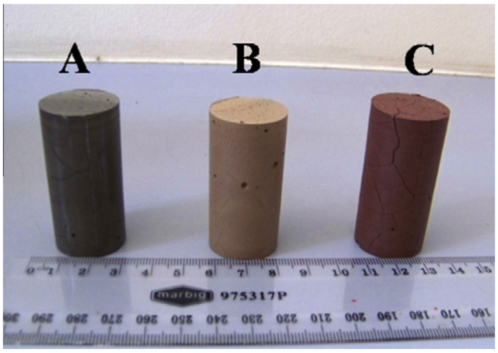

Fig. 1. As prepared geopolymer (A), 600 °C (B) and 1000 °C (C) calcined geopolymer samples.

Samples were removed from acid and alkaline solutions after designated days and washed with tap water until the pH of the wash water became neutral. Weight change of the acid and alkali treated samples was determined after 1 day drying at ambient temperature. Initial weights of samples were measured just before the acid and alkali immersion. As prepared geopolymer exhibited weak resistance against alkaline leaching which was apparent as the solution became very cloudy. Chemical analysis of acid and alkali leached solutions were performed by ALS Chemex Pty Ltd. with an ICP–AES analyser. Samples used for the chemical analysis were denoted as *R-nA*, *R-nAl*, *C-nA*, *C-nAl*, where *R* denotes the as-prepared geopolymer, *C* means calcined geopolymer, *n*-leached days, *A* and *Al* represents the acid or alkaline environments, respectively.

2.2. Characterisation

The phase composition of the Collie fly ash and crushed calcined geopolymer were determined by Rietveld refinement with X-ray diffraction (XRD) data. Rietveld refinement was performed using Bruker AXS Topas version 4. Zincite (ZnO) was used as an internal standard. XRD patterns were collected with a Bruker D8 Advance diffractometer using Cu Kα radiation (40 kV and 40 mA), LynxEye detector between 10° and 120° 2θ, with a step size of 0.02° 2θ and collection speed of 0.4°/min. Samples were rotated during pattern collection.

Fracture surfaces of the samples were studied with a Zeiss EVO 40XVP scanning electron microscope. Compressive strength of the as-prepared and chemically treated geopolymer samples was determined with an EZ-50 Universal testing machine (Lloyd Instruments). The uncertainty in the measurement was taken as the standard deviation of the average of the compressive strength of four samples.

3. Results and discussion

3.1. Effect of calcination on mineralogical content of geopolymer

Table 3 shows phase composition of the as-prepared and calcined geopolymer samples determined by quantitative XRD.

Table 3
Phase composition of as-prepared and calcined geopolymer. Values in brackets indicate the uncertainty.

Component (wt.%)	As-prepared geopolymer	Calcined geopolymer
Amorphous	63.4 (0.7)	61.6 (0.7)
Quartz (low)	19.7 (0.8)	20.7 (0.8)
Mullite	11.2 (0.2)	12.0 (0.2)
Maghemite C	3.0 (0.1)	2.0 (0.2)
Magnetite	1.4 (0.1)	1.4 (0.1)
Hematite	1.3 (0.1)	2.2 (0.1)

Minor changes in the phase composition resulted from the calcination of the geopolymer with levels generally within experimental uncertainty. The minor change in composition of the geopolymer is consistent with observations of calcined Collie fly ash (500 °C and 800 °C) which also showed less than 3% change in amorphous content [11]. The amorphous component in geopolymer is believed to be the sum of residual or non-reacted fly ash and geopolymeric gel formed by the geopolymerisation reaction. But, it is not clear how much of the amorphous component reacted with the alkali to form geopolymeric gel and thus how much of amorphous aluminosilicate is still present in the microstructure.

It is speculated that surface changes of the geopolymeric gel and non-reacted fly ash spheres occur due to calcination but the volume of the material changed is below XRD detection limits. Fig. 2 shows SEM micrographs of the as-prepared and 600 °C calcined geopolymers.

The fracture surface of the as prepared sample shows features typical of fly ash based geopolymers i.e. undissolved fly ash spheres distributed within geopolymeric gel. The microstructure of the calcined geopolymer resembles the microstructure of as prepared geopolymer except the presence of additional porosity within the geopolymeric gel. The porosity in the geopolymeric gel is thought to arise from dehydroxylation caused by a release of structural water. It is apparent that the calcination did not cause a significant change within the geopolymer microstructure except increased porosity. The observed microstructural changes of the geopolymer sample are in agreement with the changes in the mineralogical composition determined by XRD (Table 3).

3.2. Leaching behaviour of the samples

Fig. 3 shows percentage weight change of the as-prepared and calcined geopolymers after immersion in acid or alkali. Calcination of the geopolymers at 600 °C caused about 12% weight reduction which is in agreement with Rickard's findings where he examined the thermal response of the same fly ash based geopolymer [13]. Weight reduction of the geopolymers occurred as result of dehydration and dehydroxylation of geopolymeric gel.

Acid or alkali leaching caused weight reduction of the as-prepared geopolymer samples, while weight gains were observed in calcined geopolymer samples. Weight gains of the calcined samples are believed to be due to permeation of liquid phases into pores previously occupied by alkaline pore water before calcination. The retention of alkali or acid in the pores of geopolymer is likely to continue microstructural degradation which might be decreased by preliminary rinsing in water before acid and alkali immersion. The calcined and alkali treated samples gained more weight than the calcined and acid treated samples which is thought to be related with the relatively higher density of the sodium hydroxide solution compared with HCl. As-prepared geopolymer exhibited weak resistance against alkali attack, forming a muddy surface layer after just 1 day immersion in 14 M NaOH while calcined geopolymer did not show any surface change. Immersion of as-prepared and calcined geopolymer in 18% HCl did not result in any visible changes.

Fig. 4 shows the concentration of dissolved elements from the geopolymer samples after immersion in acid or alkaline solutions. Although, Na is part of the geopolymer structure its concentration has not been displayed after alkali immersion because of the difficulty in distinguishing sodium leached out from the geopolymer structure and sodium from the alkaline solution. The ICP results show high concentrations of Fe, Al and Ca after acid exposure which increases with time. The high concentration of Fe in solution is consistent with the high level of amorphous and crystalline Fe oxides in the fly ash. It is clear that in acid the amorphous components will react preferentially, consequently amorphous iron and un-reacted fly ash spheres were leached from the geopolymer.

When Fe concentration is plotted (not shown here) versus time the gradient is almost the same (i.e. the rate of Fe dissolution is the same) for as-prepared and calcined geopolymer (same for Ca and Al) suggesting that the same dissolution mechanism is taking place. The only difference is the starting point. As we have previously stated partial surface crystallisation of the geopolymeric gel and non-reacted fly ash spheres occur due to calcination but the volume of the material changed is below XRD detection limits. It is proposed that the difference in the amount of Fe, Al and Ca leached from the as prepared and calcined geopolymer is due to the partial crystallisation of the surface of amorphous constituents in the geopolymer.

Generally acid and alkali leaching characteristics of the geopolymers present here can be described as:

1. *As-prepared geopolymer in acid solution* – High level of Fe, Al and Na leached from samples that increase with time in a linear function.
2. *Calcined geopolymer in acid solution* – The calcination has resulted in a slight decrease in the level of Fe leached from the samples but the amount leached is still strongly correlated with time. The amount of Al and Na leached from samples has dropped significantly.
3. *As-prepared geopolymer in alkali solution* – Si is found to leach at high levels, increasing with time while leach rates for Al and Fe are lower. Leaching rate of the Si and Al after 5 days of immersion is a little bit lower than those after 3 days immersion. At present, we do not have any explanation on this behaviour.

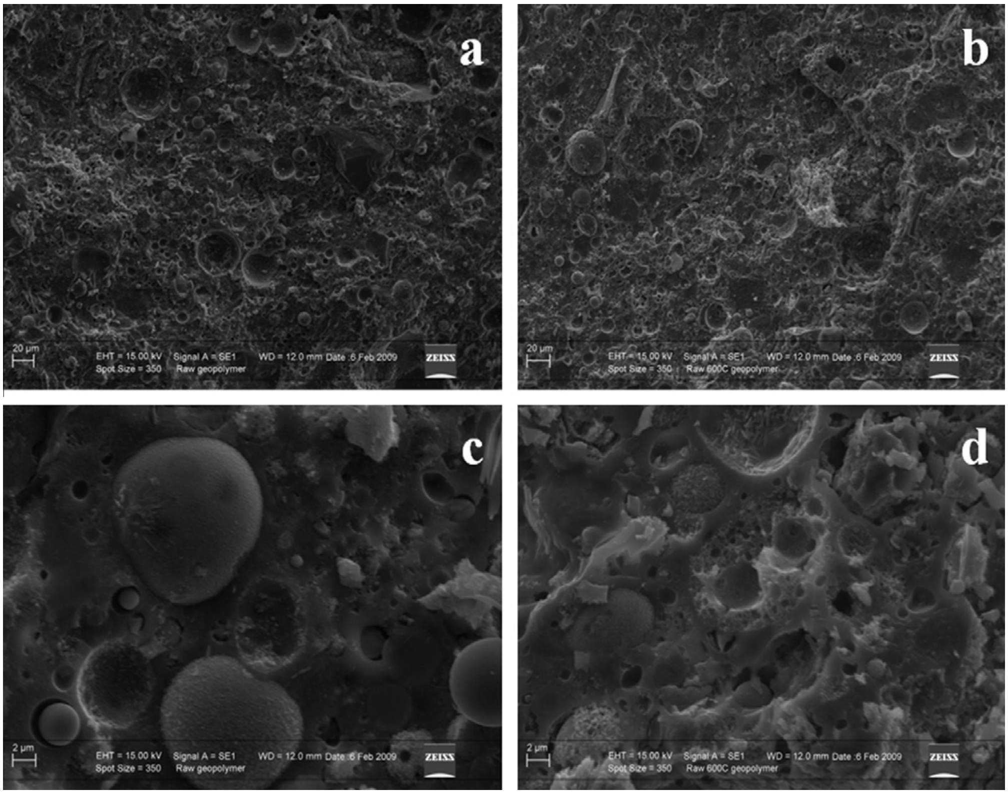

Fig. 2. SEM micrographs of fracture surfaces of as-prepared (a, c) and 600 °C calcined (b, d) geopolymer samples.

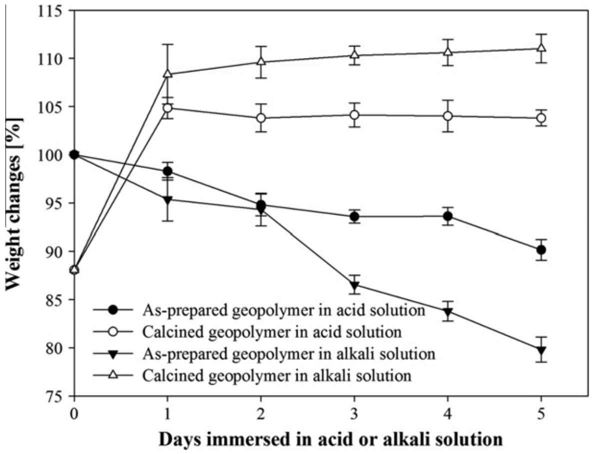

Fig. 3. Weight changes of samples after immersion in acid or alkali solution.

4. *Calcined geopolymer in alkali solution* – Leach rates for all elements have dropped to less than 1 g/L even for 5 days immersion with Si exhibiting the biggest drop.

Based on the increase of Na leached from the as-prepared geopolymer in acid with time it can be speculated that the geopolymeric gel as well as the non-reacted fly ash was also affected by the acid.

Although, Rietveld analysis revealed that the change of the mineralogical composition of as-prepared and calcined geopolymer is not significant their resistance to acid and alkali improves. Alkali resistance improves remarkably especially in terms of Si dissolution.

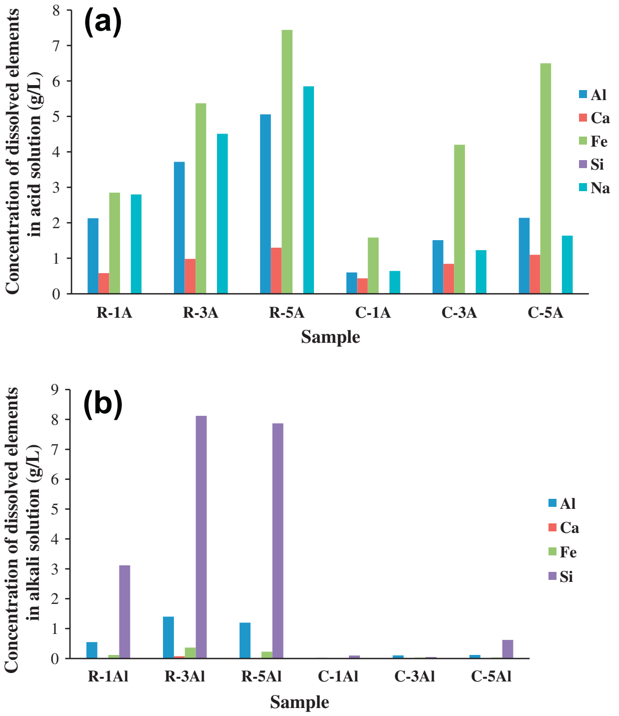

Fig. 4. Concentration of elements dissolved from geopolymer samples, (a) in acid solution; (b) in alkali solution.

XRD patterns of the acid and alkali leached geopolymers (Fig. 5) indicate that the crystalline components are not affected by the acid or alkali leaching.

NaCl was identified in the acid leached samples clearly originating from neutralisation reaction of sodium hydroxide with the

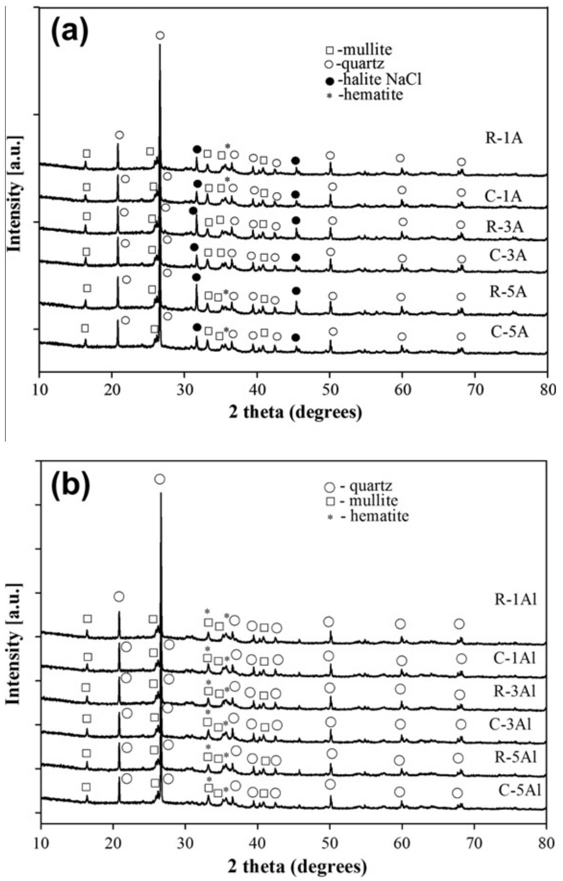

Fig. 5. XRD patterns of the acid (a) and alkali (b) leached geopolymers.

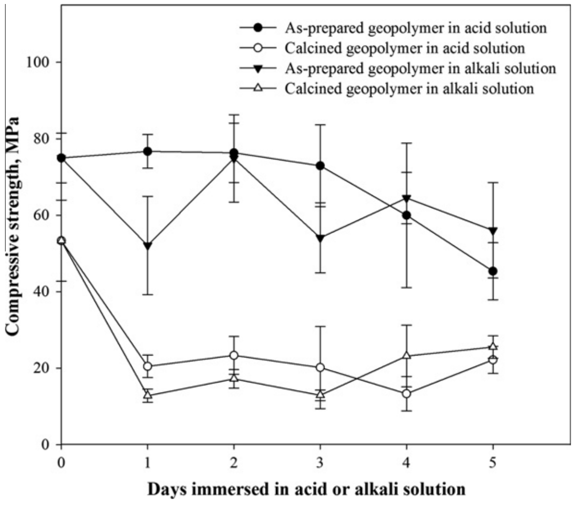

Fig. 6. Compressive strength of geopolymer samples.

hydrochloric acid. Generally, the intensity of this peak is higher in as-prepared geopolymer indicating a higher level of available sodium possibly in the pore water.

Fig. 6 shows compressive strength measured after acid and alkali immersion. An obvious outcome of calcination is an almost 30% reduction in compressive strength probably related to the presence of cracks. Unfortunately the compressive strength of the alkali immersed geopolymers had high standard deviations making it difficult to draw any conclusions with confidence. Nevertheless, compressive strengths of the acid and alkali immersed as-prepared geopolymers are higher than calcined geopolymer samples even after 5 days of continuous immersion. This result is unexpected because of the high leaching rate of the cations from as-prepared geopolymers which could leave behind a porous microstructure and a concomitant lower compressive strength. However, it would appear that any porosity created by acid or alkali dissolution of as prepared sample is less damaging to the microstructure than cracking induced by calcinations. It is also possible the drop in compressive strength of the geopolymer with calcination was caused not only by cracking, but also loss of structural water of the geopolymeric gel.

Calcination of the Collie fly ash based geopolymers will result in several processes such as dehydration, dehydroxylation, polymorphic transition of quartz with expansion and a partial oxidation of the amorphous iron. A number of these processes will cause internal stresses leading to cracking and loss of compressive strength. For Collie fly ash the outcome of the calcination process is undesirable but for fly ash with lower iron oxide content the effect of calcination will be considerably milder. In addition, much of the quartz can be removed by sieving so that the impact of this phase on cracking due to calcination can also reduced. Rickard has demonstrated that geopolymer pastes produced by using Australian fly ashes with lower iron and quartz contents exhibited a ceramic like behaviour (i.e. increased in compressive strength with calcination at 1000 °C without cracking [14]) and is thus expected to show beneficial acid and alkaline resistant properties. Nevertheless a 50 MPa geopolymer prepared from the Collie fly ash, even after calcination, can still be used for many applications.

4. Conclusions

Acid and alkali resistance of fly ash based geopolymer pastes can be increased substantially by calcination at 600 °C. Calcining geopolymer reduced compressive strength by approximately 30%, because of crack appearance and loss of the structural water. Calcination of geopolymer reduces solubility of the Al and Si cations in 14 M NaOH from 1.4 g/L and 8.1 g/L to 0.1 g/L and 0.5 g/L, respectively. Exposure of the non calcined and calcined samples to 18% HCl reduces solubilities of Al and Fe cations from 5.1 g/L and 7.4 g/L to 2.1 g/L and 6.6 g/L, respectively. Acid and alkaline resistance of the calcined geopolymer increases due to the partial crystallisation of the surface of amorphous constituents in the geopolymer. Acid or alkali resistance behaviour of the geopolymers can also be improved by regulating the amount of quartz impurity and level of iron oxides in the fly ash thus assisting the geopolymer calcination process.

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