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Thermal behaviour of geopolymers prepared using class F fly ash and elevated temperature curing

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Abstract

This article reports a study of thermal stability of properties upon firing at 800–1200 °C of geopolymer materials prepared using class F fly ash and Na and K alkaline activators. Compressive strength and shrinkage measurements, XRD, SEM (BEI), TGA and MIP were utilised in these studies. The materials were prepared at water/binder ratios in a range of 0.09–0.35, using compaction pressures up to 10 MPa and curing temperatures 80 and 100 °C. Thermal stability of the studied geopolymer materials was rather low. In the samples prepared using sodium-containing activators rapid deterioration of strength at 800 °C was observed, which was connected to a dramatic increase of the average pore size. Initially amorphous structures were replaced by the crystalline Na-feldspars. In materials prepared using fly ash and potassium silicate compressive strength was significantly increased on heating, deterioration of strength started at 1000 °C. After firing these materials remained amorphous with reduced average pore size and significantly increased compressive strength. Compaction at 1–10 MPa reduced shrinkage on firing in all materials. Geopolymer materials prepared using class F fly ash and alkaline activators showed high shrinkage as well as large changes in compressive strength with increasing fired temperature in the range of 800–1200 °C. Thus the materials were found unsuitable for refractory insulation applications.

Keywords: Fly ash; Alkali activated cement; Thermal resistance; Mercury porosimetry; Microstructure; Compressive strength

1. Introduction

Recently discovered geopolymers are ceramic materials that are produced by alkali activation of aluminosilicate raw materials, which are transformed into reaction product by polymerisation in a high pH environment and hydrothermal conditions at relatively low temperatures (up to 120 °C). Because of the low energy requirements of production from common raw materials and their inflammability at high temperatures, these compounds are attracting increasing interest as ecologically friendly fireproof building materials, sound and heat insulators and materials for encapsulating hazardous wastes for storage or disposal [1,2].

Previous investigations by Davidovits et al [3,4], Barbosa and MacKenzie [5,6] reported very good heat resistant properties of materials prepared using sodium silicate, potassium silicate and metakaolin, having thermal stability up to 1200–1400 °C. Geopolymers can be prepared using fly ash and metakaolin as raw materials. Fly ash is a waste of energy manufacture and is produced in millions of tonnes in every developed country, only 20% of it is utilised. If compared with metakaolin it has low cost and environmental factor of utilisation of waste material polluting the environment. However, it may contain significant amount of impurities like iron oxide in a form of hematite and magnetite, and it is also less reactive than metakaolin. Previous work by Krivenko and Kovalchuk [7] investigated heat resistant geopolymer materials manufactured using class F fly ash, which had good thermal resistance properties up to 800 °C. The aims of this study was to investigate thermal stability up to 1200 °C of geopolymer materials prepared using local fly ashes and compare their thermal behaviour to that of geopolymers prepared using metakaolin.

Geopolymers prepared using either fly ash or metakaolin have framework structures originating from condensation of tetrahedral aluminosilicate units of varying Al/Si ratio such as (Al–O–Si–O–)M^+, (Al–O–Si–O–Si–O–)M^+, (Si–O–Al–O–Si–O–Si–O–)M^+ etc. M^+ is an alkali ion, typically Na or K, which balances the charge of the tetrahedral Al [1]. Geopolymers prepared using class F fly ash are largely amorphous, but depending on the activator used in its preparation, may contain areas of semi-crystalline zeolites such as sodalite, gismondine, and chabazite [8]. This paper investigates the effect

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

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	Loss on ignition
Fly ash 1[1]	50.0	28.0	12.0	6.5	1.3	0.7	0.2	–	–	–
Fly ash 2[2]	61.4	33.0	1.1	0.6	0.3	0.1	0.1	2.0	–	1.4

1—Gladstone, Queensland, Australia.
2—Tarong, Victoria, Australia.

of the composition and processing conditions on strength and heat resistant properties at temperatures 800–1200 °C of geopolymer materials prepared using class F fly ashes.

2. Experimental

2.1. Materials

The chemical and mineral compositions of two fly ashes used in the investigation are shown in Table 1 and Fig. 1, respectively. Fly ash 1 was sourced from Gladstone in Queensland; Australia. It is mainly glassy with some crystalline inclusions of mullite, hematite and quartz, with particles size range of 1–7 μm. Fly ash 2 was sourced from Tarong power station in Australia. It is glassy with considerable crystalline inclusions of quartz and mullite with particles size range of 1–10 μm. Fly ash 1 contained 50% silicon oxide and 13% iron oxide, while Fly ash 2 contained 61% silicon oxide and 1% iron oxide. Sodium hydroxide and potassium hydroxide (Sigma), sodium silicate type D with M_s (ratio of silica oxide to sodium oxide) equal to 2.02, 14.7% Na_2O, 29.4% SiO_2, and potassium silicate 13.5% K_2O, 27% SiO_2 both supplied by PQ Australia were used in materials preparations.

2.2. Specimen preparation and test conditions

2.2.1. Preparation of specimens

Two series of test samples were made, differing in their composition and method of moulding. Table 2 shows the details of the samples and moulding conditions. In Series1 samples were prepared using sodium hydroxide, potassium silicate and sodium silicate solutions, providing 8–9%Na or K in mixtures and water/binder ratios of 0.27–0.345. Water/binder ratio given in this paper was calculated as a ratio of total mass of water to mass of fly ash. The pastes were cast in plastic cylinders and sealed with the lid. Because of low flow ability of mixes hand compaction using cylindrical plunger was utilised at a filling stage. The compaction was used to eliminate visible voids in the moulding material. In Series 2 Fly ash samples were prepared, providing 8–9%Na or K in mixtures and water/binder ratios of 0.09–0.166. In series 2 mixes of very dry consistency were used, thus some of test samples were pressure compacted. The compaction pressure varied from 1 to 10 MPa (Table 2). The pastes were moulded in plastic cylinders and sealed with the lid. The method of heat curing was developed before in Ref. [8]. It was shown that prolonged initial curing of samples at room temperature before the application of heat was beneficial for strength development of geopolymer samples prepared using fly ash. The method of curing of mixtures of series 1 and 2 was the same, initially samples were cured for 24 h at room temperature, after that the mixtures were ramped either to 80 or 100 °C for series cured, respectively, at 80 and 100 °C, and cured at this temperature for 24 h. After heat curing the oven was turned off and the materials cooled down inside the oven, afterwards the materials were held at room temperature before being used in tests.

2.2.2. Testing conditions

Table 3 shows the summary of experimental programme. The $\phi 25\times 50$ mm cylinder samples were exposed to firing at 800, 1000 and 1200 °C for 4 h at a heating rate 10 °C/min. The compressive strength of $\phi 25\times 50$ mm cylinder samples was measured before and after firing. At least three samples were used for each data point in these tests. Before and after firing tests dimensions of the cylinder samples were measured using Vernier callipers. Using these measurements shrinkage of the materials

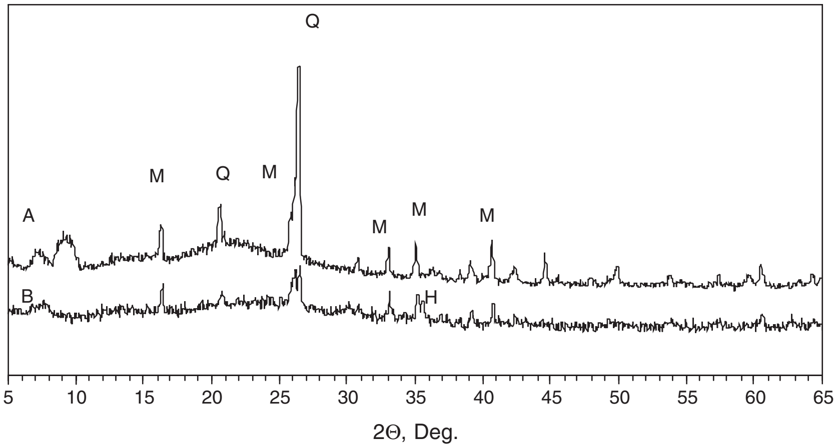

Fig. 1. XRD traces of fly ashes: A=Tarong fly ash, B=Gladstone fly ash; Q=quartz, M=mullite, H=hematite.

Table 2
Sample composition

Series 1

Sample ID	Aluminosilicate source	Curing temperature, °C	Water/binder ratio	Molar ratio			
			w/b	K_2O/Al_2O_3	Na_2O/Al_2O_3	SiO_2/Al_2O_3	H_2O/Al_2O_3
FKSS	Fly ash 1	80	0.345	0.32		4	7
FASS	Fly ash 1	80	0.3		0.47	4	5.1
FA	Fly ash 1	80	0.27		0.645	3.036	5.5
T	Fly ash 2	80	0.27		0.582	3.344	4.99
GT2	80% fly ash 1, 20% fly ash 2	80	0.27		0.564	3.125	4.83
GTFA	50% fly ash 1, 50% fly ash 2	80	0.27		0.623	3.068	3.575
TG2	20% fly ash 1, 80% fly ash 2	80	0.27		0.564	3.125	4.83

Series 2

Sample ID	Aluminosilicate source	Curing temperature, °C	Water/binder ratio,	Molar ratio				Compaction pressure, MPa
			w/b	K_2O/Al_2O_3	Na_2O/Al_2O_3	SiO_2/Al_2O_3	H_2O/Al_2O_3	
G1.PSS	Fly ash 1	100	0.166	0.173		3.5	3.38	–
G1.P1	Fly ash 1	80	0.166	0.173		3.5	3.38	2
G1.P2	Fly ash 1	80	0.166	0.173		3.5	3.38	6
G1.P3	Fly ash 1	80	0.166	0.173		3.5	3.38	10
G1	Fly ash 1	100	0.09		0.645	3.036	1.88	–
G1.1.80	Fly ash 1	80	0.09		0.645	3.036	1.88	1
G1.2.80	Fly ash 1	80	0.09		0.645	3.036	1.88	2
G1.3.80	Fly ash 1	80	0.09		0.645	3.036	1.88	3
G1.1.100	Fly ash 1	100	0.09		0.645	3.036	1.88	1
G1.2.100	Fly ash 1	100	0.09		0.645	3.036	1.88	2
G1.3.100	Fly ash 1	100	0.09		0.645	3.036	1.88	3
G2	Fly ash 1	80	0.18		1.28	3.042	3.76	
T1.5	Fly ash 2	80	0.14		0.806	3.142	2.39	
GT2.0	80% Fly ash 1, 20% fly ash 2	100	0.18		0.564	3.125	3.23	
GT2.1	80% fly ash 1, 20% fly ash 2	100	0.09		0.623	3.068	1.82	

due to firing was calculated as an average shrinkage of the three samples exposed to the firing test. Three numbers, which characterize shrinkage, were calculated: S_D-shrinkage in diameter direction, S_L-shrinkage in the length direction, and volumetric shrinkage S_V calculated based on S_D and S_L ($S_V=(2\ S_D+S_L)/3$).

Before and after heat exposure materials G1, KFSS and G1.PSS were examined using TGA, SEM, MIP and XRD. Thermogravimetric analysis was performed using Setaram TG2 unit (Setaram, France) with temperature range of 30–1000 °C in floating air and heating rate of 10 °C/min. Microstructural studies utilised SEM (Hitachi S-2300, Japan) in a BEI mode. The polished specimens were used for the SEM examinations. To prepare the polished specimens, 1 mm thick slices were cut from cylinder samples using a low speed diamond saw, impregnated with ultra-low viscosity resin and then polished using a number of steps (240, 400 and 600 grit SiC, 6, 3, 1 μm diamond paste). For the examination using SEM the polished specimens were carbon coated. X-Ray diffraction analyses of powdered specimens were made using a Rigaku Geigerflex D-max II automated diffractometer (Rigaku, Japan) 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). The slow scanning rate was used to improve resolution of peaks. The materials were also analysed using mercury intrusion porosimetry to study porosity and average pore diameter before and after firing. The geopolymeric samples crushed to a size of 5–10 mm were dried at 105 °C prior to MIP test. As it was found that for materials with pores less than 0.1 μm the pore size distribution result from MIP is markedly affected by the drying treatment, the most severe of the drying techniques, oven drying at 105 °C was selected. Previously it was found that some geopolymer materials contain pores of average size 4.5 nm [9]. In addition, low water/binder ratio was used in this investigation, which also helped to reduce the average pore size. A similar drying technique was used previously by Winslow and Lovell as preparation for MIP test [10]. The MIP tests were performed using Autopore 2001 station (Micromeritics Instrument Corporation, GA USA) with pressure in the range of 0–440 MPa. The contact angle $\theta=130°$ was used for data processing.

3. Results

3.1. Materials prepared using sodium-containing activators

3.1.1. Compressive strength

Fig. 2 shows strength evolution in geopolymer specimens prepared using sodium-containing activator and water/binder

Table 3
Experimental programme

Sample ID	Compaction pressure MPa	Compressive strength after curing at				TGA	XRD	SEM	MIP	Shrinkage
		22 °C	800 °C	1000 °C	1200 °C					
FKSS	–	X	X	X	X	X	X	X	X	X
FASS	–	X	X			–	X	–	–	–
FA	–	X	X			–	X	–	–	–
T	–	X	X			–	X	–	–	–
T1.5	–	X	X	X		–	X	–	–	X
GT2	–	X	X			–	X	–	–	–
GTFA	–	X	X			–	X	–	–	–
TG2	–	X	X			–	X	–	–	–
GT2.0		X	X	X		–	X	–	–	–
GT2.1		X	X	X		–	X	–	–	X
G2	–	X	X			–	X	–	–	X
G1	–	X	X	X	X	X	X	X	X	X
G1.1.100	1	X	X	X	X	–	–	–	–	X
G1.2.100	2	X	X	X	X	–	–	–	–	X
G1.3.100	3	X	X	X	X	–	–	–	–	X
G1.1.80	1	X	X	X	X	–	–	–	–	–
G1.2.80	2	X	X	X	X	–	–	–	–	–
G1.3.80	3	X	X	X	X	–	–	–	–	–
G1.PSS	–	X	X	X	X	X	X	X	X	X
G1.P1	2	X	X	X	X	–	–	–	–	X
G1.P2	6	X	X	X	X	–	–	–	–	X
G1.P3	10	X	X	X	X	–	–	–	–	X

ratios in a range of 0.09–0.3. Visual examination of the materials prepared using sodium-containing activators after firing experiments showed that all specimens except G1 prepared at $w/b=0.09$ developed shrinkage cracking when exposed to firing to 800 °C. Shrinkage cracking increased with an increase of water/binder ratio. Samples G1 (manufactured using Gladstone fly ash), T and T1.5 (both manufactured using Tarong fly ash), TG2 (80% Tarong +20% Gladstone fly ash) prepared at w/b ratios of 0.09, 0.27, 0.14 and 0.27, respectively, had a tendency of increasing strength in the firing experiment up to 800 °C, strength of all other specimens was deteriorating upon firing. However, after exposure to temperature above 800 °C strength of all specimens prepared using Na-containing activator deteriorated rapidly.

Fig. 3 shows strength evolution in specimens prepared using sodium hydroxide at water/binder ratio 0.09 and using compaction pressure 1, 2 and 3 MPa, and specimen G1, which was compacted by hand. Specimens cured at 100 °C had initial strength 50–100% higher than that of the specimens cured at 80 °C. All specimens had a tendency of increasing strength upon firing. After firing the compressive strength of the pressure compacted specimens was lower than that of the hand compacted specimen. On firing, specimens manufactured using pressure 1–3 MPa increased strength up to 30%, while specimens G1 had

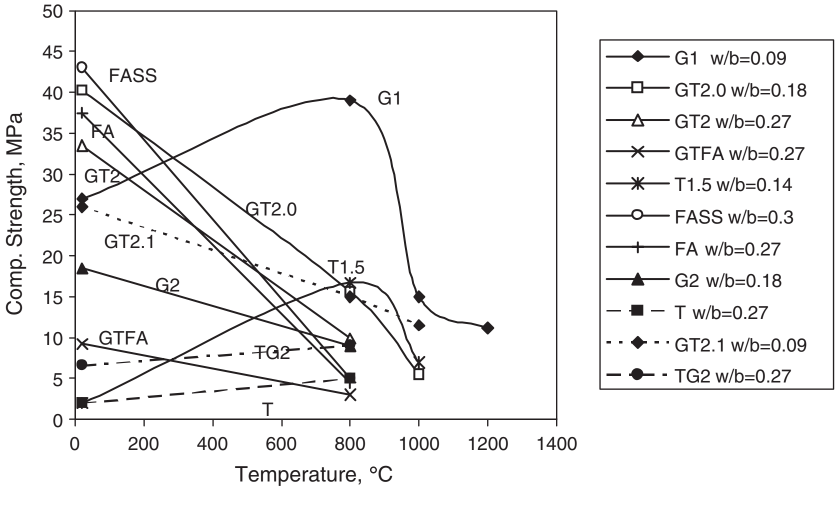

Fig. 2. Compressive strength of geopolymer materials of $w/b=0.09$–0.3 prepared using class F fly ash and sodium silicate or/and sodium hydroxide before and after firing experiments.

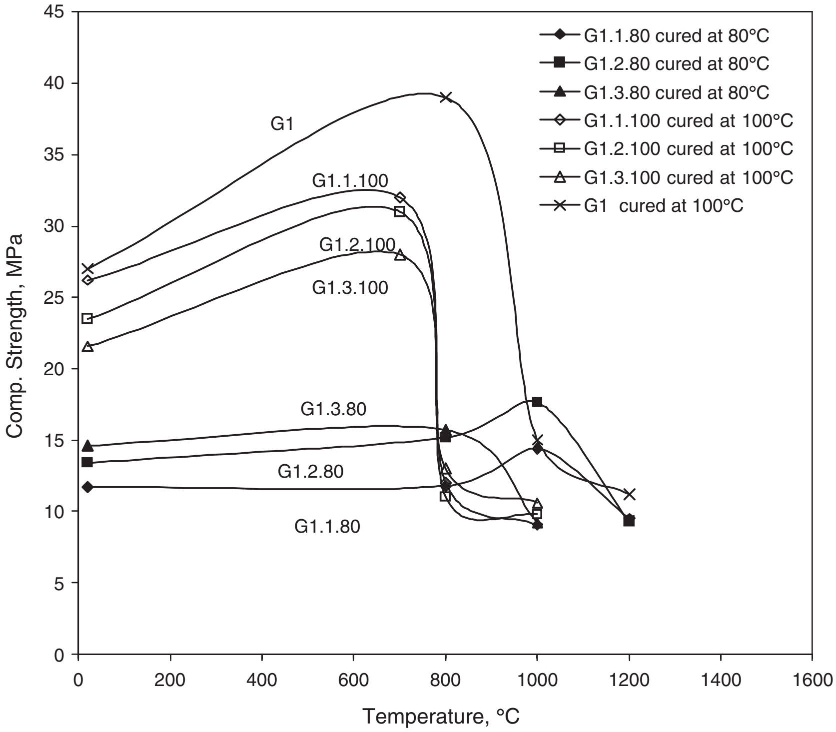

Fig. 3. Compressive strength of geopolymer materials of $w/b=0.09$ prepared using class F fly ash and sodium hydroxide before and after firing experiments. Specimens G1 was not pressure compacted, while all other specimens were pressure compacted.

strength increased 44%. However, after exposure to temperature above 800 °C strength of specimens prepared using Na-containing activator rapidly deteriorated. Strength loss was rapid in specimens prepared using heat curing at 100 °C, which had higher initial strength than specimens cured at 80 °C.

3.1.2. Thermal gravimetric analysis

Fig. 4 presents typical results of thermal gravimetric analysis of geopolymeric materials G1 prepared using sodium hydroxide activator and Gladstone fly ash. There was a continuous loss of weight up to 700 °C, with the rate of weight loss increasing around 100 and 700 °C and total weight loss about 12% at 1000 °C. Fig. 4 also presents results of thermal gravimetric analysis of geopolymeric materials FKSS and G1.PSS prepared using potassium-containing activators and Gladstone fly ash. There was a continuous loss of weight up to 700 °C, with the rate of weight loss increasing around 100 and 600 °C and total weight loss about 5% (G1.PSS) and 8% (FKSS) at 1000 °C.

3.1.3. XRD

Fig. 5 presents a selection of typical XRD traces for the geopolymer material G1 ($w/b=0.09$) prepared using Gladstone fly ash and sodium-containing activator before and after exposure to firing at 800, 1000 and 1200 °C. Traces of amorphous aluminosilicate gel and semi-crystalline hydroxysodalite were present in the initial sample, in addition to the residue of fly ash, quartz, mullite and hematite. After exposure to 800 °C peaks for hydroxysodalite started to disappear and crystalline nepheline $AlNaSiO_4$ was present in the specimen. After exposure to 1000 °C traces of $NaAlSi_2O_6$ was found, while after exposure to 1200 °C strong peaks for albite $NaAlSi_3O_8$ in addition to Na-feldspars $AlNa(SiO_4)$ and $NaAlSi_2O_6$, were evident.

Fig. 6 presents XRD traces of the geopolymer material GT2 ($w/b=0.27$) prepared using 80% Gladstone fly ash and 20% Tarong fly ash before and after exposure to firing at 800 and 1000 °C. The amorphous aluminosilicate gel with inclusions of semi-crystalline hydroxysodalite and Na–P1 zeolite formed the initial material. After firing at 800 °C peaks of nepheline $AlNaSiO_4$ and $NaAlSi_2O_6$, were present, while after exposure to 1000 °C traces of $AlNaSiO_4$ were found, further heating to 1200 °C caused melting of the specimen.

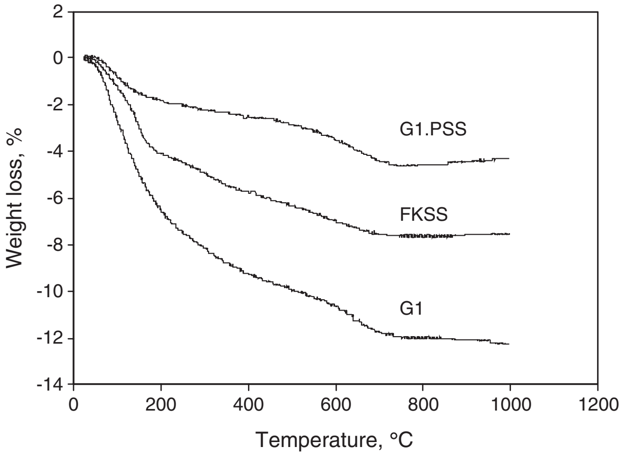

Fig. 4. Thermal gravimetric analysis of geopolymeric materials prepared using potassium-containing activators G1.PSS ($w/b=0.166$) and FKSS ($w/b=0.345$), and sodium-containing activator G1 ($w/b=0.09$).

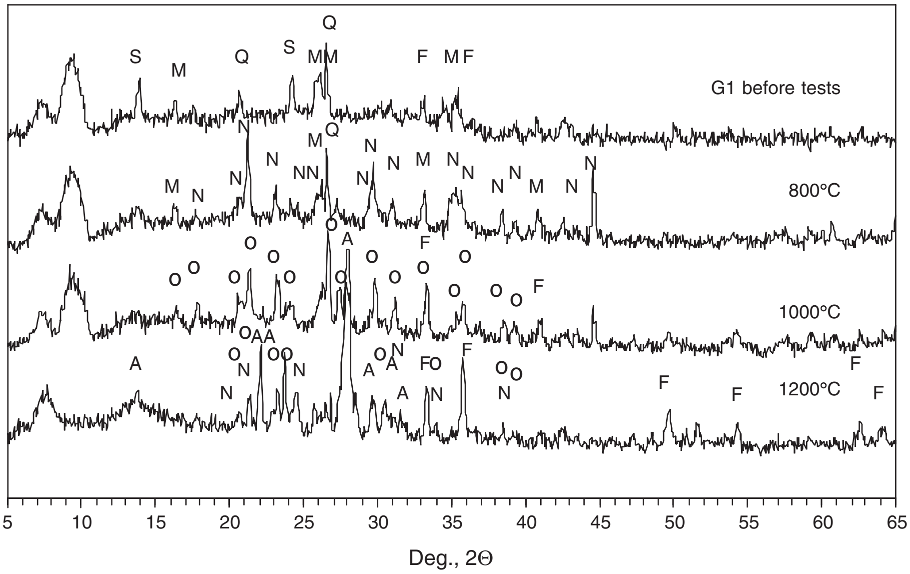

Fig. 5. XRD traces of G1 material prepared using fly ash 1 and sodium hydroxide before tests and after exposure to 800, 1000 and 1200 °C: M=mullite, Q=quartz, F=hematite, N=nepheline AlNa(SiO$_4$), o=NaAlSi$_2$O$_6$, A=albite NaAlSi$_3$O$_8$, S=hydroxy sodalite.

3.1.4. Porosity by MIP and SEM

Fig. 7 presents cumulative intrusion in the MIP experiment for G1 specimens prepared using sodium hydroxide and Gladstone fly ash at $w/b=0.09$. The total porosity measured by MIP in G1 specimen before and after exposure to 800 and 1000 °C slightly increased from 26% to 29%, while the average pore size increased significantly from 37.6 nm in initial specimen to 121 and 1835 nm after exposure to 800 and 1000 °C, respectively (Fig. 8).

Fig. 9(a–d) presents the SEM images obtained in back-scattered electrons of the polished sections of the G1 specimen before and after firing experiments at 800, 1000 and 1200 °C. The G1 matrix containing mostly unreacted material presented in Fig. 9(a) was transformed into a matrix containing more reacted material with crystalline reaction products (Fig. 9(b)). A significant increase in porosity was observed after firing at 1000 °C with pores up to 10 μm, while after firing at 1200 °C arrears of low porosity and large pores (50–200 μm) dominated the matrix (Fig. 9(c,d)). Development of these large pores is possibly connected to the decomposition of the material on heating.

3.1.5. Shrinkage

Table 4 presents a summary of shrinkage measurements of geopolymer specimens. Three numbers, which characterize shrinkage, are presented: S_D-shrinkage in diameter direction,

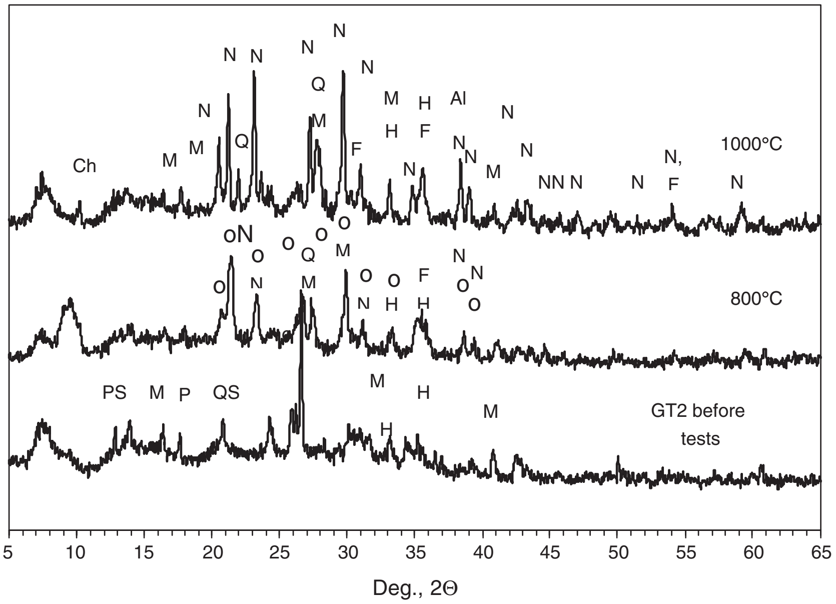

Fig. 6. XRD traces of GT2 material before tests and after exposure to 800 and 1000 °C: M=mullite, Q=quartz, F=magnetite, H=hematite, N=nepheline AlNa(SiO$_4$), o=NaAlSi$_2$O$_6$, Al=aluminium syn., P=Na–P1 zeolite (gismondine), S=hydroxy sodalite.

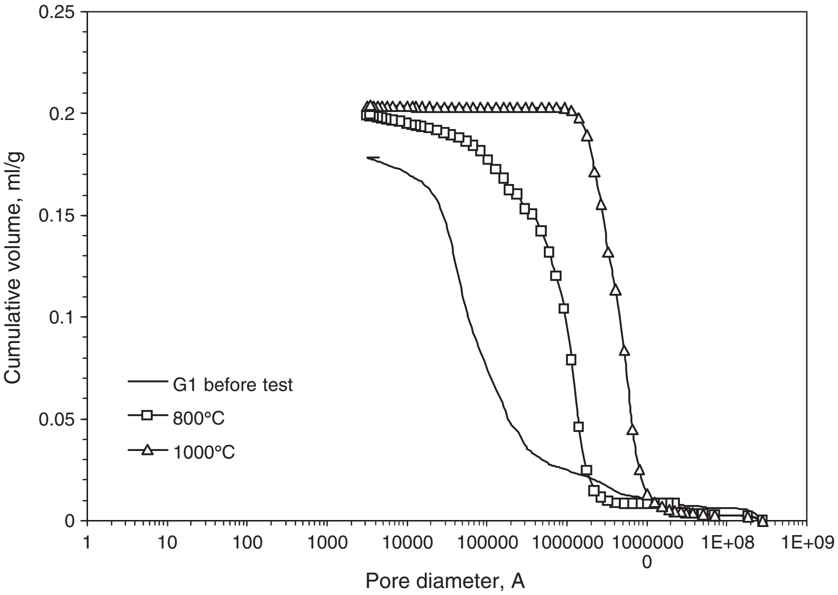

Fig. 7. Cumulative volume of intrusion vs pore diameter in the MIP experiment for the G1 specimens prepared using Gladstone fly ash and sodium hydroxide at $w/b=0.09$.

S_L-shrinkage in the length direction, and volumetric shrinkage S_V calculated based on S_D and S_L. For geopolymer materials prepared using K activators, shrinkage in length and diameter directions were reduced if pressure compaction was used in the manufacturing. With an increase of the compaction pressure, shrinkage S_L and S_D declined. For geopolymer materials prepared using Na-containing activators and utilising pressure compaction in the manufacturing, shrinkage in the length direction was reduced, while shrinkage in diameter direction slightly increased. For materials prepared using Na- and K-containing activators, shrinkage increased with an increase of firing temperature from 800 to 1200 °C, increase of water/binder ratio and the alkali content of the material. Melting occurred at lower temperature if the sodium content of the specimens was increased as in the case of G2 and T1.5 specimens. Specimens prepared using Tarong fly ash (T1.5) with a high silica content had an expansion on firing (T1.5 specimen), which was attributed to expansion on heating of uncombined silica. This expansion increased with an increase of the firing temperature to a point, when a large volume of foam was produced at 1200 °C.

3.2. Materials prepared using potassium-containing activator

3.2.1. Compressive strength

Fig. 10 presents compressive strength of the specimens prepared using potassium silicate and Gladstone fly ash at $w/b=0.166$–0.345 and cured at 80 and 100 °C. Specimens manufactured using $w/b=0.166$ were compacted using applied pressure of 2, 6 and 10 MPa (specimens G1.P1, G1.P2 and G1.P3, respectively). The initial strength of 2–5 MPa was measured for materials prepared at $w/b=0.166$ and 0.345 and cured at 80 °C, while for the material prepared at $w/b=0.166$ and cured at 100 °C the highest compressive strength of 12 MPa was achieved. Materials prepared at $w/b=0.345$ and 0.166 and cured at 80 °C had a similar strength evolution after exposure to 800, 1000 and 1200 °C, achieving maximum strength of 53 MPa after firing at 1000 °C, while further increase of firing temperature caused deterioration of strength. Specimens G1.PSS ($w/b=0.166$) compacted by hand and cured at 100 °C had an increasing strength up to 1200 °C. Observation of the strength evolution of the specimens compacted at 2–10 MPa show that pressure compaction does not induce significant improvement of initial strength, but can be detrimental for strength development on firing.

3.2.2. XRD

Figs. 11 and 12 show XRD traces of the geopolymer samples FKSS ($w/b=0.345$) and G1.PSS ($w/b=0.166$), respectively, prepared using Gladstone fly ash and potassium-containing activators before and after firing at 800, 1000 and 1200 °C. 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 17–35° 2θ arising from the glassy phase of the fly ash and broad

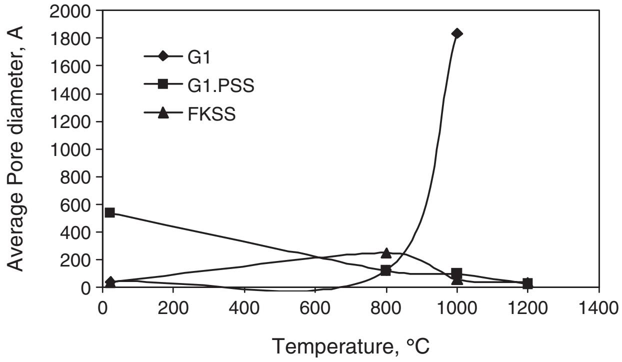

Fig. 8. Evolution of the average pore diameter (A) in geopolymer materials prepared using sodium hydroxide (G1) and potassium silicate (G1.PSS, FKSS) before and after firing, based on results of MIP experiments.

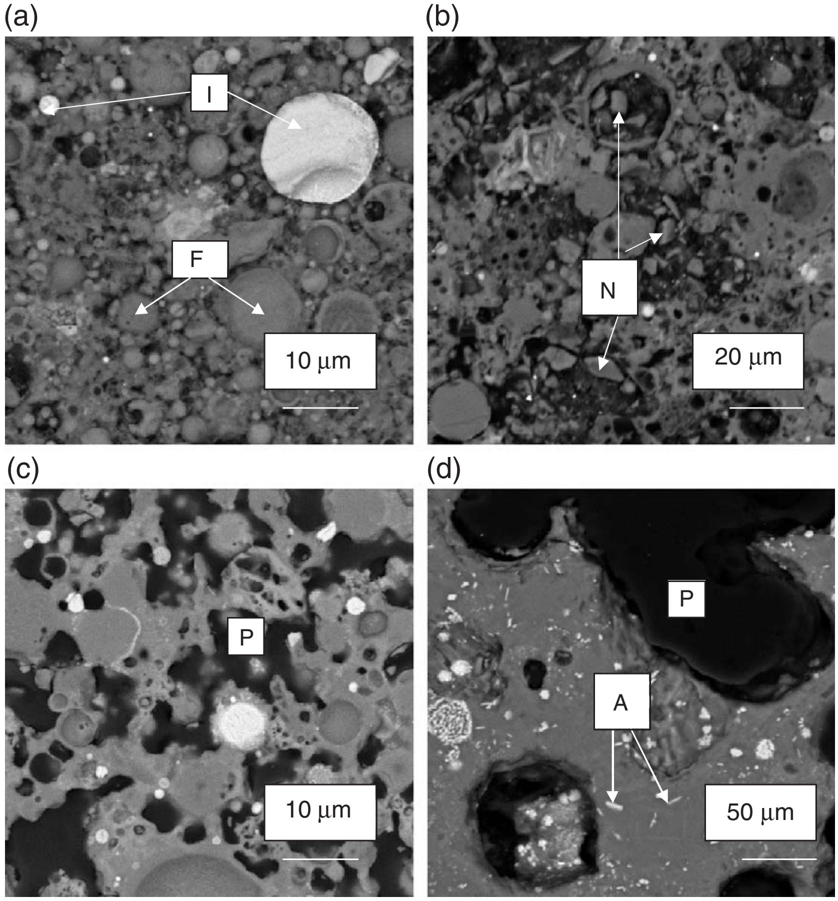

Fig. 9. (a–d). Representative SEM BEI of the polished sections of G1 specimen prepared using sodium hydroxide and class F fly ash (a) before test, and after exposure to (b) 800 °C, (c) 1000 °C, (d) 1200 °C. F—fly ash particle, I—fly ash particle with high content of iron impurity, P—porosity; N, A—Na-feldspars.

peaks in the regions 6–10° 2θ arising from aluminosilicate gel. Some modification of peaks in the region 6–10° 2θ was observed in FKSS specimen after firing at 800 and 1200 °C indicating of changes in the aluminosilicate gel (Fig. 11). No such changes were found in G1.PSS specimen (Fig. 12), where traces of crystalline kalsilite and leucite appeared after firing at 1200 °C. In both FKSS and G1.PSS specimens peaks for hematite and quartz increased their intensity after firing.

3.2.3. Porosity by MIP and SEM

Fig. 13(a–b) shows cumulative intrusion in MIP experiment before and after firing of the FKSS (w/b=0.345) and G1.PSS

Table 4
Summary of shrinkage measurements, %

Sample ID	Compaction pressure, MPa	800 °C			1000 °C			1200 °C		
		S_D	S_L	S_V	S_D	S_L	S_V	S_D	S_L	S_V
G1	N/A	2.06	5.19	3.10	3.95	5.14	4.35	5.33	−4.55	N/A
G1.1.100	1	2.50	3.30	2.76	4.28	3.7	4.08	7.83	5.70	7.12
G1.2.100	2	2.37	2.79	2.51	4.02	2.7	3.58	5.32	3.94	4.86
G1.3.100	3	2.23	2.75	2.40	3.04	2.94	3.01	Melted		
G1.PSS	N/A	1.77	1.86	1.8	2.66	3.58	2.96	8.05	13.96	10.02
G1.P1	2	1.03	0.74	0.933	4.42	3.90	4.25	6.53	7.78	6.94
G1.P2	6	0.2	0.2	0.2	3.52	3.53	3.52	6.17	7.80	6.71
G1.P3	10	0.0	0.0	0.0	3.25	4.62	3.71	6.04	7.45	6.51
FKSS	N/A	2.07	2.96	2.36	3.23	4.18	3.54	9.65	15.45	11.58
G2	N/A	4.08	2.08	3.41	4.4	2.56	3.79	Melted		
GT2.1	N/A				4.06	2.08	3.4	Melted		
T1.5	N/A	−3.85	−11.9	−6.53	−4.11	−13.53	−7.24	Melted (after large expansion)		

S_D=Shrinkage in the diameter direction of the cylinder, %.
S_L=Shrinkage in the length direction of the cylinder, %.
S_V=$(2\ S_D+S_L)/3$ Average volumetric shrinkage, %.

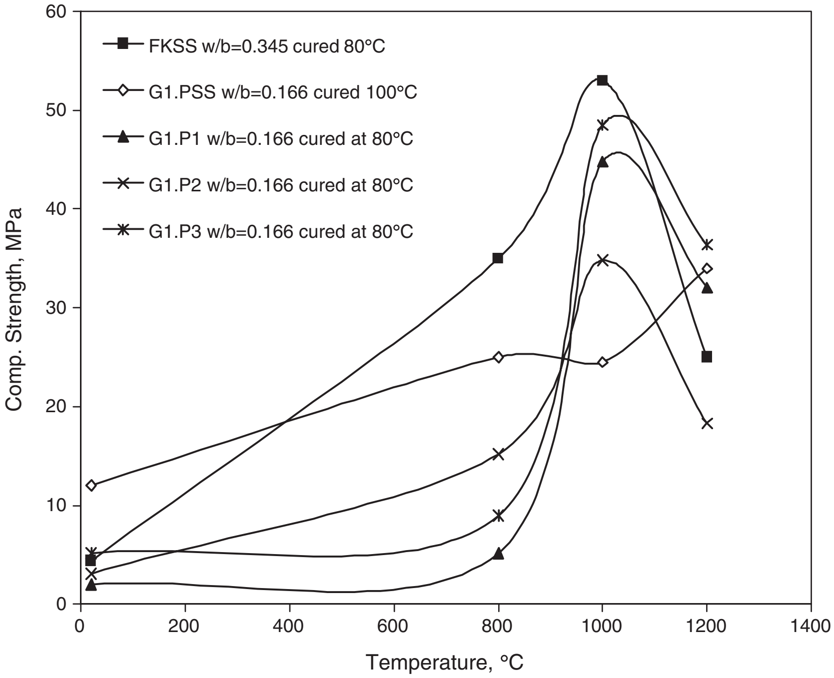

Fig. 10. Compressive strength of geopolymer materials of $w/b=0.166$–0.345 prepared using class F fly ash and K-containing activator before and after firing experiments.

($w/b=0.166$) specimens at 800, 1000 and 1200 °C. The total volume intruded in MIP experiment had a high variation in case of FKSS specimen, with significant increase after firing at 800 °C, and significant reduction after firing at 1000 and 1200 °C as compared to initial value. These changes of volume were associated with some increase of the average pore diameter at 800 °C, followed by reduction of the average pore size at 1000 and 1200 °C (Fig. 8). In the case of G1.PSS there was a significant reduction of the total volume of intrusion after firing at 1200 °C, while after firing at 800 and 1000 °C pore volume was not different from that of the initial material (Fig. 13(b)). The average pore size was continuously reduced in case of G1.PSS sample (Fig. 8). Fig. 14 presents evolution of total porosity measured by MIP. A significantly decreased porosity was observed in case of FKSS specimen after treatment at 1000 °C. In the case of G1.PSS and G1 specimens, the specimen's porosity was only slightly reduced after treatment at 1000 °C.

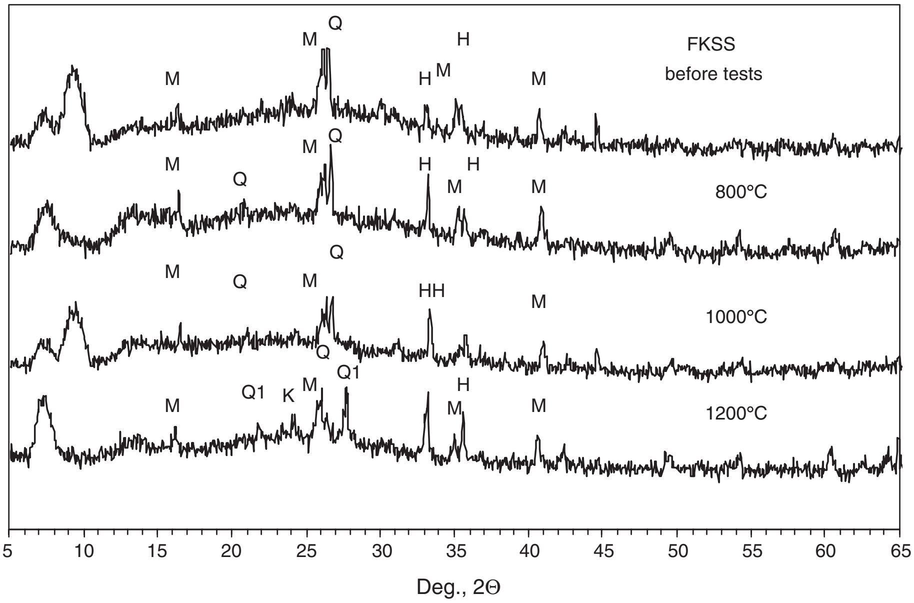

Fig. 11. XRD traces of FKSS material before test and after exposure to 800, 1000 and 1200 °C: M=mullite, Q=quartz (PDF No. 1-649), Q1=SiO_2 (PDF No. 85-462), H=hematite, K=kalsilite ($KAlSiO_4$) (PDF No.11-579).

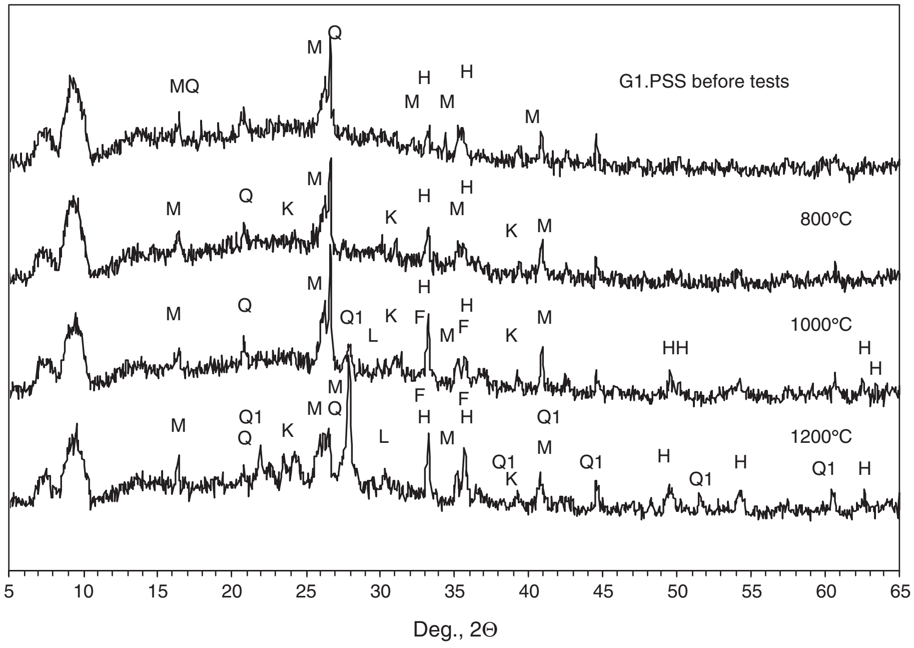

Fig. 12. XRD traces of G1.PSS material before tests and after exposure to 800, 1000 and 1200 °C: M=mullite, Q=quartz (PDF No. 1-649), Q1=SiO_2 (PDF No. 85-462), F=magnetite, H=hematite, K=kalsilite ($KAlSiO_4$) (PDF No.11-579), L=leucite ($KAlSi_2O_6$) (PDF No.38-1423).

Figs 15(a–d) and 16(a–d) present SEM images in backscattered electrons of the polished sections of the G1.PSS and FKSS specimens, respectively, before and after the firing experiments. Fig. 15(a–d) indicates that the microstructure of G1.PSS ($w/b=0.166$) specimen did not experience large changes after firing at 800 and 1000 °C, while significant densification was observed after firing at 1200 °C. Fig. 16(a–d) shows changes that took place in the microstructure of FKSS ($w/b=0.345$) after firing at 800, 1000 and 1200 °C. In agreement with the measurement of the average pore diameter in MIP experiment (Fig. 8) the SEM images (Fig. 16(a–d)) show a significant increase of the average pore size after treatment at 800 °C, which was progressively reduced after treatment at 1000 and 1200 °C. A very dense matrix was produced in the result of treatment at 1200 °C. However large pores of size 20–100 μm which appeared in the microstructure may cause degradation of strength evident in Fig. 10.

4. Discussion

The term fire resistance is frequently used to assess the behaviour after firing of different samples. However, the criteria used to assess fire resistance could be defined differently. For example, in a refractory context, the linear and volume changes are important indicators of fire resistance. If material has linear shrinkage which exceeds the limit of <1.5%, the material could not be classed as resistant. Stability of strength after firing is also an indication of good fire resistance in refractory context. While fire resistance in a fire-protection context is based upon heat conduction through a sample when exposed to standard fire defined by ISO 834. Then a simple relation can be established between the thermal resistance ($R=\delta/k$) of the protection layer and the thickness of an equivalent concrete protection. The equivalent concrete thickness yields the same time for reinforcement bars to reach 500 °C as the corresponding thermal protection layer when the structure is exposed to a standard ISO 834 fire [11]. In this article the samples were investigated considering fire resistance in a refractory context, however, fire resistance of these materials in a fire-protection context was not evaluated.

Two different class F fly ashes were utilised in this study. Gladstone fly ash contained 50% SiO_2, 28% Al_2O_3, and 12% Fe_2O_3, while Tarong fly ash contained about 61.4% SiO_2,33% Al_2O_3 and 1% Fe_2O_3. Examination of XRD traces of the fly ashes (Fig. 1) indicated that Gladstone fly ash had mainly amorphous structure, while Tarong fly ash had a considerable crystalline component. The strength of materials prepared using these fly ashes was also different: materials utilising Gladstone fly ash had good initial strength of 35–45 MPa, while materials utilising Tarong fly ash had a low strength of 2 MPa. Thus significant crystalline component of the Tarong fly ash negatively influenced its activation and produced low initial strength. In addition, particle size may also have an influence on the performance of the materials, as Gladstone fly ash had particle size range of 1–7 μm, while that for Tarong fly ash was 1–10 μm. Fine particles have a better dissolution, which is a first step in geopolymerisation process. In addition, it is possible that particles size, their crystalline state and composition had a significant influence on the amount of Si- and Al-monomers which come into solution and become the building blocks in the structure of geopolymers.

The evolution of the compressive strength after exposure to 800, 1000 and 1200 °C for geopolymer specimens showed again a significant difference in the performance of materials prepared using two fly ashes. The specimens utilising Gladstone fly ash and sodium-containing activators with good initial

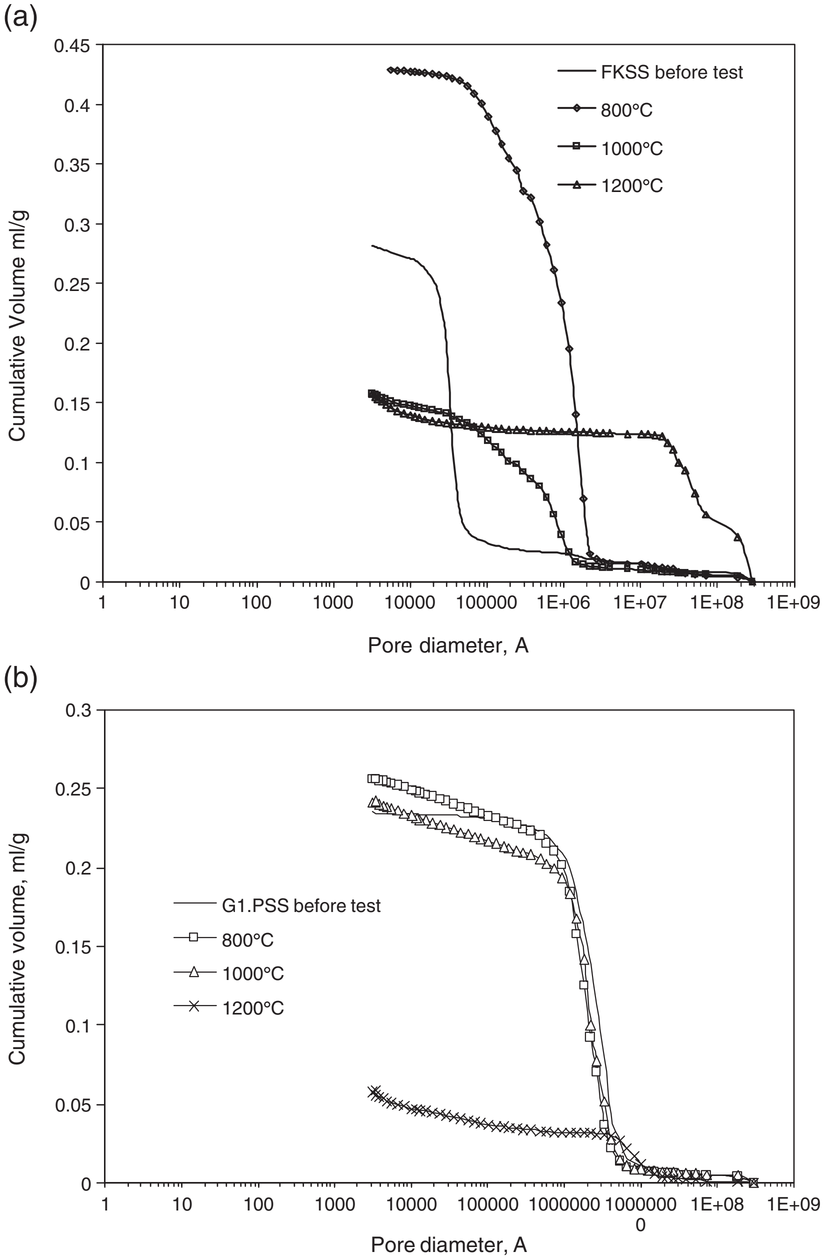

Fig. 13. (a,b). Cumulative volume of intrusion vs pore diameter in the MIP experiment for the specimens prepared using Gladstone fly ash and potassium silicate (a) FKSS at w/b=0.345, (b) G1.PSS at w/b=0.1666 before and after exposure to firing at 800, 1000 and 1200 °C.

strength (35–45 MPa) before the firing experiments, had a very high strength loss after exposure to 800 °C, while geopolymers prepared using Tarong fly ash with low initial strength (2 MPa) improved strength after firing at 800 °C (5–16 MPa). Geopolymers prepared using potassium-containing activator utilised only Gladstone fly ash. They had quite low initial strength (2–5 MPa), but had significantly improved strength in the result of firing at 1000 °C (up to 53 MPa). Thus observations of geopolymer materials manufactured using Gladstone fly ash indicated that the behaviour of materials prepared using Na- and K-containing activators when exposed to firing was different. Materials prepared using K-containing activators had significantly increased their initial strength, while materials prepared using sodium-containing activators had very high loss of strength at temperatures exceeding 800 °C. Previously, materials prepared using metakaolin showed thermal resistance up to 1300 °C for sodium polysialate geopolymers and up to 1300–1400 °C for potassium polysialate geopolymers [5,6].

The initial materials prepared using Na-containing activators were mostly amorphous, only traces of hydroxy-sodalite were present in some of the studied materials. However, after firing at 800 °C the materials prepared using sodium-containing activators and class F fly ash showed reduced strength and presence of Na-felfdspars $NaAlSiO_4$ and $NaAlSi_2O_6$, which remain to the onset of melting at 1100–1200 °C. In some of materials traces of albite $NaAlSi_3O_8$ appeared at 1200 °C. SEM images in back scattered electrons showed presence of significant amount of crystalline phases after firing at 800 °C.

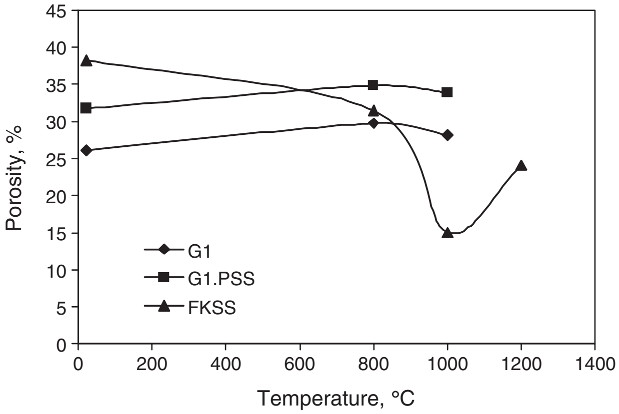

Fig. 14. Evolution of porosity (%) in geopolymer materials prepared using sodium hydroxide (G1) and potassium silicate (G1.PSS, FKSS) before and after firing, based on results of MIP experiments.

Evidently, feldspars crystallisation contributed to the increase of porosity and deterioration of strength (Fig. 9(b)). It is possible that presence of unreacted sodium in these materials caused crystallisation of Na-feldspars on firing. Barbosa and MacKenzie [5] described similar thermal behaviour of poorly reacted formulations of metakaolin and sodium silicate mixtures. However, in their investigation well-reacted geopolymer material did not show formation of crystalline phases up to 1300 °C, only small amounts of mullite and corundum was found at 1200–1300 °C, attributed to reaction of unreacted metakaolin. Barbosa and MacKenzie reported that increased amounts of water and/or sodium and silicon could cause reduced thermal resistance of geopolymer material when exposed to firing [5]. The investigation showed that the performance of geopolymer materials was improved when low water/binder ratios were utilised. It is seen in the performance of geopolymer materials of water/binder ratios 0.166 and 0.09. Experimental results indicated that curing at elevated temperature increased the initial strength and fire resistance of the geopolymer materials. Loss of strength on firing was possibly connected to the deterioration of aluminosilicate gel. After decomposition of aluminosilicate gel freed sodium, silicon and aluminium produced Na-feldspars. Performance of materials prepared using sodium-containing activators and class F fly ash was significantly lower than that of materials prepared using metakaolin possibly due to incomplete polymerisation of geopolymers and presence of high iron content in the fly ash.

It was previously investigated that materials prepared using Gladstone fly ash and sodium-containing activators have very small average pore size of about 4.5 nm [9], therefore these materials have a low permeability. It is possible that on firing

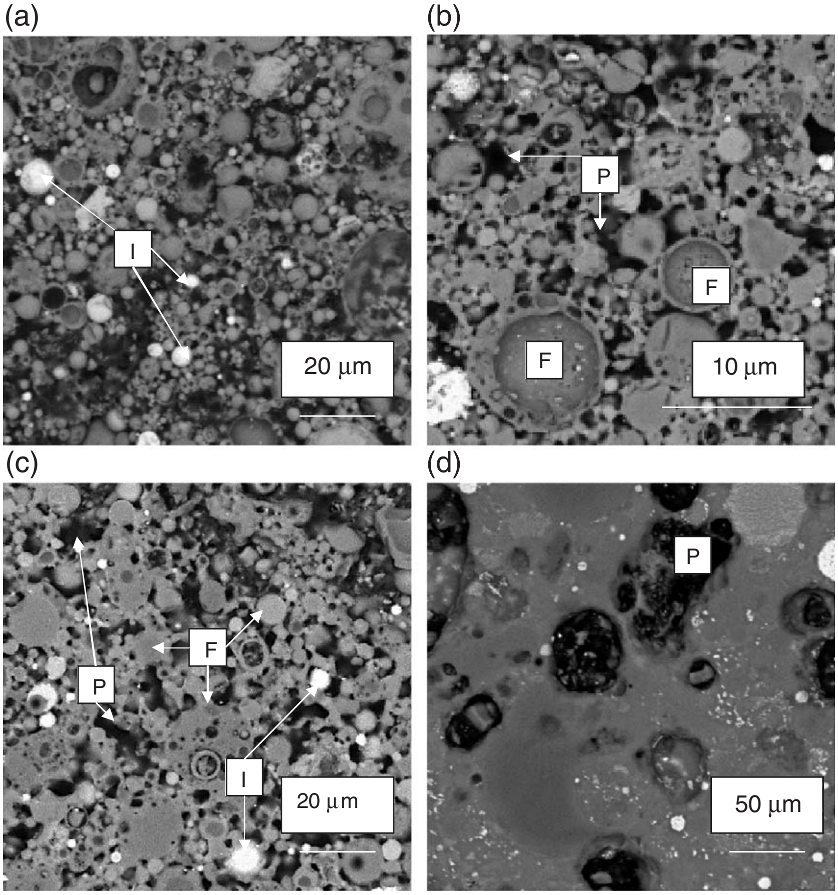

Fig. 15. (a–d). Representative SEM BEI of the polished sections of G1.PSS specimen prepared using potassium silicate and a class F fly ash (a) before test, and after exposure to (b) 800 °C, (c) 1000 °C, (d) 1200 °C firing tests. F—fly ash particle, I—fly ash particle with high content of iron impurity, P—porosity.

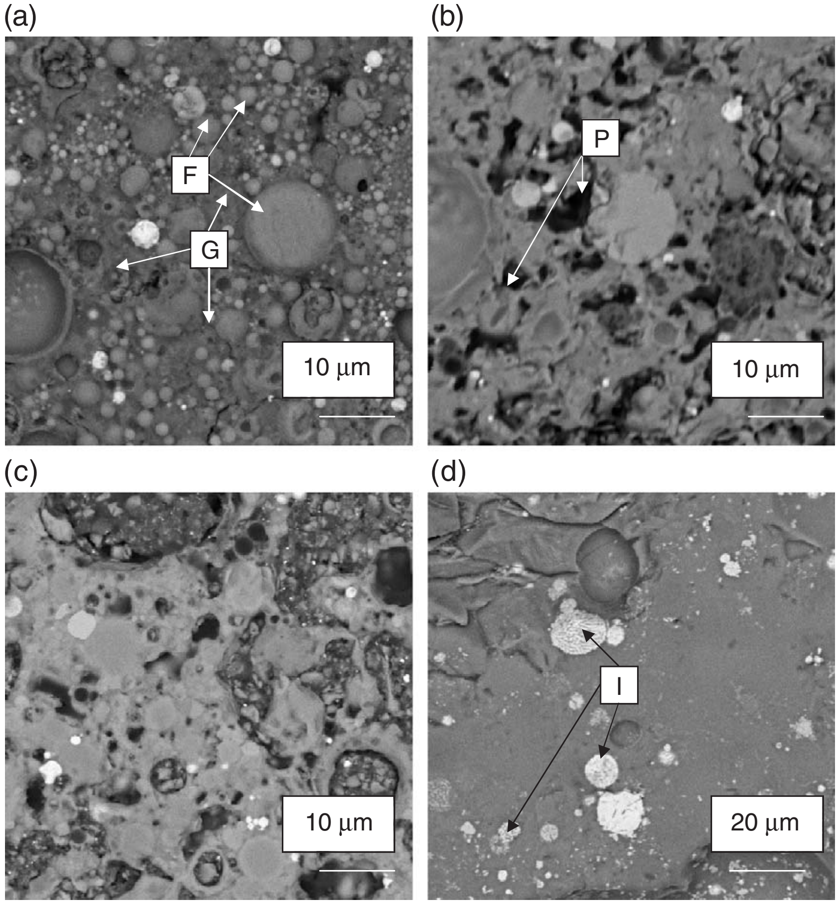

Fig. 16. (a–d). Representative SEM BEI of the polished sections of FKSS specimen prepared using potassium silicate and class F fly ash (a) before test, and after exposure to (b) 800 °C, (c) 1000 °C, (d) 1200 °C. G—aluminosilicate gel, F—fly ash particle, I—fly ash particle with high content of iron impurity, P—porosity.

high stresses are developed in the pore walls due to movement of uncombined water on heating, while aluminosilicate geopolymers deteriorate and their strength is decreased. These causes collapse of fine pores and development of shrinkage cracking. The experimental results indicated that a loss of compressive strength in materials prepared using Na-containing activator when exposed to firing was associated with a significant increase of the average pore size and shrinkage cracking. Although material G1 performed better than all others in the firing experiments, it had a high increase of the average pore size when compared before and after firing experiments (Fig. 8). Therefore materials prepared using sodium-containing activators had rapidly deteriorating strength when exposed to firing at 800 °C.

Contrary to that, materials prepared using potassium-containing activators had significantly increased strength regardless of water/binder ratio used in their preparation (Fig. 10). Investigation of matrix development showed a decreasing average pore size and dropping porosity of the specimens after firing at 800, 1000 and 1200 °C (Figs. 8 and 14). However, significant changes of the strength at high temperatures and porosity may indicate liquid formation, which is an indication of reduced thermal resistance. The materials prepared using K-containing activators remained mostly amorphous up to 1200 °C, and had an increasing strength up to 1000 °C, while in some materials a loss of strength was observed after firing at 1200 °C. Contrary to these results, Barbosa and MacKenzie reported very high thermal stability of potassium sialate geopolymers up to 1300–1400 °C, and in this investigation geopolymer specimens experienced recrystallisation to feldspars leucite and kalsilite at 1000 °C [6]. The recrystallisation was less complete in the silica-rich K-Polysilicatedisiloxo samples, which retained a degree of amorphous geopolymer content on heating and had more evident melting behaviour at 1400 °C [6]. Once again, performance of geopolymers prepared using class F fly ash was lower than that of geopolymer materials prepared using metakaolin. Evidently, presence of significant amounts of iron oxide in the fly ash used for materials preparation and poor polymerisation of geopolymers in samples utilising fly ash caused degradation of fireresistance properties of the geopolymer materials if compared with that of geopolymer materials prepared using metakaolin.

Appearance of Na and K feldspars in the geopolymer materials on firing indicate decomposition of the initial aluminosilicate gel and presence of free Na, K, Si and Al. It appears that on firing decomposition of geopolymers in materials formed using Na-containing activators happened more readily. This can be attributed to higher diffusion coefficient of Na^+ than that of K^+ in the matrix on firing [12].

Compaction at 1–10 MPa caused reduced shrinkage on firing. Compaction used in specimen preparations influenced the compressive strength of geopolymer materials. In most cases it had a negative effect on the strength of specimens exposed to firing, while the initial strength of the specimens was sometimes increased. Densification reduced shrinkage of materials on firing in case of materials activated by Na- and K-containing activators (Table 4). Curing at 80 and 100 °C was utilised in the specimen's preparation. Curing at 100 °C led to an increased initial compressive strength, and improved fire resistance, which were attributed to improved activation of fly ash at elevated temperature. It is possible that deterioration of materials prepared using class F fly ash was more rapid than that in case of materials prepared using metakaolin due to lower degree of reaction of fly ash, incomplete polymerisation of geopolymers and because of impurities present in the fly ash, which lowed melting temperature of these materials [12].

The geopolymer materials prepared using class F fly ash were found not suitable for the manufacturing of refractory bricks, due to large changes in compressive strength on firing and high shrinkage which exceeds in most cases 1.5%. However, the G1 and G1.PSS materials may be suitable to be used as fire-protection layer due to low heat conduction through the geopolymer. Additional tests need to be performed to verify heat conduction through the layer of geopolymer when exposed to standard heating curve. The investigation showed that prepared geopolymer materials compare favourably with organic polymers, they are nonflammable, do not release toxic fumes and have very low weight loss 5–12% as compared to 50–80% for fire-resistant polymer nanocomposites when heated up to 1000 °C [13]. The geopolymer materials were found superior to Portland cement concretes in their thermal properties when exposed to 800–1000 °C [14]. However, the presented results show that tested geopolymer materials utilising class F fly ash are not suitable for refractory applications due to high shrinkage and large changes in compressive strength, which were possibly caused by negative influence of large amount of iron impurity present in the fly ash.

Volume expansion was observed in some of geopolymer specimens with increased content of silica, such as in T1.5 specimens. It was attributed to expansion on heating of uncombined silica. In case of T1.5 specimens this expansion increased with an increase of the firing temperature to a point, when large volume of foam was produced at 1200 °C. This observation showed that T1.5 composition utilising Tarong fly ash could be used to produce artificial lightweight aggregates.

5. Conclusions

The thermal stability of the geopolymer materials prepared with sodium-containing activators was rather low, and significant changes in the microstructure took place. In the geopolymers prepared using sodium-containing activators, rapid deterioration of strength at 800 °C was observed, which was connected to a dramatic increase of the average pore size. Initially amorphous structures were replaced by the crystalline Na-feldspars. Materials prepared using fly ash and potassium silicate had better thermal stability than geopolymers prepared using Na-containing activators, materials remained mostly amorphous up to 1200 °C. After firing these materials had reduced average pore size and improved compressive strength. Compaction at 1–10 MPa reduced shrinkage on firing in all materials. Geopolymer materials prepared using class F fly ash and sodium and potassium silicate show high shrinkage as well as large changes in compressive strength with increasing fired temperature in the range 800–1200 °C. Thus materials were found unsuitable for refractory insulation applications; their use for fire-protection needs further investigation.

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