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Geopolymeric materials prepared using Class F fly ash and elevated temperature curing

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Abstract

This paper reports the results of the study of the influence of elevated temperature curing on phase composition, microstructure and strength development in geopolymer materials prepared using Class F fly ash and sodium silicate and sodium hydroxide solutions. In particular, the effect of storage at room temperature before the application of heat on strength development and phase composition was studied. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and SEM were utilised in this study.

Long precuring at room temperature before application of heat was beneficial for strength development in all studied materials, as strength comparable to 1 month of curing at elevated temperature can develop in this case only after 24 h of heat curing. The main product of reaction in the geopolymeric materials was amorphous alkali aluminosilicate gel. However, in the case of sodium hydroxide activator in addition to it, traces of chabazite, Linde Type A, Na-P1 (gismondine) zeolites and hydroxysodalite were also present. The type of zeolite present and composition of aluminosilicate gel were dependent on the curing history.

Keywords: Thermal treatment; Hydration products; Microstructure; Fly ash; Alkali-activated cement

1. Introduction

First scientific studies of geopolymeric materials indicated a certain potential for these materials to become cement for the future [1–5]. Davidovits [5–7] first used the term "geopolymers" in describing synthetic minerals similar to those that form in the Earth's crust. Geopolymers belong to the same silicoaluminates family as zeolites but have a significant difference from them: they are essentially amorphous polymers. Their properties are also different: they possess high strength, thermal stability, high surface smoothness and precision, and high surface hardness. [6,7]. These mineral polymers with empirical formula: $M_n[\text{–}(SiO_2)_z\text{–}AlO_2]_n \cdot wH_2O$, where z is 1, 2 or 3; M is an alkali cation, such as potassium or sodium, and n is the degree of polymerisation, were called polysialates [5–7].

Geopolymer materials can be formed from silica–alumina oxides mixed with alkali hydroxides and alkali silicates. Davidovits [6,7] used the silica–alumina oxide mixture, specially prepared highly reactive clay, for example, neokaolinite, parakaolinite, halloysite, milanite, and chamoisite, calcined and milled to increase its reactivity. The resulting silica–alumina oxide has the aluminium cation in fourfold coordination and in tetrahedral position. When this silica–alumina oxide is mixed with alkali silicates, reactions of dissolution and copolymerisation occur and polysialates, polysialate–siloxo and polysialate–disiloxo are formed [5]. Compared to the described patents, this paper presents an investigation of the properties of geopolymeric materials utilising Class F fly ash and the alkaline activators, such as sodium silicate and sodium hydroxide, and cured at elevated temperature.

Previous research reported that heat is an important factor for the activation of fly ash, because of the activation barrier, which has to be overcome for the reaction to take place [8]. It was reported that the activation energy is higher

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for fly ash than for slag, and thus heat treatment is more important for the activation of fly ash.

There were a number of researchers studying activation of fly ash by alkalies utilising elevated temperature curing [1–3]. The study by Swanepoel and Strydom [2] investigated utilisation of fly ash and kaolinite clay in a geopolymeric material cured at temperatures up to 70 °C. The compressive strength achieved after 28 days was 8 MPa. Palomo et al. [1] presented a study of alkali-activated fly ashes cured at 65 and 85 °C at two liquid/solid ratios: 0.25 and 0.3. The study indicated formation of an amorphous alkali aluminosilicate similar to that obtained in the alkali activation of metakaolin. The strength developed was in the range of 60 MPa. No crystalline zeolitic products were observed, but the Fourier transform infrared spectroscopy (FTIR) spectra indicated a possibility of their presence. The investigations showed the importance of elevated temperature curing particularly for samples exposed to 2 and 5 h curing, where a significant increase in strength was observed at 85 °C as compared to 65 °C. It was found that the rise of strength at 85 °C as compared to 65 °C was much smaller when curing time was 24 h. This study continues the investigation of the effect of different curing regimes and types of activator on the strength development and hydration products of Class F fly ash activated by sodium silicate and sodium hydroxide. It investigates the effect of precuring at room temperature before the application of heat on strength development and products of reaction and the effect of different heat treatment regimes and activators on long-term properties of geopolymer materials.

2. Experimental

2.1. Materials

The chemical and mineral compositions of fly ash are shown in Table 1 and Fig. 1, respectively. Fly ash used was sourced from Gladstone in Queensland, Australia. It is mainly glassy with some crystalline inclusions of mullite, hematite and quartz. Laboratory grade sodium silicate solution type D with Ms (ratio of silica oxide to sodium oxide) equal to 2.02, 14.7% Na_2O, 29.4% SiO_2 was supplied by PQ Australia, while 60 w/v% sodium hydroxide solution was supplied by Sigma. Sodium hydroxide and sodium silicate solutions were used for fly ash activation.

Table 1
Composition of fly ash (mass%) by XRF

Oxide	Fly ash
SiO_2	50.0
Al_2O_3	28.0
Fe_2O_3	12.0
CaO	6.5
MgO	0.6
K_2O	1.5
Na_2O	0.2
TiO_2	–
P_2O_5	0.7
MnO	–
SO_3	–
Sulphide sulphur as S^{2-}	–
Cl	0.2
Loss on ignition	–

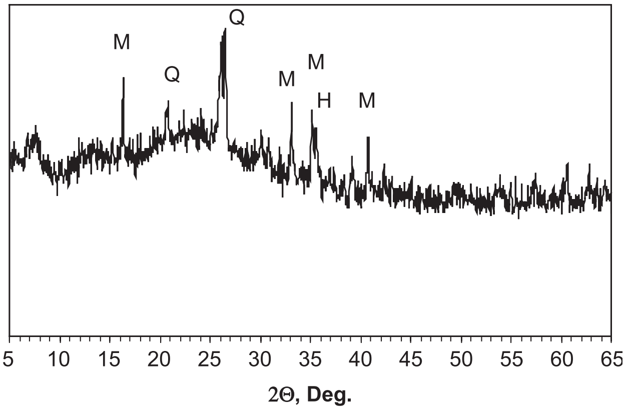

Fig. 1. XRD traces of fly ash. Q=quartz, M=mullite, H=hematite.

2.2. Procedures

Fly ash was mixed with sodium hydroxide and sodium silicate solutions, providing up to 10% Na in mixtures and water/binder ratio of 0.3; Table 2 shows the details of the samples and curing conditions. The pastes were cast in plastic cylinders and sealed with the lid. Three types of curing were used. In the first case, the mixtures were cured for 2 h at room temperature and then ramped to 75 °C and exposed to heat curing at 75 °C for 1 month (Case I 75C). In the second case, the mixtures were cured for 24 h at room temperature after that the mixtures were ramped to 75°C (Case II 75C) or 95 °C (Case II 95C) and cured at these temperatures for 24 h; after that, the materials cooled down with the oven and were cured at room temperature afterwards. In the third case, mixtures were cured for 24 h at room temperature and then were ramped to 75 °C (Case III 75C) or 95 °C (Case III 95C) and exposed to that temperature for 6 h; they were cooled down with the oven and were cured at room temperature afterwards. In all cases, the samples were sealed in plastic tubes and cured hydrothermally. Two types of curing were utilised after exposure to heat. In one case, the cylindrical samples were covered with hydrophobic film and wrapped in thin plastic to prevent moisture evaporation and tested for compressive strength at indicated times; in the second case, the cylinders were stored in tap water, and when required, were taken out of water and tested.

Table 2 shows the summary of the experimental programme. The compressive strength of ø25×50 mm cylinders was measured at 1, 2, 7, 14, 28, 60 and 120 days. The materials were analysed by X-ray diffraction (XRD),

Table 2
Summary of experimental programme

Type of activator and w/b ratio	Concentration	Curing regime	Compressive strength	XRD	SEM	SEM X-ray microanalysis	FTIR
Liquid sodium silicate, w/b=0.3	2%, 4%, 6%, 8% Na	Case I 75 °C	1, 2, 7, 30	X	X	X	
NaOH, w/b=0.3	2%, 4%, 6%, 8% Na	Case I 75 °C	1, 2, 10, 30	X	X		
Liquid sodium silicate, w/b=0.3	8% Na	Case II 75 °C	1, 2, 7, 14, 30, 45, 60, 120	X	X	X	X
NaOH, w/b=0.3	8% Na	Case II 75 °C	2, 10, 20, 30, 45, 60, 120, 140	X	X	X	X
Liquid sodium silicate, w/b=0.3	8% Na	Case II 95 °C	1, 2, 7, 14, 30, 45, 60, 120	X	X	X	X
NaOH, w/b=0.3	8% Na	Case II 95 °C	2, 10, 20, 30, 45, 60, 120, 140	X	X	X	X
Liquid sodium silicate, w/b=0.3	8% Na	Case III 95 °C	1, 2, 7, 14, 30, 45, 60, 120	X	X		X
NaOH w/b=0.3	8%, 10% Na	Case III 75 °C	2, 10, 20, 30, 45, 60, 120, 140	X	X		
NaOH, w/b=0.3	8%, 10% Na	Case III 95 °C	2, 10, 20, 30, 45, 60, 120, 140	X	X		X

FTIR and SEM. XRD analyses were made with a Rigaku Geigerflex D-max II automated diffractometer with the following conditions: 40 kV, 22.5 mA, Cu–Kα radiation. The XRD patterns were obtained by scanning at 0.1° (2θ) per min and in steps of 0.05° (2θ). FTIR was performed for the samples after 28 days on Perkin Elmer 1600 FTIR spectrometer using the KBr pellet technique (3 mg powder sample mixed with 100 mg KBr).

Microstructural studies utilised SEM (Hitachi S-2300, Japan) equipped with EDS analyser (Oxford Image Analysis). Secondary electron images were collected of the fractured specimens, and microanalysis studies utilised polished specimens. To prepare polished specimens, 1-mm-thick slices were cut using a low-speed saw. The samples were first impregnated with ultra-low viscosity resin and then polished. All the specimens were carbon coated. X-ray microanalyses were carried out at an accelerating voltage of 20 kV for 100 s; matrix corrections were applied by ZAF procedure. For hydrated phases, each spot analysed relates to a region of 1 μm across in diameter.

3. Results

3.1. Compressive strength

The studied pastes did not show hardening after 1 day of curing at room temperature; thus, three cases of heat curing described above were employed. Figs. 2 and 3 show the results of the compressive strength measurements for materials prepared with sodium silicate and sodium hydroxide solutions and cured as described in Case I 75C. There was an increase in strength with increase in concentration from 2% to 8% Na in the mixtures prepared with the sodium silicate and sodium hydroxide solutions. For sodium hydroxide, a gradual increase in strength was observed corresponding to the increase in sodium concentration, while for sodium silicate, the strength was low at 2%, 4% and 6% Na, and rapidly developed at 8% Na concentration.

Fig. 4 presents the results of the strength measurements for materials cured according to Case II 75C, Case II 95C, Case III 75C and Case III 95C procedures for fly ash activated by sodium hydroxide solution. Fig. 5 presents the results of the strength measurements for materials cured according to Case II 75C, Case II 95C and Case III 95C procedures for fly ash activated by sodium silicate solution. The increase in Na concentration above 8% Na in mixtures of fly ash and sodium hydroxide caused slow strength gain at early ages in materials prepared with 10% Na (Case III 75C, Fig. 4).

It was found that long precuring at room temperature was beneficial for strength development, and there was about 300% increase in strength after 24 h of heat curing in Case II 75C and Case II 95C as compared to Case I 75C for materials with both activators. The strength was significantly higher if materials were stored 24 h at room temperature before application of heat.

Strength of materials was increased in Case II 75C and Case II 95C as compared to Case III 75C due to longer period of elevated temperature treatment (Figs. 3 and 4), 24 vs. 6 h. For both types of activators, materials formed at 95 °C had higher strength than materials formed at 75 °C if 24 h heat treatment was employed. However, this trend was inversed for materials formed with sodium hydroxide when 6 h heat treatment was employed (Case III 95C and Case III 75C). Materials cured at 75 °C (Case III 75C) had higher strength than materials cured at 95 °C (Case III 95C). An

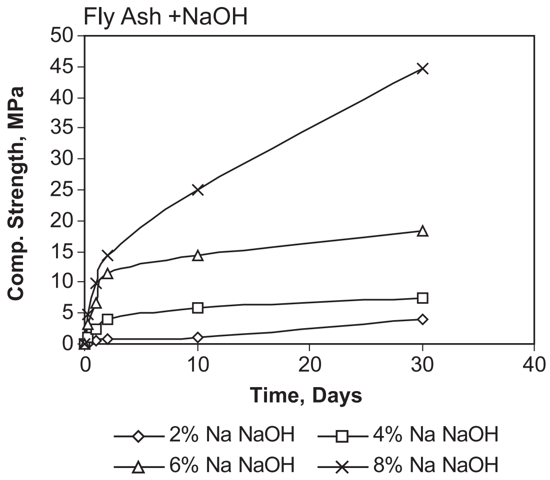

Fig. 2. Compressive strength development in fly ash activated by sodium hydroxide and cured at 75 °C after 2 h precuring at room temperature (Case I 75C).

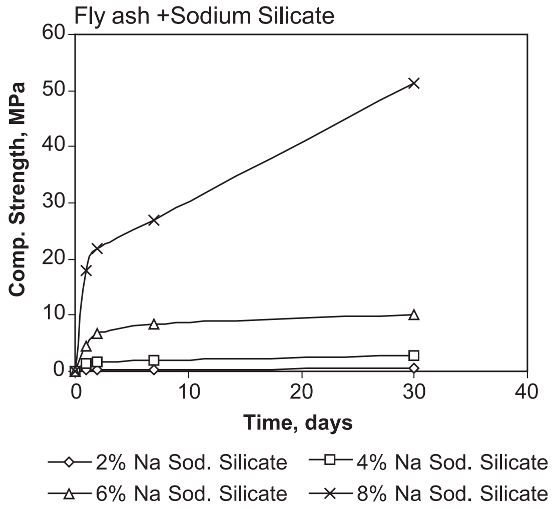

Fig. 3. Compressive strength development in fly ash activated by sodium silicate and cured at 75 °C after 2 h precuring at room temperature (Case I 75C).

interesting observation was for the sodium hydroxide activated system with 10% Na cured at 75 °C (Case III 75C). In the first month, the strength of the samples with 10% Na was below the strength of the samples formed with 8% Na; however, when cured at 95 °C (Case III 95C), mixtures with 10% Na had higher strength than those with 8% Na concentration.

Materials with both activators showed deterioration of strength if moisture evaporation is allowed during or after heat curing. The material's surface has to be covered by thin plastic or hydrophobic film to prevent surface drying. This investigation also revealed that strength of the materials prepared with sodium silicate depends on the storage conditions after exposure to heat and a loss of up to 25% of the strength can occur after heat curing. Materials prepared with sodium hydroxide did not show loss of strength after heat curing (Fig. 4).

When stored at room temperature in air, Case II 95C samples prepared with sodium silicate had up to 20% loss of strength, as shown in Fig. 5. These samples were stored covered by hydrophobic film and by thin plastic. Materials prepared with the sodium silicate activator had up to 25% loss of strength when stored at room temperature in tap water after heat curing as in Case II 75C or Case II 95C (Fig. 6). However, fly ash activated by sodium silicate and cured 6 h at 95 °C (Case III 95C) did not have strength reduction and had 25% strength gain when stored in tap water at room temperature. When stored in air, materials prepared with sodium silicate and cured as in Case II 75C or Case III 95C had no strength loss; for materials cured as in Case III 95C, some strength gain was observed. Thus, materials activated by sodium silicate and heat cured for 6 h had a steady strength growth afterwards compared to samples cured at 95 °C for 24 h, which had up to 25% strength loss afterwards.

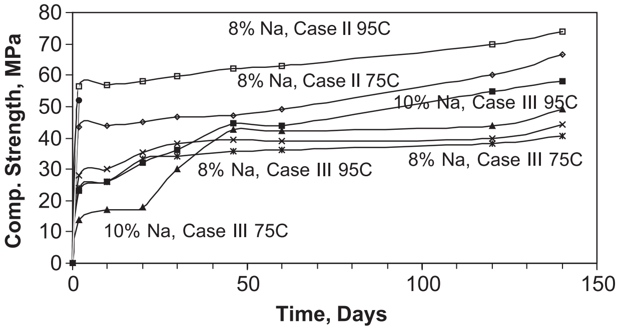

Fig. 4. Compressive strength development in fly ash activated by sodium hydroxide and cured as in Case II 95C, Case II 75C, Case III 95C and Case III 75C. The specimens were held at room temperature in tap water after the heat treatment.

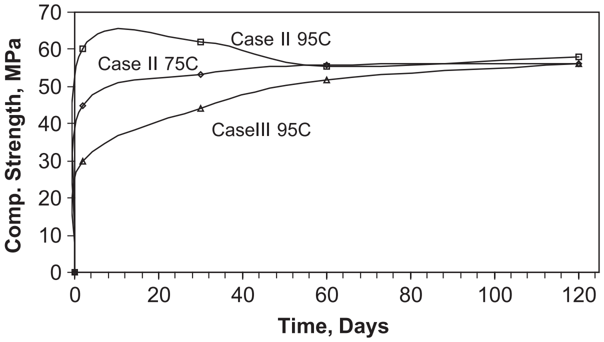

Fig. 5. Compressive strength development in fly ash activated by sodium silicate and cured as in Case II 95C, Case II 75C and Case III 95C. The samples were held at room temperature RH=70% after the heat treatment.

3.2. XRD

Figs. 7 and 8 present XRD traces of the samples prepared with sodium silicate and sodium hydroxide solutions, respectively. It was found that the main phases formed in the samples are amorphous, and only in the case of materials prepared with sodium hydroxide solution were semicrystalline zeolitic phases present after 1 month of storage. The zeolitic products formed depended on the curing regime. In materials with 2 h precuring at room temperature and

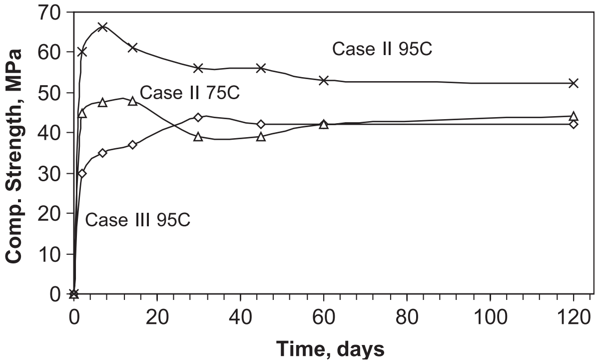

Fig. 6. Compressive strength development in fly ash activated by sodium silicate and cured as in Case II 95C, Case II 75C and Case III 95C. The specimens were held at room temperature in tap water after the heat treatment.

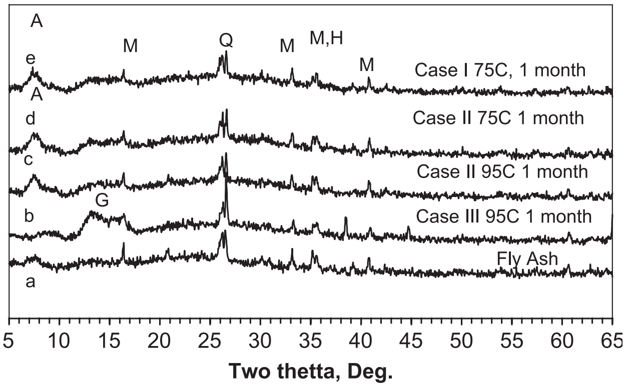

Fig. 7. XRD traces of (a) Class F fly ash, and Class F fly ash mixed with sodium silicate activator and cured; (b) as in Case III 95C, 1 month; (c) as in Case II 95C, 1 month; (d) as in Case II 75C, 1 month; (e) as in Case I 75C, 1 month. A=poorly crystalline Linde Type A precursor, G=poorly crystalline aluminosilicate gel, Q=quartz, M=mullite, H=hematite.

afterwards exposed to elevated temperature curing as in Case I 75C, Linde Type A and chabazite were found, while in materials with 24 h precuring and 6 or 24 h of heat treatment as in Case II 75C, Case II 95C and Case III 95 C, traces of chabazite, Na-P1 (gismondine) and hydroxysodalite were present. Fig. 7 shows that regardless of regime of elevated temperature curing, all materials prepared with sodium silicate were essentially amorphous for X-ray. Peaks due to quartz, mullite and hematite of the crystalline component of the fly ash can be seen in addition to a broad peak in the region 20–32° 2θ arising from the glassy phase of the fly ash and broad peaks in the region 6–10° and 12–16° 2θ arising from aluminosilicate gel.

3.3. FTIR

Fig. 9a and b presents the IR spectra of samples prepared with sodium hydroxide and sodium silicate solutions, respectively. The FTIR spectrum of the alkali-activated fly ash samples shows some differences when compared to the spectrum of the starting fly ash. During the reaction, the band at 800 cm^{-1} due to AlO_4 vibrations disappears and a new band at around 700 cm^{-1} appears, while the band at 1200 cm^{-1} due to asymmetric stretching Si–O–Si and Al–O–Si in fly ash shifts to lower frequencies (960–1000 cm^{-1}). The shift was higher in the fly ash activated by sodium hydroxide than in the fly ash activated by sodium silicate. In all geopolymeric materials, new bands appeared in the regions of 1600 and 3450 cm^{-1} which were attributed to bending vibrations (H–O–H) and stretching vibration (–OH), respectively. These changes are consistent with the formation of the aluminosilicate network in a polymer structure.

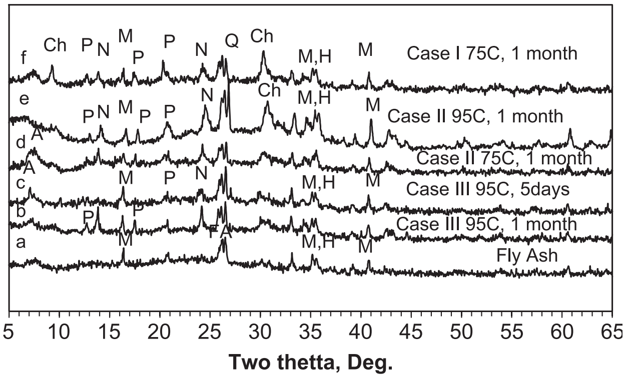

Fig. 8. XRD traces of (a) Class F fly ash, and Class F fly ash mixed with sodium hydroxide activator and cured; (b) as in Case III 95C, 1 month; (c) as in Case III 95C, 5 days; (d) as in Case II 75C, 1 month; (e) as in Case II 75C, 1 month; (f) as in Case I 75C, 1 month. Ch=chabazite, P=Na-P1 (gismondine), N=hydroxysodalite, A=Linde Type A, Q=quartz, M=mullite, H=hematite.

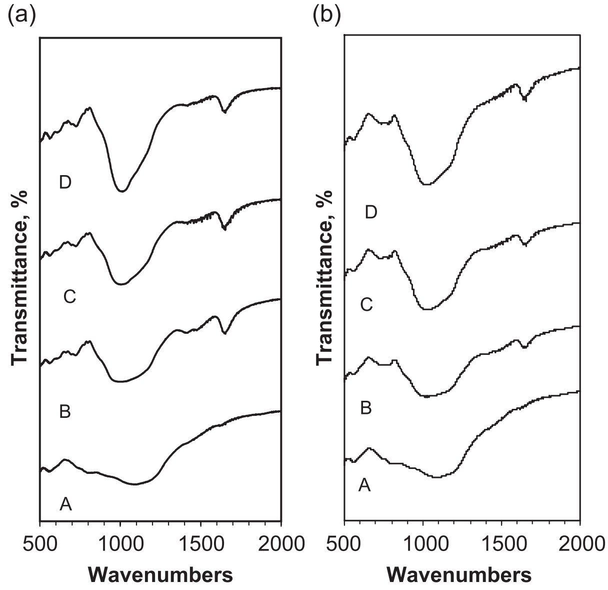

Fig. 9. FTIR spectra of (a) Class F fly ash mixed with sodium hydroxide activator and (b) Class F fly ash mixed with sodium silicate activator: A=initial material fly ash, and materials cured 1 month, B as in Case III 95C, C as in Case II 75C, D as in Case II 95C.

Comparison of Fig. 9a and b shows that the intensity of the bands at 960–1000, 750, 600 and 500 cm^{-1} frequencies are significantly enhanced in the case of fly ash activated by sodium hydroxide and cured as in Case II 95C compared to the spectra of material formed with sodium silicate activator cured as in Case II 95 C. The increase in intensity indicates increase in chain length and more aluminosilicate gel formed in this case.

3.4. SEM

The geopolymer samples were examined using secondary and backscattered electron imaging. Figs. 10–12a and b, present the fracture surface of the materials prepared with sodium silicate and sodium hydroxide solutions and cured as in Case II 95C, Case II 75 C and Case III 95C, respectively. The micrographs show that materials are heterogeneous and contain a large proportion of unreacted fly ash (Figs. 10–12a and b). A significant difference in the

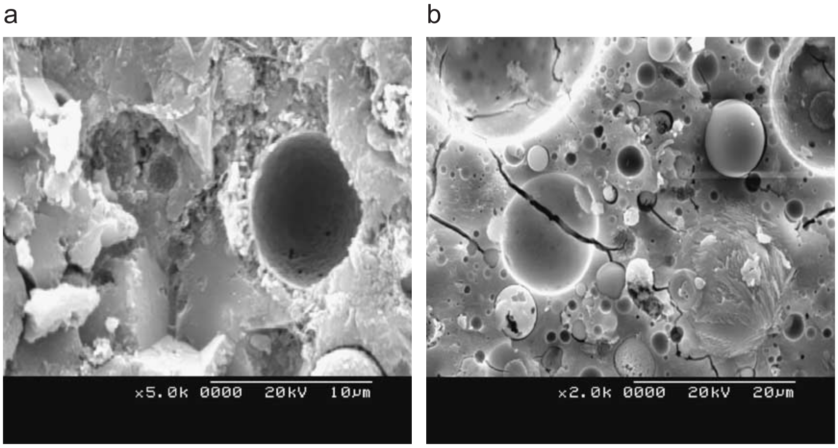

Fig. 10. SEI of geopolymer materials formed by reaction of Class F fly ash with (a) sodium hydroxide solution, and (b) sodium silicate solution and cured as in Case II, 95 °C.

appearance of the matrix-forming phases was observed for these two activators. In the material with sodium silicate, a glass-like matrix with imbedded fly ash spheres was present, while in the material with sodium hydroxide, a composite matrix containing some glass-like areas and more crystalline areas was formed and fly ash spheres were imbedded in it. Comparison of these images to micrographs of the fly ash activated in Ref. [1] shows that long precuring at room temperature in this investigation induced significant dissolution of fly ash and formation of a continuous matrix phase. This was beneficial because it increased homogeneity in the geopolymeric materials.

3.5. X-ray microanalysis (EDS)

Some of the microanalyses were of residue of fly ash particles, which were defined as "fly ash"; most were of the materials present in the matrix, which were described as "gel". The microanalyses confirmed that the major hydration product was aluminosilicate gel in all samples. In addition to Al, Si, amounts of Fe, Na, Ca, K, Mg, P and Cl were found in all analyses. Of the species detected, Na and K are likely to be present in significant quantities in the solution. During specimen preparation, species dissolved in the solution will precipitate out on the surface of the hydration products. Some of the free alkali may be removed from the specimen while cleaning and polishing. Consequently, it was impossible to accurately determine degree of sodium incorporation in the aluminosilicate gel.

Fig. 13a and b shows plots of the (Na+K+Ca)/Al vs. Si/Al ratios for the specimens prepared using sodium hydroxide activator, and cured as in Case II 75C and Case II 95C. There was a linear relationship between the two ratios for the specimen cured as at 95 °C, while no clear linear relationship was observed in the case of the fly ash activated by sodium hydroxide and cured at 75 °C, where data points fall in a circular area. Fig. 14a–c presents the plots of the (Na+K+Ca)/Al vs. Si/Al ratios for the specimens prepared using sodium silicate activator, and cured as in Case I 75C, Case II 75C and Case II 95C. For specimens cured at 75 °C, the linear relationships were not well defined. The relationships are consistent with the view that the analyses

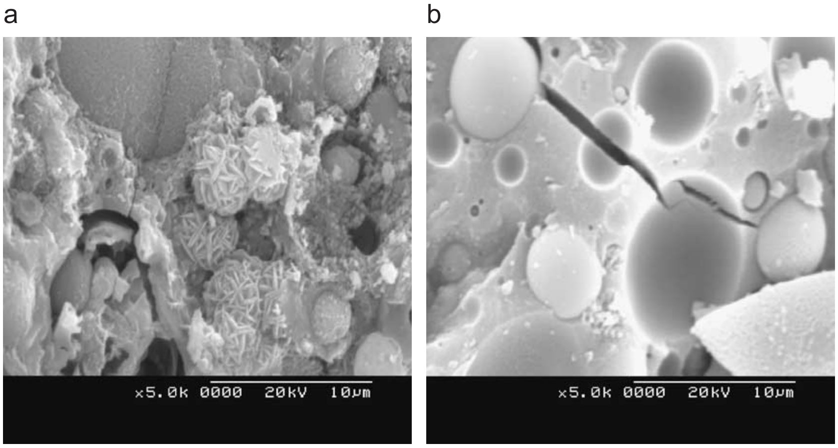

Fig. 11. SEI of geopolymer materials formed by reaction of Class F fly ash with (a) sodium hydroxide solution, and (b) sodium silicate solution and cured as in Case II, 75 °C.

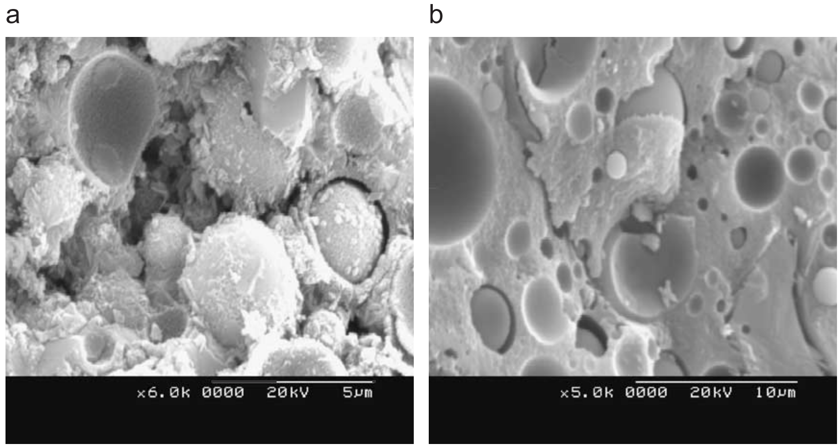

Fig. 12. SEI of geopolymer materials formed by reaction of Class F fly ash with (a) sodium hydroxide solution, and (b) sodium silicate solution and cured as in Case III, 95 °C.

are of aluminosilicate gel with variable composition. Table 3 summarises the observations of the Si/Al ratios of the analyses presented in Figs. 13a and b and 14a–c.

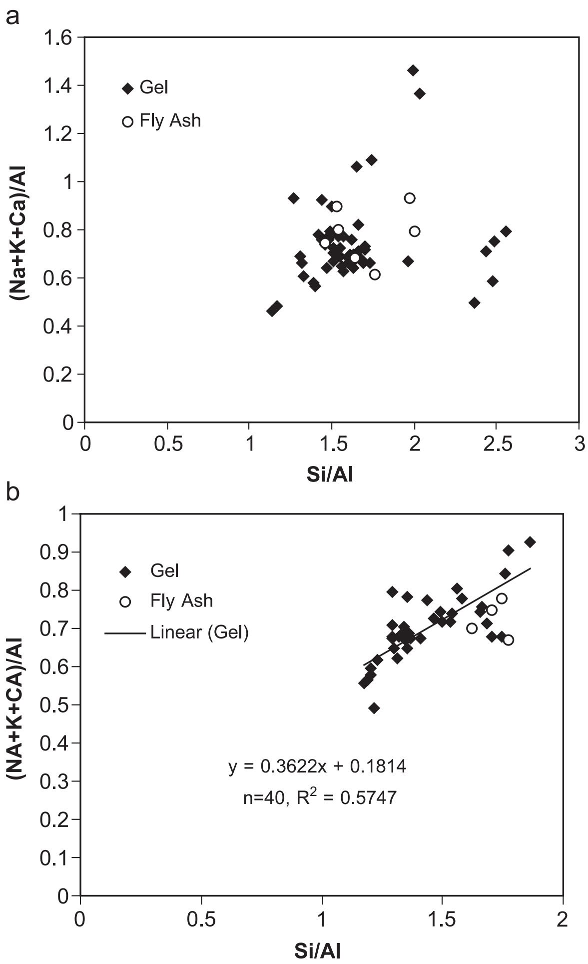

Fig. 13. Results of X-ray microanalysis plotted in the axis (Na+K+Ca)/Al vs. Si/Al, atomic ratios, for specimens prepared using sodium hydroxide solution, 8% Na, and cured (a) 24 h at room temperature, and 24 h at 75 °C (Case II 75C), and (b) 24 h at room temperature, and 24 h at 95 °C (Case II 95C).

4. Discussion

4.1. Strength development

The experiments showed that long precuring as room temperature was beneficial for strength development of all tested samples. In agreement with previous reports, the investigation showed that the first 6 h of heat curing induced significant changes in the geopolymeric materials. The reactions that occurred in the first 6 h of curing did not stop after heat exposure, but continued, and is evident from the further strength growth in samples cured as in Case III 75C and Case III 95C for sodium hydroxide and as in Case III 95C for sodium silicate activators. In fact, the changes which occurred after 24 h of heat treatment were reversible in the case of sodium silicate activator, as up to 20% loss of strength was observed afterwards for Case II 75C and Case II 95C samples cured in water and Case II 95C samples cured in air.

Although the main product of reaction in all geopolymeric samples was amorphous aluminosilicate, there was a significant difference in properties and even in appearance of these aluminosilicates in samples formed with sodium silicate and sodium hydroxide activator. The matrix-forming phases in the case of sodium hydroxide appeared to be more crystalline with more stable strength properties than in the case of sodium silicate activator. Presence of traces of zeolitic products in these materials was indicated by XRD. The inversed dependence of the strength development vs. temperature found in Case III 75 and Case III 95C samples activated by sodium hydroxide and slow strength growth in the Case III 75C sample with 10% Na are believed to be related to the formation of these crystalline phases, that interfered with strength development at the early stages.

4.2. XRD and FTIR

In previous investigations, zeolitic phases chabazite and Na-P1 (gismondine) coexisting with C-S-H were identified in fly ash–NaOH and fly ash–NaOH–cement systems [9].

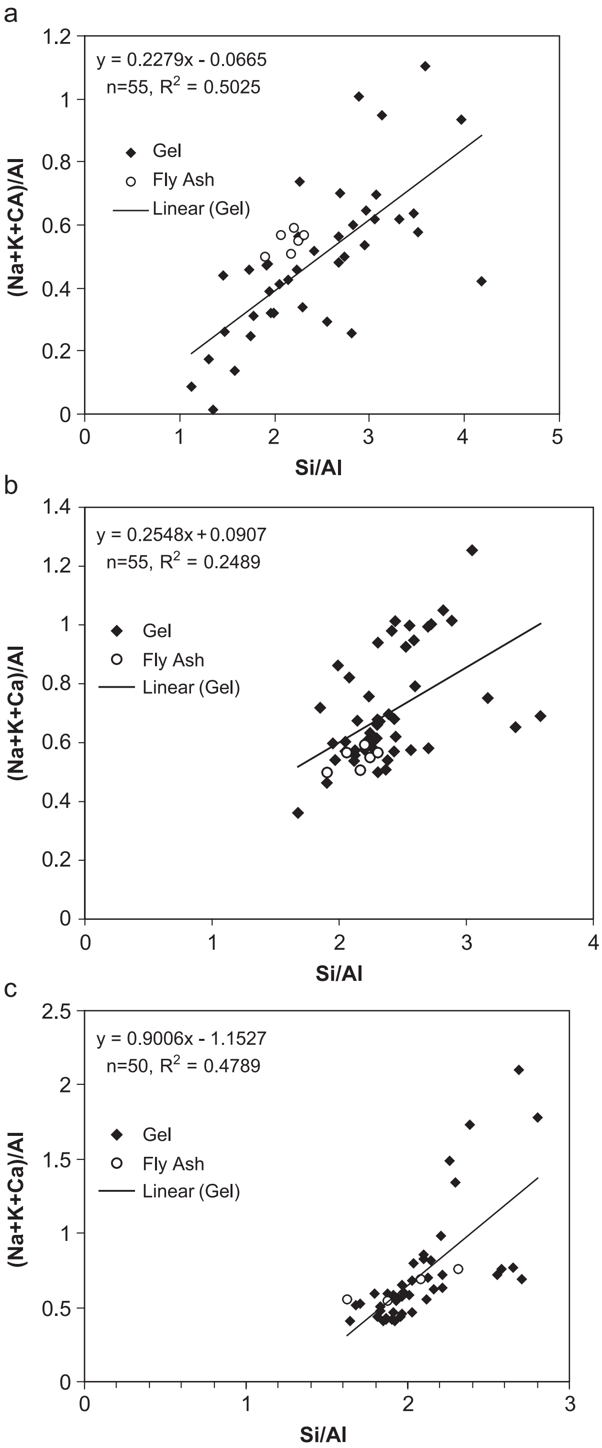

Fig. 14. Results of X-ray microanalysis plotted in the axis (Na+K+Ca)/Al vs. Si/Al, atomic ratios, for specimens prepared using sodium silicate solution, 8% Na, and cured (a) 2 h at room temperature and 1 month at 75 °C (Case I 75 °C), (b) 24 h at room temperature, and 24 h at 75 °C (Case II 75C), and (c) 24 h at room temperature, and 24 h at 95 °C (Case II 95C).

Considerable amounts of zeolites were formed in cement–fly ash system blend activated by highly alkaline multi-compound activator (pH 14) and cured at 70 °C in the study by Katz et al. [11] and Brough et al. [10]. At later ages, tobermorite, hydroxysodalite and Na-P1 (gismondine) were present in the mixtures. Apparently, appearance of considerable amounts of the crystalline zeolitic products in these investigations is connected with the high water/solid ratio of 1 used as compared to water/binder ratio of 0.3 in the present study, because presence of excess amounts of water is an important factor inducing crystallisation in Me_2O–Al_2O_3–SiO_2–H_2O and Me_2O–CaO–Al_2O_3–SiO_2–H_2O (Me—the alkali metal) systems.

In the previous research of geopolymeric materials utilising fly ash, amorphous aluminosilicate gel and zeolite formation was reported [1–3,9]. In this study, some crystalline products appeared after 1 month of curing in the sodium hydroxide activated systems; in the materials activated by sodium silicate, only amorphous aluminosilicate products were observed. However, immediately after heat curing, only amorphous aluminosilicate products were present in all systems. The type of zeolite phase in samples prepared with sodium hydroxide depended on the curing history.

The observations of changes in FTIR spectra of geopolymeric materials agree well with the previous research [1,2,4]. However, in the present study, despite the shown presence of zeolites in some of the samples, there were no drastic modification of the band in the 1600 cm^{-1} range corresponding to bending vibrations (H–O–H) similar to changes, which were observed by Palomo et al. in one of the samples cured at 85 °C. In the present study, this band was modified for all studied geopolymer materials. The appearance of this band was similar for all geopolymer materials, some of them contained only amorphous reaction products, and others contained some zeolites in addition to amorphous aluminosilicates.

4.3. X-ray microanalysis (EDS)

The microanalyses showed a significant difference between the samples in the composition of aluminosilicate

Table 3
Summary of X-ray microanalysis

Type of activator	Curing conditions	Range of Si/Al (atomic ratio)	Range of most frequent Si/Al ratios
NaOH, 8% Na	24 h room temp., 24 h 75 °C, Case II 75C	1.2–2.6	1.4–1.7
	24 h room temp., 24 h 95 °C, Case II 95C	1.2–1.8	1.2–1.5
Sodium silicate, 8% Na, SiO_2/Na_2O=2	2 h room temp., 1 month at 75 °C, Case I 75C	1.0–3.8	Even distribution in the range 1.0–3.5
	24 h room temp., 24 h 75 °C, Case II 75C	1.8–3.6	2–3
	24 h room temp., 24 h 95 °C, Case II 95C	1.6–2.8	1.8–2.2

gel. There was dependence in the Si/Al ratio of the aluminosilicate gel upon temperature of curing for specimens activated by both activators (Table 3). A reduction in Si/Al ratios was observed for specimen cured at 95 °C as compared to specimen cured at 75 °C. For specimens activated by sodium hydroxide, Si/Al ratio was in the range 1.2–2.6 and 1.2–1.8, respectively, for specimens cured as in Case II 75C and Case II 95C. Most frequent values of Si/Al ratio were also reduced with increase of curing temperature.

There was also a difference in the composition of the aluminosilicate gel in specimens prepared using sodium silicate, with the points falling in the range of Si/Al ratios 1–4, 1.8–3.6 and 1.6–2.8, respectively, for the specimens cured as in Case I 75 °C, Case II 75 °C and Case II 95 °C. The results indicated that utilisation of long precuring before heat treatment allowed to narrow the range of Si/Al ratios in the aluminosilicate gel, e.g., Si/Al=1–4 (2 h precuring) compared to Si/Al=1.8–3.6 (24 h precuring). An increase of curing temperature also caused reduction in Si/Al ratios, e.g., Si/Al=1.8–3.6 (75 °C) compared to Si/Al=1.6–2.8 (95 °C). These observations are consistent with the view that the analyses were of aluminosilicate gel with variable composition, which depended on the treatment history and composition of the initial materials. Specimens prepared using sodium silicate activator had the higher average Si/Al ratio than specimens prepared using sodium hydroxide activator.

The plots in Figs. 13a and b and 14a–c show that (Na+K+Ca)/Al ratios in the specimens were in the range 0.5–1 for most data points. Davidovits [5–7] proposed that geopolymers consist of a polymeric Si–O–Al framework, with SiO_4 and AlO_4 tetrahedra joint by sharing O atoms. Al is tetrahedrally coordinated in this network and has a net negative charge. Thus, to maintain electroneutrality, the presence of cations, such as Na^+, K^+ and Ca^{2+}, is essential for charge balance of tetrahedrally coordinated Al, and therefore (Na+K+Ca)/Al atomic ratio in geopolymer must be close to 1. Figs. 13a and b and 14a–c show that (Na+K+Ca)/Al ratios in the specimens are approaching 1 and thus support this model.

5. Conclusions

Long precuring at room temperature is beneficial for strength development of geopolymeric materials utilising fly ash and cured at elevated temperature as it allows shortening the time of heat treatment for achievement of high strength. For materials utilising fly ash activated by sodium silicate, 6-h heat curing is more beneficial for the strength development than 24-h heat treatment. Fly ash samples formed with sodium hydroxide activator had more stable strength properties than fly ash samples formed with sodium silicate.

Samples prepared with the sodium hydroxide activator had traces of zeolite phases in addition to amorphous alkali aluminosilicate that was the only phase present in fly ash activated by sodium silicate activator. Composition of aluminosilicate gel depended on the treatment history. An increase of temperature of heat treatment caused a decrease of Si/Al ratios in aluminosilicate gel, and long curing at room temperature narrowed the range of distribution of the Si/Al ratios.

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