



Effect of fly ash preliminary calcination on the properties of geopolymer

J. Temuujin*, A. van Riessen

Centre for Materials Research, Department of Imaging and Applied Physics, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

ARTICLE INFO

Article history:

Received 13 June 2008

Received in revised form 7 August 2008

Accepted 14 August 2008

Available online 27 August 2008

Keywords:

Fly ash

Calcination

Geopolymer

Mechanical properties

ABSTRACT

The influence of preliminary calcination of fly ashes on the geopolymerisation process has been studied. Preliminary calcination at 500 and 800 °C causes decarbonation of the fly ash while it also leads to a decrease of the amorphous content of the fly ashes from 60 to 57%. Geopolymer prepared using raw fly ash exhibited a compressive strength 55.7(9.2) MPa, while for 500 and 800 °C calcined samples it reduced to 54(5.8) and 44.4(5.4) MPa, respectively. The decrease in compressive strength of the geopolymers is discussed in terms of partial surface crystallisation of the fly ash particles. Reactivity of the fly ash also has been correlated with the shrinkage rate and presence of efflorescence on the surface of geopolymers.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

As demand for concrete as a construction material increases the production of Portland cement will also increase. However, production of Portland cement liberates a considerable amount of greenhouse gas as a result of decarbonation of limestone in the kiln during manufacturing of cement and the combustion of fossil fuels. Furthermore, Portland cement is also among the most energy-intensive construction materials, after aluminium and steel [1]. Therefore, the search for an alternative binder to replace Portland cement binder is important endeavour. Initially, Glukhovskiy followed by Davidovits suggested that artificially synthesised alkaline activated aluminosilicate cementitious systems can have excellent durability and may exhibit many other useful properties such as high compressive strength, low shrinkage, acid and fire resistance, etc. [2,3]. Importantly, such so-called “geopolymer” materials not only have comparable or superior properties to traditional cementitious binders, but also have low greenhouse emissions. In the past decade a large number of publications including many review papers on geopolymer synthesis and characterisation have been published [4,5]. Most of the researchers used metakaolin and fly ashes for source materials [4,5]. Fly ash is thought to be good candidate for source materials because it is the residue from coal burnt in a thermal power plant and regarded as a waste product. Fly ash has a complex microstructure comprising of a mixture of amorphous and crystalline components. The fly ash accumulates rapidly

and can pose serious disposal problems. It would be highly advantageous to be able to use these by-products through resource recovery programs [6]. A moderate level of fly ash is utilised as a filler in the production of the Portland cement. It is apparent that the chemical and mineralogical composition of coal varies significantly depending on its origin, thus it is expected that the chemical and mineralogical composition of fly ash will also vary with coal source. The composition of fly ash, especially the content of the unburnt carbon residues is dependent on the performance of the thermal power plant and its efficiency. Van Jaarsveld et al. have suggested that the final structure and physical properties of fly ash based geopolymers are dependent upon a variety of material parameters including water content, thermal history, particle size, and degree of amorphicity [7]. Fly ash also contains different amount of unburnt carbon which may reach up to 17% [8]. The Portland cement concrete industry will use fly ash if the loss-on-ignition (LOI) values are less than 6%. Unburnt carbon is responsible for ignition loss and is also an undesirable constituent of fly ash that causes the following effects:

- increases the electrical conductivity of concrete;
- changes colour of mortar and concrete (may appear black);
- requires increased water and additives [9].

Obviously all these effects manifest themselves in the fly ash based geopolymer made from high carbon fly ash. Moreover, controlling the water content in fly ash based geopolymer concrete is extremely important because a high water to solids ratio results in deterioration of mechanical properties [10,11]. Therefore, carbon free fly ash based geopolymers are expected to have better mechanical properties than carbon containing fly ash based geopolymers [12].

* Corresponding author. Tel.: +61 8 9266 3673; fax: +61 8 9266 2377.
E-mail address: jtemuujin@yahoo.com (J. Temuujin).

In this study we characterised geopolymer properties prepared from carbon free fly ash.

2. Experimental procedures

Geopolymer samples were made from Collie fly ash supplied by Western Power, Western Australia. The chemical composition of the fly ash as determined by XRF is shown in Table 1. The total carbon was determined by total combustion analysis, prior to XRF analysis and it was equal to 3 wt%.

Major and minor elements in the ground bulk samples of the fly ash were determined using a Philips PW1400 XRF spectrometer fitted with a rhodium tube. The elemental composition was determined by comparison with certified reference materials and the spectrometer drift corrected by regular measurement of an external monitor sample. Matrix effects were corrected using α -factors provided by Philips and adjusted for this sample preparation procedure [13].

As it mention in the introduction, the fly ash consists of the crystalline and amorphous constituents and also unburnt carbon. The amorphous component is the important part for fly ash reactivity and a higher proportion amorphous equates to high reactivity [7,14]. In order to determine the mineralogical composition of the fly ash the Rietveld method was used for quantitative phase analysis with XRD patterns using Rietica 1.7.7 software (Rietica Home, Retrieved 8th June 2006 from <http://www.rietica.org>). Zincite was used as an internal standard to enable absolute phase abundance estimates to be obtained. The XRD patterns were collected on a Siemens D-500 with Bragg-Brentano geometry using a Cu K α source, with a post sample K β filter. The angular range collected was 10° to 120° 2 θ , with a step size of 0.02° 2 θ and collection speed of 0.4°/min. Tube conditions were set at 40 kV and 30 mA.

Fly ash samples were calcined at 500 and 800 °C temperatures for 20 h in order to remove the residual unburnt carbon. Fly ash samples were calcined in a fired clay basket. Heating and cooling rates were set at 5 °C/min. Calcination caused a partial crystallisation of the amorphous part into crystalline mullite and hematite. DTA–TG of the Collie fly ash shows an exothermic event around 500 °C (decarbonation) accompanied by a weight loss followed by a weight gain after 600 °C [15]. The Collie fly ash calcined at 800 °C is considered to be carbon free [16]. DTA/TG measurements indicate that the fly ash calcined at 500 °C is also carbon free. Therefore, 500 and 800 °C calcined fly ash can be considered as carbon free, but with slightly different amorphous and crystalline compositions.

Since the most reactive part of the fly ash is its amorphous part, the main chemical composition of the amorphous part was calculated by subtracting the crystalline component, as measured by QXRD (quantitative X-ray diffraction), from the bulk composition, as measured by XRF. This is achieved by converting the

Table 1
Chemical composition of the fly ash, wt%

Al ₂ O ₃	23.63
CaO	1.74
Fe ₂ O ₃	15.3
K ₂ O	0.84
MgO	1.2
MnO	0.13
Na ₂ O	0.38
P ₂ O ₅	1.31
SiO ₂	51.5
SO ₃	0.28
TiO ₂	1.32
LOI	1.78

Table 2
Chemical composition of the amorphous part of the fly ash, wt%

Al ₂ O ₃	11.64 ± 1
SiO ₂	26.49 ± 1
Fe ₂ O ₃	12.7 ± 0.5
All other oxides + carbon	9.2 ± 0.5

crystalline phase compositions to equivalent oxide composition to make them comparable to XRF results. The main chemical composition of the amorphous component in the raw fly ash is shown in Table 2.

To determine the correct amount of activator required to manufacture the geopolymer we have used the amorphous composition of the fly ash, because if there is too much activator, the excess, after dissolution, would remain in the sample weakening the structure [17]. However, if there is not enough alkaline activator, not all the aluminosilicate material undergoes geopolymerisation. In principle to cater for the reduced amorphous component in the calcined samples less alkaline solution should be used. However for this experiment we have used same amount of the alkali assuming that the newly formed crystalline compounds might exhibit the same reactivity as untreated raw fly ash. Geopolymer compositions used for the experiments are shown in Table 3.

For the geopolymer composition calculation we have used ratios known to give the highest compressive strength in Collie fly ash based geopolymer concrete, but recalculated for just the amorphous content of the fly ash. Therefore, the present research utilised less alkali than previous studies [10,11]. The alkaline compounds used were 14 M NaOH and D-grade sodium silicate solution from PQ Australia Pty Ltd.

Carefully weighed components were mixed and de-foamed in a high velocity centrifuge mixer (Thinkey mixer) and placed in cylindrical plastic moulds with 25 mm diameter. The closed moulds then cured at 70 °C for 24 h. After curing, the samples were removed from the oven and kept in their moulds for 3 days before being cut with a diamond saw to a height of 50 mm. Compressive strength testing was done 7 days after processing using a compression testing instrument (Lloyds Instruments 6000R). The uncertainty in the measurement was taken as the standard deviation of the compressive strength of three samples. SEM examination was carried out with a Philips XL30 scanning electron microscope, incorporating an energy dispersive spectrometer (EDS, Oxford Instruments) using gold coated samples. EDS analysis of efflorescence scratched from the geopolymer surface was performed without coating.

Densities and apparent porosities of the sectioned geopolymers were measured by the Archimedes principle using de-ionised water. However, saturation with water was considered inappropriate because of possible leaching in water for ions such as Na [18]. Therefore, measured densities and apparent porosities are not regarded as absolute values but relative values. Shrinkage of the samples was evaluated by measuring dimensional changes. Dimensions of the samples were measured after demoulding and then again after 3 days. Values in brackets for either mechanical properties or porosities indicate the standard deviation of repeated measurements.

Table 3
Geopolymer composition of this study

Fly ash	Si/Al (molar)	Na/Al (molar)	Water/geopolymer solid (mass)
Raw	2.3	0.88	0.19
500 °C calcined	2.3	0.88	0.19
800 °C calcined	2.3	0.88	0.19

Table 4
Mineralogical composition of the fly ashes

	Amorphous (%)	Quartz low (%)	Mullite (%)	Hematite (%)	Maghemite Q (%)
Raw fly ash	60 (1)	20 (1)	17 (1)	0.9 (0.5)	1.7 (0.5)
500 °C calcined fly ash	59 (1)	20 (1)	18 (1)	1.3 (0.5)	1.8 (0.5)
800 °C calcined fly ash	57 (1)	20 (1)	19 (1)	2.8 (0.5)	1.2 (0.5)

3. Results and discussion

3.1. Effect of calcination on fly ash

Table 4 shows mineralogical composition of the raw and calcined fly ashes.

As shown in Table 4, calcination caused approximately a 3% decrease of the amorphous component of the fly ash while at same time increasing the crystalline phases mullite and hematite. As discussed before, DTA–TG of the Collie fly ash shows a weight gain after 600 °C. The weight gain of the fly ash can be explained in terms of hematite crystallisation from the amorphous part of the fly ash involving the oxidation reaction Fe^{2+} to Fe^{3+} . Therefore, LOI of the fly ash (1.78%) was lower than total carbon content (3%). However, considering the time allocated for calcination the crystallisation rate of the fly ash is rather low. Fig. 1 shows SEM micrographs of the raw and calcined fly ash. There are almost no changes in terms of morphology.

There are some cenospheres with crystallised surfaces in the 500 and 800 °C calcined fly ashes which may indicate some degree of higher crystallisation. With calcination the original grey colour of the fly ash changes to a red brown colour possibly caused by hematite crystallisation.

3.2. Effect of the calcination on the microstructure of geopolymers

After 3 days the geopolymer samples show different volume shrinkages. Geopolymer prepared using raw fly ash shows 0.54 (0.1)% volume shrinkage while for the 500 and 800 °C calcined fly ash samples the shrinkage was 0.83 (0.25) and 5.45 (0.40)%, respectively. Calcination of the fly ash thus caused increasing shrinkage of the prepared geopolymers which is unusual as geopolymers generally exhibit little drying shrinkage. In fact for the 800 °C calcined fly ash geopolymer the large shrinkage resulted in the samples cracking. Density of the 800 °C calcined fly ash geopolymer was little bit higher (1.98 (0.14) g/cm³) than those calcined at 500 °C (1.97 (0.03) g/cm³) and raw fly ash based geopolymer (1.94 (0.01) g/cm³). Apparent porosities of these samples were 14.7 (0.6)%, 14.1 (0.95)% and 10.2 (2.1)% for the raw, 500 °C and 800 °C calcined fly ash based geopolymers, respectively. However, the small difference between the densities and apparent porosities of the present samples suggest that the high shrinkage of the 800 °C calcined fly ash based geopolymer does not correlate with the density of the samples. It is possible that the shrinkage could be related to the presence of the chemically bound water with the geopolymer gel and higher shrinkage may be an indication of insufficient geopolymerisation reaction. Because geopolymer gel retains water in its

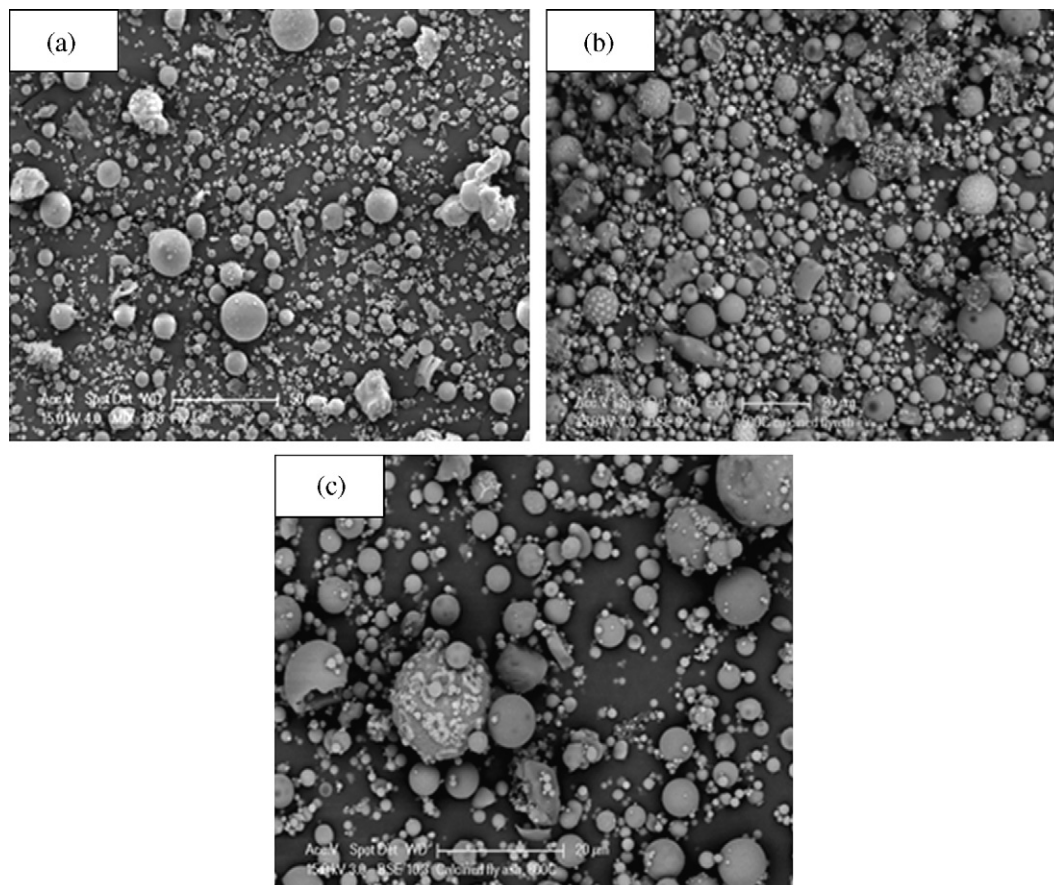


Fig. 1. SEM micrographs of the raw and calcined fly ashes. (a) Raw, (b) 500 °C, and (c) 800 °C.

Table 5
Summary of shrinkage, density and apparent porosity measurements

Sample	Drying shrinkage (%)	Density (g/cm ³)	Apparent porosity (%)
Raw fly ash based	0.54 (0.1)	1.94 (0.01)	14.7 (0.6)
500 °C calcined fly ash based	0.83 (0.25)	1.97 (0.03)	14.1 (0.95)
800 °C calcined fly ash based	5.45 (0.4)	1.98 (0.14)	10.2 (2.1)

structure within cavities the drying shrinkage will be small. Collie fly ash based geopolymer showed approximately 2% linear shrinkage upon heating to 550 °C and this shrinkage is mainly due to the water content in geopolymer [15]. Therefore the high drying volumetric shrinkage of the 800 °C calcined fly ash based geopolymer is an indication of a low geopolymerisation rate. Since, there was insufficient geopolymerisation, the excess solution migrates to the surface causing high shrinkage and cracks. It is apparent that lower apparent porosity of the 800 °C calcined fly ash based samples result from high shrinkage. Shrinkage, density and apparent volume measurements of the geopolymers are summarised in Table 5.

Fig. 2 shows how the compressive strength of the geopolymer reduces with increase in calcination temperature of the fly ashes.

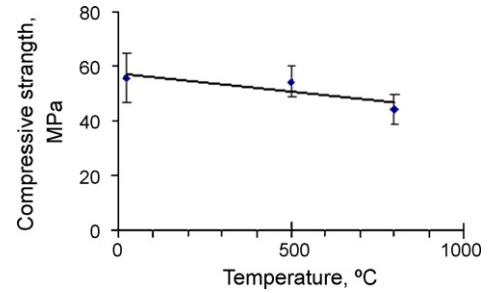


Fig. 2. Influence of fly ash calcination temperature on compressive strength of the geopolymers.

Generally, in most ceramics strength decreases with increasing porosity. However, for geopolymer samples described here the opposite trend occurs which may be related to cracking of samples after demoulding in conjunction with a lower geopolymerisation rate in the calcined fly ash based samples.

Fig. 3 shows SEM micrographs of the samples. For the raw fly ash based samples the microstructure appears homogeneous and more of the fly ash has reacted while for the 800 °C calcined fly ash based sample there are more cracks and less fly ash has reacted. It would appear that the structural integrity of 800 °C calcined fly ash based

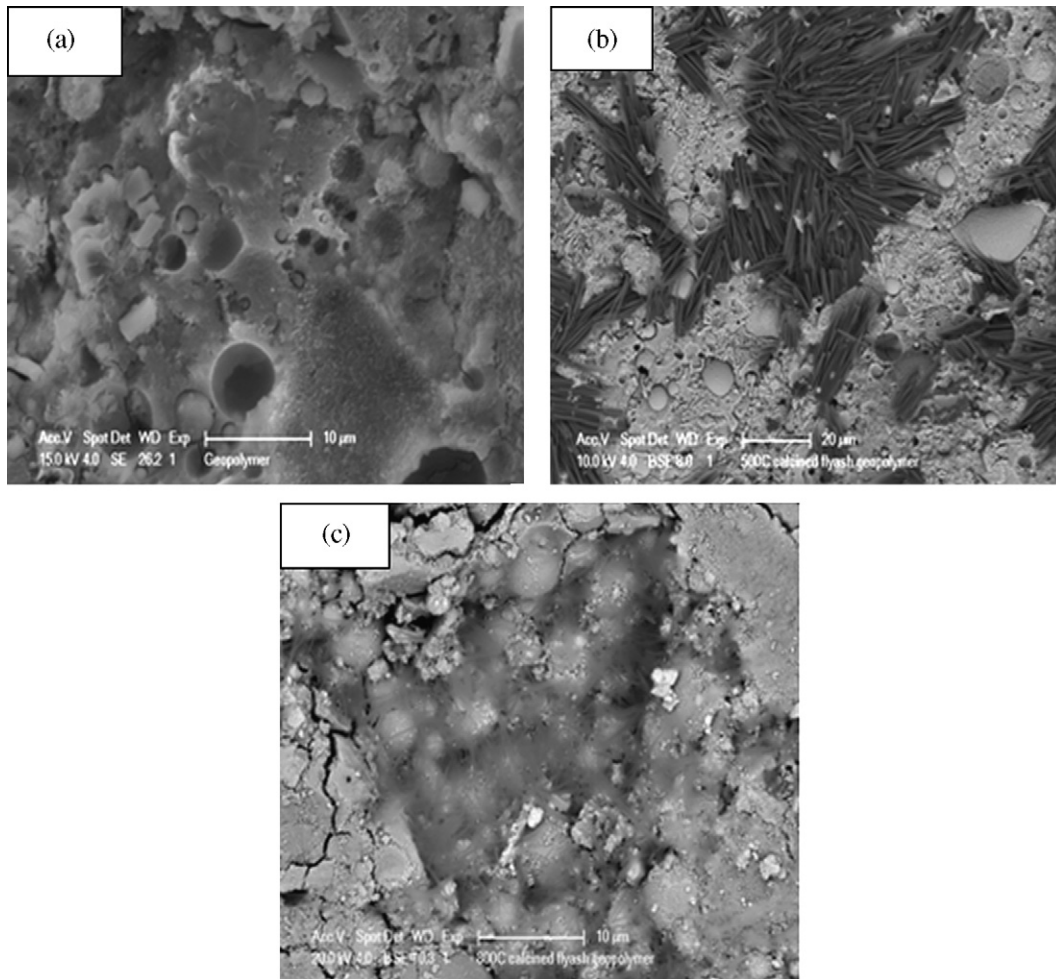


Fig. 3. Microstructure of the raw and calcined fly ash based geopolymers. (a) Raw fly ash based, (b) 500 °C calcined, and (c) 800 °C calcined fly ash based samples.

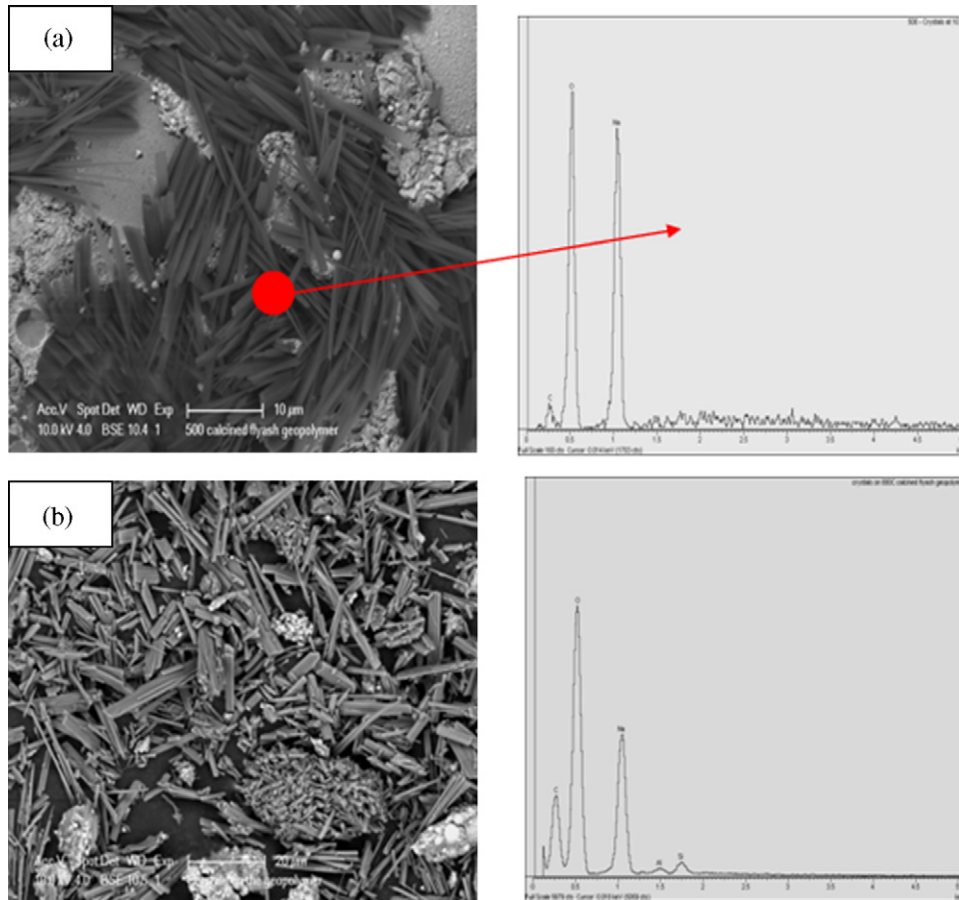


Fig. 4. SEM images and EDS spectra of efflorescence products. (a) 500 °C and (b) 800 °C calcined fly ash based geopolymers (backscattered mode at 15 kV).

geopolymer has been compromised. Efflorescence can be observed (thin crystals) in micrographs (Fig. 3b and c) of the geopolymers based on calcined fly ash.

3.3. Characterisation of the efflorescence

Visible surface efflorescence was observed on the surface of the 800 °C calcined fly ash sample, while for the 500 °C calcined fly ash sample it could only be observed by SEM. However, no efflorescence was observed in raw fly ash based samples. The presence of efflorescence in calcined fly ash samples is clear evidence that excess alkali was used to create the geopolymer.

The efflorescence product was characterised to enable a better understanding of the geopolymerisation process. SEM micrographs and EDS spectra of the efflorescence are shown in Fig. 4. For the 500 °C calcined fly ash based geopolymer the efflorescence was characterised by collecting EDS spectra directly from the fractured surface, while for 800 °C calcined sample there was sufficient material for it to be scratched off the surface and then analysed.

The spectra strongly suggest the presence of sodium carbonate. The spectra from the 800 °C calcined fly ash sample contained some Al and Si peaks believed to arise from scratching of the geopolymer surface. X-ray diffraction of the efflorescence crystals shows the presence of the sodium carbonate hydrate ($\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$) (Fig. 5). Also there is a halo around 2θ 15–25°, indicating either an amorphous constituent of the efflorescence or amorphous geopolymer constituent from the surface.

The present study suggests that the geopolymerisation reaction depends strongly on the surface conditions of the fly ash. The difference between the raw and 800 °C calcined fly ash in terms of

the amorphous and crystalline components is only ≈ 3 wt%. But there are very large differences in terms of geopolymerisation. The reason for this behaviour is believed to arise from changes of the fly ash's surface. During the combustion of coal, minerals impuri-

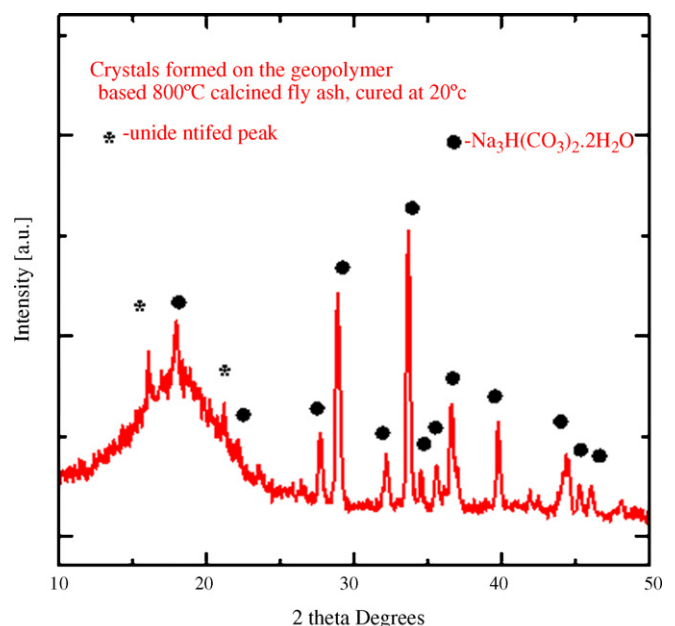


Fig. 5. XRD pattern of the efflorescence removed from the surface of the 800 °C calcined fly ash based geopolymer.

ties partially melt and form fly ash particles in which crystalline phases such as quartz and mullite remain in the core; while glassy aluminosilicates covers the surface [6]. It is also likely that a proportion of the amorphous iron oxide also covers the surface. The heat treatment or calcination causes crystallisation of the aluminosilicates and hematite on the surface of the spherical particles. It is very likely that such crystallised aluminosilicate (mullite) and hematite prevent dissolution of the aluminate and silicate species by the activating alkali [19], consequently there is excess alkali which is able to migrate to the surface of the geopolymer during curing which then crystallises as sodium hydrate carbonate. Clearly crystallisation of this compound occurs after demoulding when excess alkali is able to react with air. Since there was insufficient dissolution of the aluminate and silicate species no zeolitic compounds were formed. Based on the fly ash calcination experiments presented here it is suggested that removal of unburnt carbon from fly ash by calcination is counter productive. The calcination may remove the carbon but the concomitant changes to the surface of the fly ash limit the degree of polymerisation that is possible.

4. Conclusions

Calcination of the fly ash at 500 and 800 °C causes crystallisation of the mullite and hematite on the fly ash surfaces, lowering the reactivity of the fly ash and decreasing the level of geopolymerisation. Calcination of the fly ashes also results in a decrease of the compressive strength of the samples from 55.7(9.7) MPa in non-treated fly ash based geopolymer to 44.3(5.4) MPa for 800 °C calcined fly ash based samples.

Acknowledgements

The present research was funded by the Cooperative Research Centre for Sustainable Resource Processing. The authors are indebted to R. Williams for assistance with the Rietveld XRD analysis.

References

- [1] D. Hardjito, S.E. Wallah, D.M.J. Sumajouw, V. Rangan, Fly ash-based geopolymer concrete, *Aust. J. Struct. Eng.* 6 (2005) 1–9.
- [2] V.D. Glukhovskiy, *Soil Silicates*, Gosstroyizdat Ukrainy Publishing, Kiev, 1959 (in Russian).
- [3] J. Davidovits, Geopolymer chemistry and properties, in: J. Davidovits, J. Orlinski (Eds.), *Proceedings of the 1st International Conference on Geopolymer'88*, vol. 1, Compiègne, France, 1–3 June, 1988, pp. 25–48.
- [4] K. Komnitas, D. Zaharaki, Geopolymerisation: a review and prospects for the minerals industry, *Miner. Eng.* 20 (2007) 1261–1277.
- [5] P. Duxson, A. Fernandez-Jimenez, J.L. Provis, G.C. Luckey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, *J. Mater. Sci.* 42 (2007) 2917–2933.
- [6] V.K. Jha, M. Matsuda, M. Miyake, Resource recovery from coal fly ash waste: an overview study, *J. Ceram. Soc. Jpn.* 116 (2008) 167–175.
- [7] J.S.G. van Jaarsveld, J.S.J. van Deventer, G.C. Lukey, The characterisation of source materials in fly ash-based geopolymers, *Mater. Lett.* 57 (2003) 1272–1280.
- [8] M.L. Gray, K.J. Champagne, Y. Soong, R.P. Killmeyer, M.M. Maroto-Valer, J.M. Andresen, M.V. Ciocco, P.H. Zandhuis, Physical cleaning of high carbon fly ash, *Fuel Process. Technol.* 76 (2002) 11–21.
- [9] T.H. Ha, S. Muralidharan, J.H. Bae, Y.C. Ha, H.G. Lee, K.W. Park, D.K. Kim, Effect of unburnt carbon on the corrosion performance of fly ash cement mortar, *Constr. Build. Mater.* 19 (2005) 509–515.
- [10] D. Hardjito, B.V. Rangan, Development and properties of low-calcium fly ash-based geopolymer concrete. Research Report GC1, Curtin University of Technology, 2005, 103 pp.
- [11] B.V. Rangan, Fly ash-based geopolymer concrete. Research Report GC4, Curtin University of Technology, 2008, 44 pp.
- [12] US Patent 5,601,643 (1997).
- [13] K. Norrish, J.T. Hutton, An accurate X-ray spectrographic method for the analysis of a wide range of geological samples, *Geochim. Cosmochim. Acta* 33 (1969) 431–453.
- [14] R. Williams, Characterisation of Fly Ash for Production of Geopolymer, Honours Thesis, Curtin University of Technology, 2006.
- [15] W. Rickard, Thermal Properties of Fly Ash Geopolymers, Honours Thesis, Curtin University of Technology, 2007.
- [16] S. Wang, Z.H. Zhu, Humic acid adsorption on fly ash and its derived unburned carbon, *J. Colloid Interface Sci.* 315 (2007) 41–46.
- [17] M. Rowles, B. O'Connor, Chemical optimisation of the compressive strength of aluminosilicate geopolymers synthesised by solution silicate activation of metakaolinite, *J. Mater. Chem.* 13 (2003) 1161–1165.
- [18] D.S. Perera, O. Uchida, E.R. Vance, K.S. Finnie, Influence of curing schedule on the integrity of geopolymers, *J. Mater. Sci.* 42 (2007) 3099–3106.
- [19] J.S.J. van Deventer, J.L. Provis, P. Duxson, G.C. Lukey, Reaction mechanism in the geopolymeric conversion of inorganic waste to useful products, *J. Hazard. Mater. A* 319 (2007) 506–513.