PREPARATION AND PROPERTIES OF FLY ASH-BASED GEOPOLYMER FOAMS

#FRANTIŠEK ŠKVÁRA*, ROSTISLAV ŠULC**, ZDENĚK TIŠLER*, PETR SKŘIČÍK*, VÍT ŠMILAUER***, ZUZANA ZLÁMALOVÁ CÍLOVÁ*

*Institute of Glass and Ceramics, Faculty of Chemical Technology, ICT Prague, Technická 5, 16628 Prague 6, Czech Republic
**Department of Construction Technology, Faculty of Civil Engineering, CVUT Prague
***Department of Mechanics, Faculty of Civil Engineering, CVUT Prague, Thákurova 7, 16629 Prague 6, Czech Republic

#E-mail: skvara@vscht.cz

Submitted May 5, 2014; accepted October 20, 2014

Keywords: Geopolymer, Foam, Macro-porosity, Fly ash

An extremely porous geopolymer material – an incombustible alumino-silicate foam – can be prepared by incorporating gas-forming agents into mixtures consisting of an alkaline activating agent (NaOH + sodium water glass) and fly ash. Aluminium powder or materials containing elemental Si (silica fume, FeSi or SiC) may be used as gas-forming agents. Macroscopic pores are given rise thanks to the release of gaseous hydrogen generated during the reaction of aluminium, respectively Si, in a strong alkaline environment. The formation of the foam becomes more intense if aluminium powder is used instead of silica fume. The effect of silica fume can only be observed at concentrations ranging from 5 to 10 percent by weight and at temperatures above 60°C because of a low content of elemental Si in silica fume. The foam formation takes place immediately after the addition of aluminium powder to the mixture but the foam collapsing must be prevented by incorporation of portland cement or lime. The Si reaction in the strong alkaline environment is boosted by the presence of an alumino-silicate material, ie the fly ash. Geopolymer foams prepared by addition of gas-forming aluminium powder or silica fume are characterized by similar pore sizes; the pore size is comparable with that observed in lime-silicate materials produced in autoclave. The volume weight of geopolymer foams is similar to that of other inorganic foams. The strength of geopolymer foams is dependent on their volume weigth. Mechanical properties of geopolymer foams were stable over the investigated period of a year. Geopolymer foams are incombustible and can resist temperatures of up to 1000°C without any sign of decomposition. Their shape does not change after exposure to temperatures ranging from 400 to 800°C. In contrast to lime-silicate foams and cement-based foams the firing of geopolymer foams is not accompanied by the formation of any cracks or by any additional changes (rehydration).

INTRODUCTION

Porous materials have been applied extensively as purification membranes, high-efficiency adsorption materials, catalysts or building materials. Macro-porous materials (the materials with pores larger than 50 nm according to the IUPAC classification [1]) can be prepared on the basis [2] of organic polymers, metals or inorganic bodies (glass, ceramics, hydrate lime materials, hydraulic binders). Organic polymer foams are usually produced by expansion in vacuum, extrusion of molten polymer into a vacuum chamber, by blowing compressed gas into the molten polymer or by adding gas-forming agent to organic materials. Thanks to their low mass, low heat conductivity and good sound proofing properties the polymer foams are suitable for the manufacture of packaging components or insulating components used in civil engineering. The combustibility of such materials represents their main drawback which limits their applications to about 50 to 120 ºC at the maximum. They start to burn at temperatures ranging from 350 to 500°C. Therefore, more resistant inorganic macro-porous materials (porous concrete) are to be used at higher temperatures. Porous concrete is prepared on the basis of lime or cement pastes into which a gas-forming agent (aluminium powder, H_2O_2, CaC_2, O_2) is incorporated. The gas released during the reaction gives rise to a macro-porous structure that is preserved even after the binder hardens. Porous concrete is produced currently by using mixture composed of silica/aluminous and lime-containing materials to which aluminium powder is added. Hydro-thermal conditions in the autoclave give rise to a strong structure composed of crystalline lime hydro-silicates. However, hydro-silicate dehydration and decomposition take place at high temperatures, which may be regarded as a drawback. There is also an alternative technology available: cement or lime pastes are mixed with an organic foam obtained by using agents suppressing the surface tension (surfactants).

It is also possible to use another type of inorganic binder for the preparation of macro-porous materials, ie alkali-activated alumino-silicates called geopolymers. The authors [3-8] investigated properties and possibilities of preparation of these macro-porous geopolymers by using meta-kaolin precursor. Silica fume, SiC and H_2O_2 were added as gas-forming agents. The present work deals with the preparation and properties of macro-porous materials on the basis of alkali-activated fly ashes – geopolymers.

EXPERIMENTAL

Fly ash rejected in the Opatovice power plant (Czech Republic) fired by brown coal was used for the preparation of geopolymer foams. The fly ash composition is given in Table 1.

Table 1. Composition of fly ash from the Opatovice power plant (wt. %).

SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	P_2O_5	SO_3
53.68	31.34	2.08	6.67	0.40	1.92	1.96	1.05	0.23	0.23

Geopolymer foams were prepared by mixing the fly ash with the alkaline activating agent and the gas-forming ingredient. The water coefficient (water-to-fly ash ratio) in the mixture amounted to 0.26. The SiO_2/Na_2O modulus was equal to 1.06 and the Na_2O content (related to the fly ash weight) corresponded to 6 percent. Aluminium powder, silica fume, SiC and FeSi powder were added as gas-forming agents. Geopolymer foams were kept at a temperature of 80°C for 12 hours. Finished foams were maintained subsequently in air at a relative humidity ranging from 40 to 50 percent. The preparation diagram is shown in Figure 1.

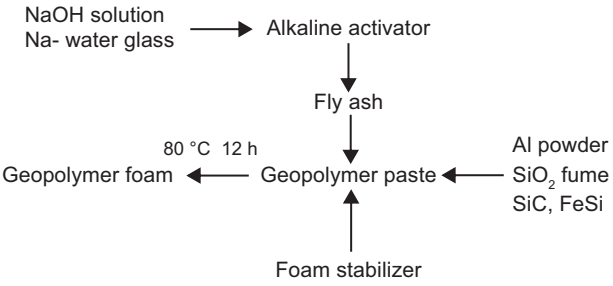
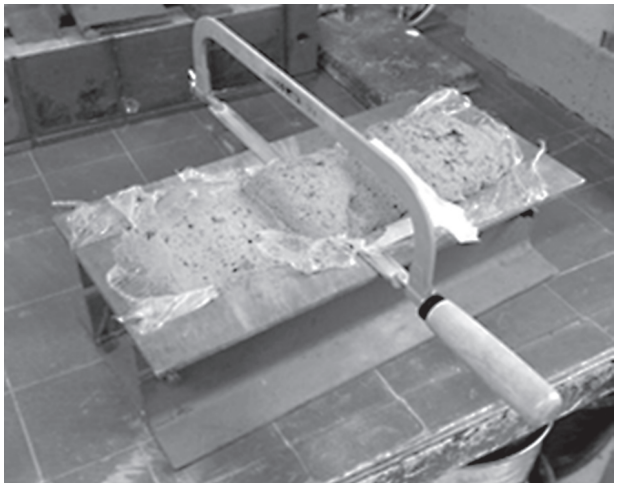


Figure 1. Preparation process of geopolymer foams.

In addition to samples measuring 100×100×100 mm also those having the dimensions of 40×40×160 mm were prepared. A foam sample obtained by using a mold with the dimensions of 100×100×100 mm is shown in Figure 2. The sample was further modified to make it suitable for measuring its strength and other properties.

a)



b)

Figure 2. Foam prepared in a a mold of 100×100×100 mm (a) and after the removal of the overflow section (b).

Aluminium powder (Aquapor 4207 and 4213, added in the manufacture of porous concrete) was used in the present work. The composition of aluminium applied as additive is given in Table 2.

Table 2. Composition of aluminium products introduced as gas-forming agents.

	Aquapor 4207	Aquapor 4213	Aluminium powder
Percentage of solid matter	68-72 %	68-72 %	98 %
D50	40-65 µm	15-22 µm	100 µm
Al content	99 %	99 %	99 %

Silica fume (Elkem) contained 95 % SiO_2 and its specific surface area was 2.500 m^2/kg (BET). SiC powder contained 92 % SiC and its average grain size was 1.1 mm. FeSi powder contained 15 % Si and 92 % of particles were below 45 µm.

Geopolymer foam samples prepared in molds with the dimensions of 100×100×100 mm and 40×40×160 mm were subjected to tests aimed at assessing their compressive strength over periods of time ranging from 7 to 180 days. Prior to the strength tests the samples of geopolymer foams were kept in air at a relative humidity of 45 to 50 %. The volume weight was also determined. Porous geopolymer foams were investigated with the aid of light microscopy and the digital image analysis (NIS Elements [9]) was applied to the determination of pore characteristics. The pores in the geopolymer foam were highlighted by filling them with a color paste. The values of heat conductivity characterizing the foams were determined, too. The foams subjected subsequently to firing at temperatures ranging from 200 to 1000°C were used for both the determination of their mechanical strength and the changes in sample dimensions caused by the firing process. Foam samples available after their destruction tests were subjected to the x-ray diffraction analysis and the morphology of fracture surfaces was investigated with the aid of the SEM technique completed by means of the point and area analysis.

RESULTS AND DISCUSSION

Preparation of geopolymer foams

The action of gas-forming aluminium agents and silicate materials in alkaline environment is different. Aluminium powder reacts in a strong aqueous alkaline environment by giving rise to gaseous hydrogen:

$$2Al + 2NaOH + 6H_2O \xrightarrow{20\text{-}30^{\circ}C} 2Na[Al(OH)_4] + 3H_2$$

The foam is formed at current temperatures (20-30°C) if aluminium powder is used as a gas-forming agent. A body characterized by a low strength is produced at such temperatures when the geopolymer structure is not formed to the full. The body may remind the so-called "false set" of portland cement. The character of the foam body changes during its heating until a stage is reached when it becomes very plastic and the foam starts caving in (see Figure 3). Other stabilizing additives (portland cement, lime) are used with the aim to avoid the uncalled-for foam destruction.

Table 3. Volume density of foam samples (kg m^{-3}) of various volumes.

	10×10×10 cm	4×4×16 cm	4×4×4 cm
Aquapor 4207	405	355	356
Aquapor 4213	468	456	455
Aluminium powder	400	320	310

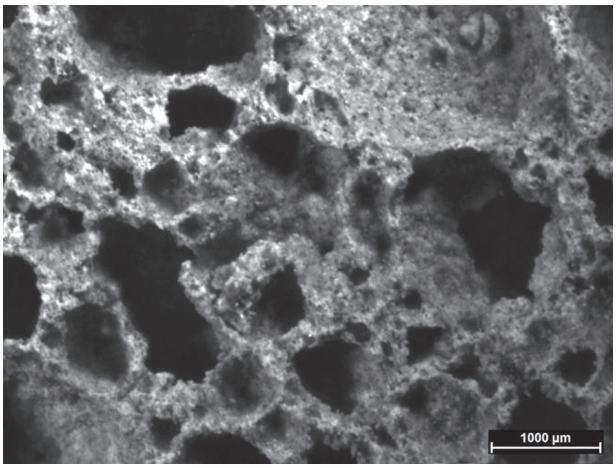


Figure 4. Defects observed in the foam. Irregular pores. A high water coefficient.

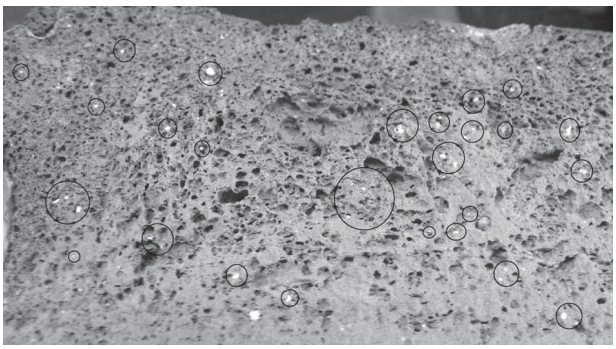
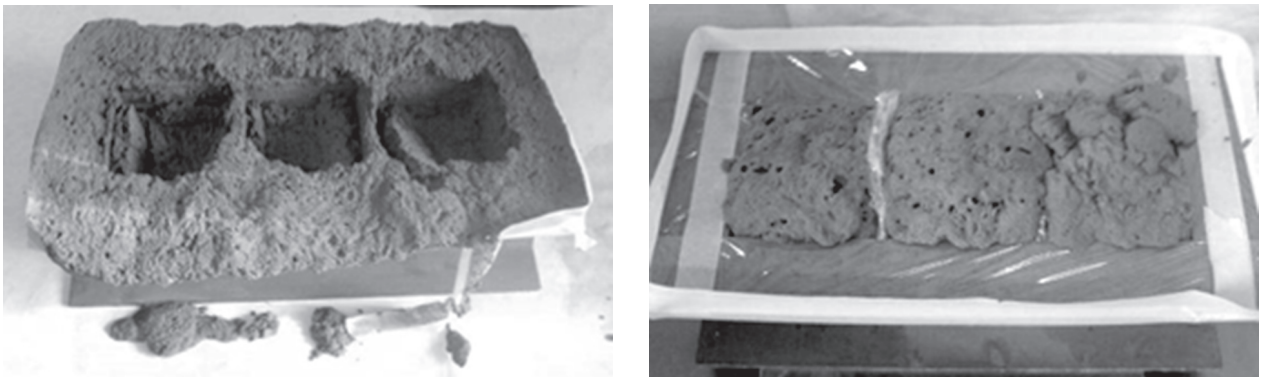


Figure 5. Defects observed in the foam. Residues of unreacted aluminium powder in the foam. Low water coefficient.



a) b)

Figure 3. The subsidence of a geopolymer foam at a water coefficient of 0.35 (a) and a well-prepared foam at a water coefficient of 0.26 (b).

The properties of geopolymer foams are influenced by the grain size of aluminium powder as well as by the water coefficient (Figures 4 and 5, Table 3). The appearance of optimally stabilized geopolymer foam exhibiting a uniform pore distribution is evident from Figure 6.

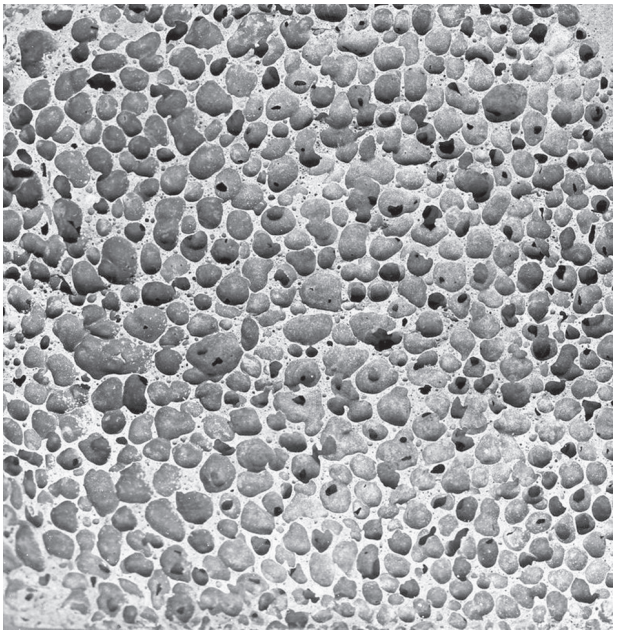


Figure 6. Stabilized geopolymer foam characterized by a uniform pore distribution, an optimum water coefficient and an optimum concentration of aluminium powder.

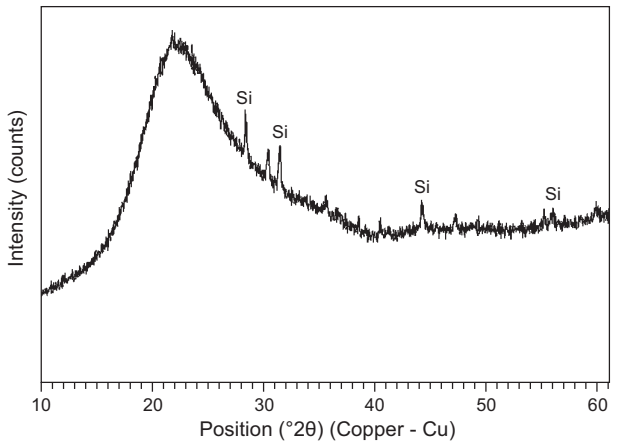


Figure 7. X-ray diffraction spectrum of silica fume.

The gas-generation mechanism in Si-containing additives is different. Elemental Si is present in silica fume recommended as a gas-forming agent for use in the preparation of geopolymer foams on the basis of metakaolin [4] as this is evident from Figure 7.

The average size of silica fume particles is 100 nm [10]. Si particles present in silica fume are evidently of a similar size. Elemental Si present in silica fume reactions in the alkaline environment by giving rise of gaseous H_2:

$$Si + 4H_2O \overset{>60°C}{\rightarrow} Si(OH)_4 + 2H_2$$

The above reaction takes place only at temperatures above 60-80°C and a strong geopolymer structure is formed at the same time. Some workers [11, 12] maintain that elemental Si gives rise to Si–H bonds in the strong alkaline environment; however, the bonds are not stable, Si–OH groups and gaseous H_2 are formed. In contrast to Al, the foam formation obtained by using SiO_2 fume is accompanied by the simultaneous formation of the geopolymer structure. H_2 generation is further boosted by the presence of a alumino-silicate material (for instance, fly ash) as this is evident from Table 4.

A visible foaming effect (Figure 8) becomes only obvious at larger additions of SiO_2 fume because of a low concentration of elemental Si in this additive.

Other Si-containing agents (SiC and SiFe powders) were also incorporated with the aim to generate gas in the geopolymer body. However, such additives exhibited little efficiency as demonstrated by Figure 9.

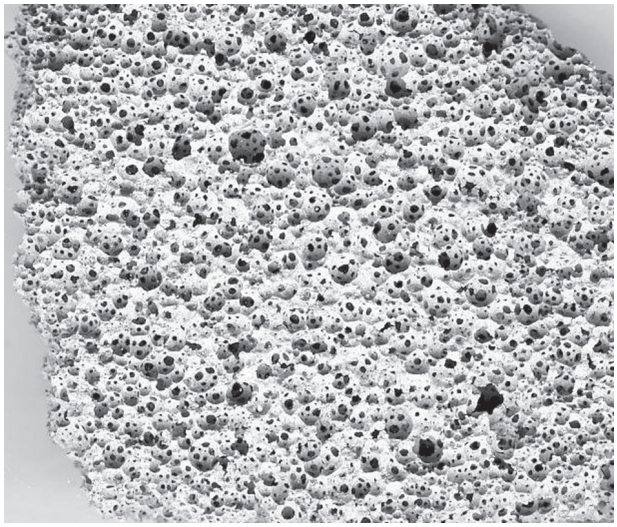


Figure 8. Geopolymer foam. SiO_2 fume.

Table 4. Gas evolution behaviour of mixtures.

NaOH solution + sodium water glass	+ silica fume	20-40°C without gas release 60-80°C gas release
NaOH solution + sodium water glass	+ silica fume + fly ash	20-40°C without gas release 60-80°C intense gas release

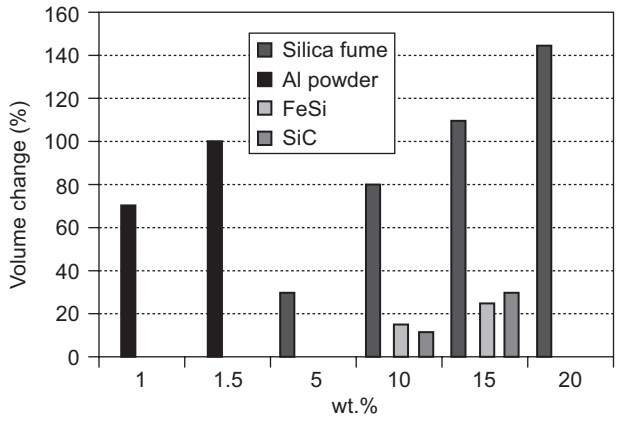


Figure 9. Influence of gas-forming additives on volume changes of geopolymer slurry.

Character of foam porosity

The microstructure of fracture surfaces of geopolymer foams prepared by additions of aluminium powder and SiO_2 fume are shown in Figures 10-13.

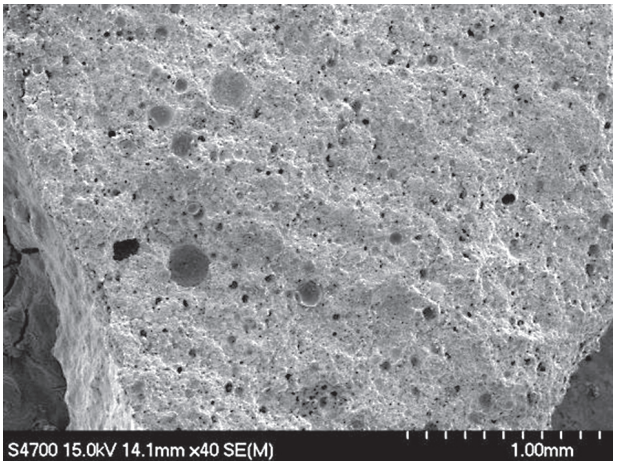


Figure 10. Microstructure of geopolymer foam (Al).

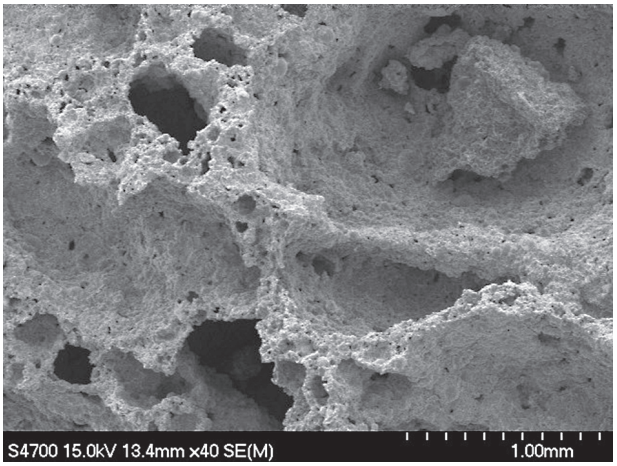


Figure 11. Microstructure of geopolymer foam (Al).

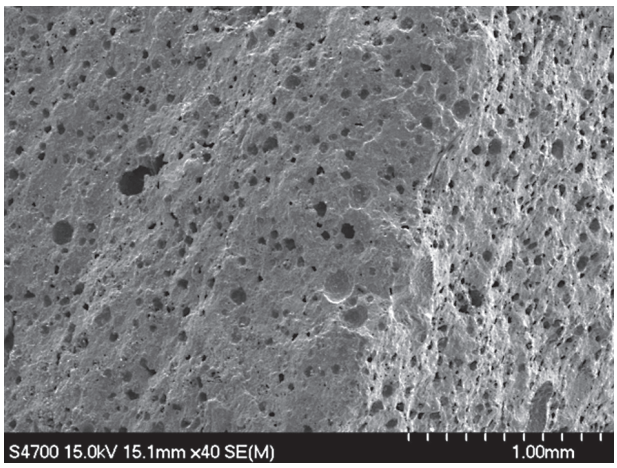


Figure 12. Microstructure of geopolymer foam (silica fume).

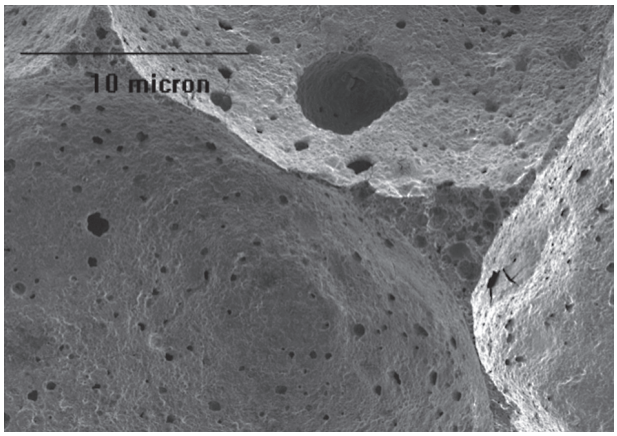


Figure 13. Microstructure of geopolymer foam (silica fume). Detailed view.

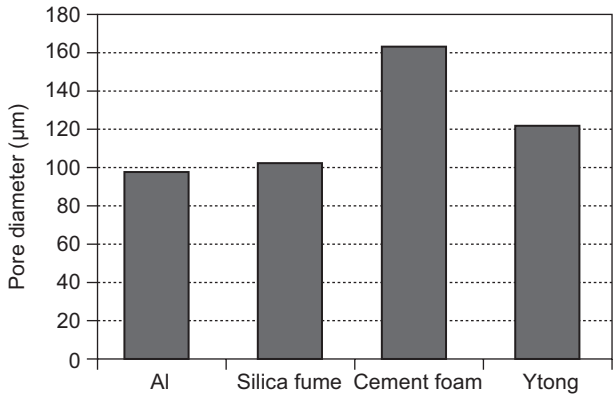


Figure 14. Pore size in geopolymer foams and reference materials.

The pore size in geopolymer foams (Figure 14) prepared by adding aluminium and silica fume gas-forming agents is practically the same; it is comparable to that observed in reference materials on the basis of lime-silicate materials (Ytong) exposed to autoclave treatment. Nevertheless, the pores in lime-silicate materials

are more symmetrical than those found in geopolymer materials where the pore roundness is slightly worse (Figure 15).

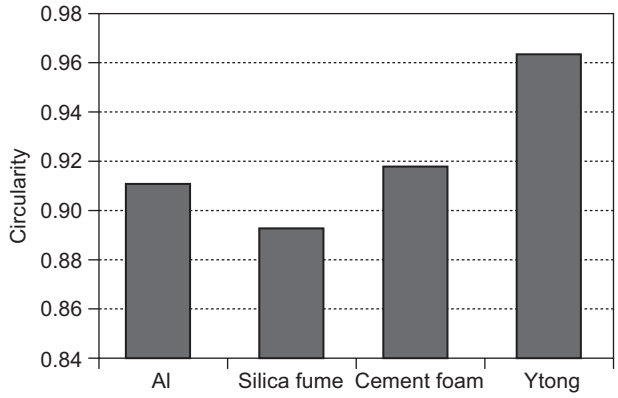


Figure 15. Pore circularity in geopolymer foams and reference materials.

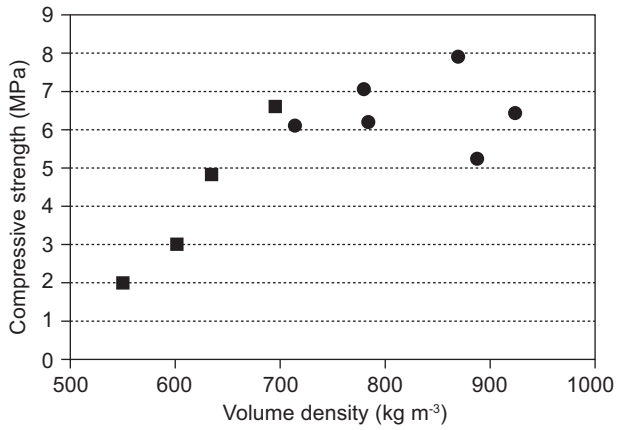


Figure 16. Dependence of the strength of geopolymer foams on their volume weight. ■ – foams prepared by using aluminium powder or, respectively, SiO_2 fume, ● – foams prepared by using aluminium powder and a stabilizing agent.

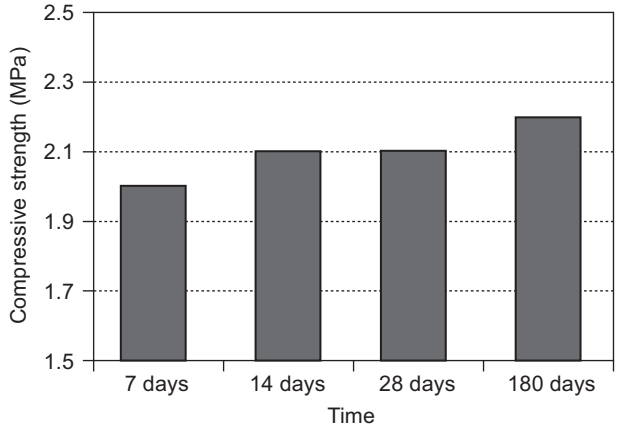


Figure 17. Time dependence of the strength of geopolymer foam (Al); volume weight of 540 kg m^{-3}.

Mechanical properties of foams

The dependence of the compressive strength on volume weight (Figure 16) shows – analogously to other macro-porous materials – a decrease in the material strength with the decreasing volume weight. The strength of geopolymer foams does not vary significantly in dependence on time (Figure 17); this behavior is in agreement with results obtained by a long-term monitoring of geopolymer strength over periods ranging from 3 to 7 years [13].

Thermal properties of geopolymer foams

Measured values of the heat conductivity of geopolymer foams and reference materials are obvious from Figure 18. The thermal properties of geopolymer foams are comparable with those characterizing other materials.

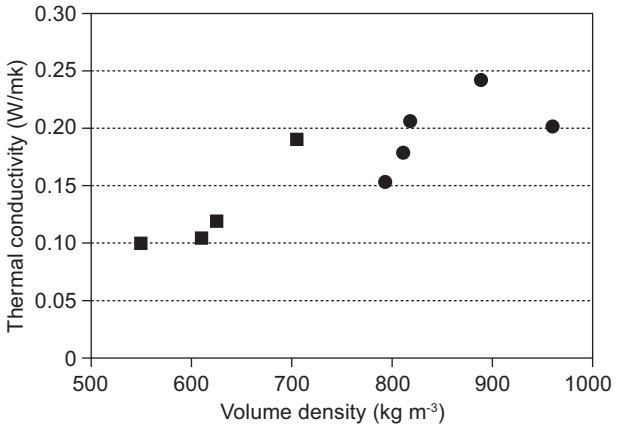


Figure 18. Dependence of the heat conductivity on volume weight. ■ – foams prepared by using aluminium powder or, respectively, SiO_2 fume, ● – foams prepared by using Al and a stabilizing agent.

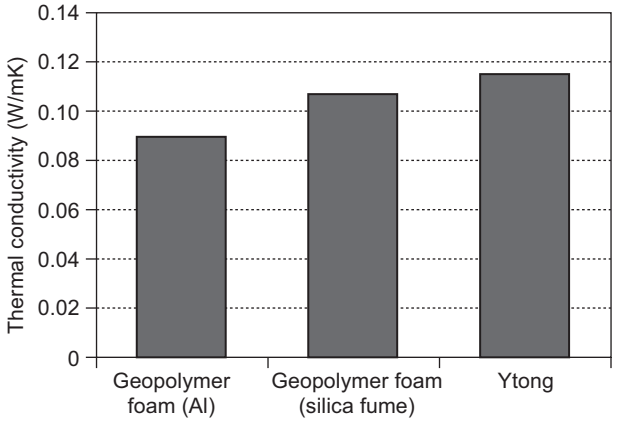


Figure 19. Comparison of the heat conductivity of geopolymer foams with that of other porous materials.

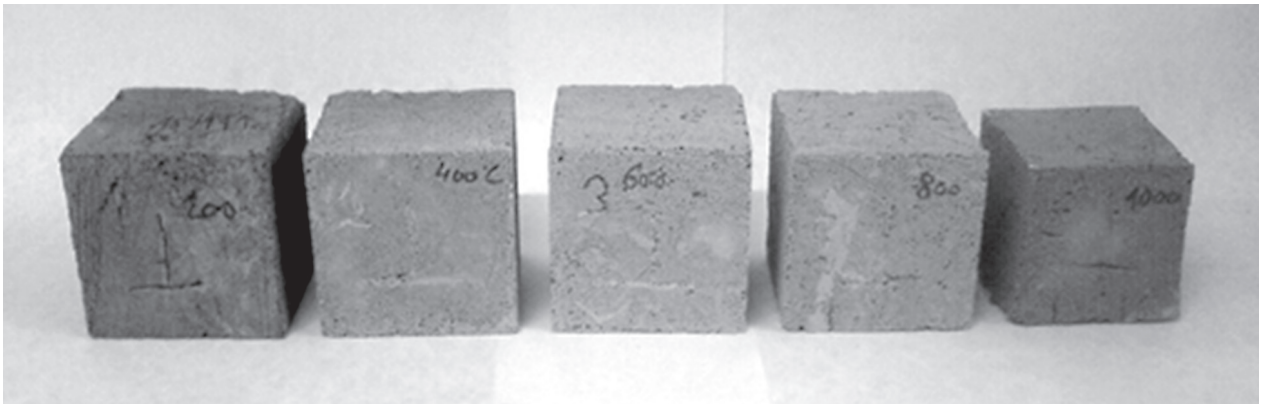


Figure 20. Geopolymer foams after firing (from the left: 200°C – grey, 400°C – light grey, 600°C – light yellow, 800°C – yellow, 1000°C – brown).

High-temperature properties of geopolymer foams

The heating of geopolymer foams to a temperature below 1000°C is not accompanied by any destruction or disintegration phenomena. The heat treatment brings about changes in the color of geopolymers from grey to dark brown (800-1000°C), see Figure 20.

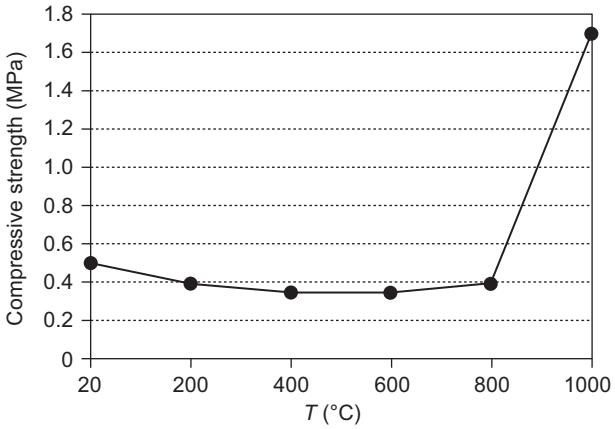


Figure 21. Temperature dependence of the compressive strength of geopolymer foams (Al) after their 2-hour firing.

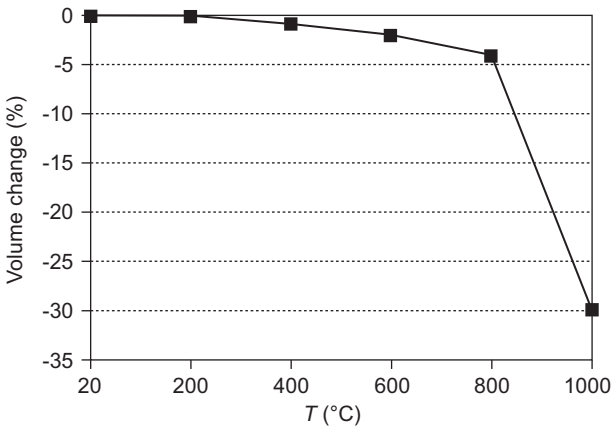


Figure 22. Temperature dependence of volume changes of geopolymer foams (the volume after firing).

The strength values of fired geopolymer foams (Figure 21) remain practically constant, only the strength of the material fired at a temperature of 1000°C grows because of its sintering. The volume of samples fired above 800°C changes (owing to the sintering), see Figure 22.

In contrast to the reference materials (cement foams or lime-silicate materials treated in autoclave) the firing of geopolymer foams results in a small loss of their mass, which happens at all temperatures up to 1000°C, see Figure 23.

The mechanical strength of geopolymer foams is related to the behavior of the geopolymer during their heating which is accompanied by a continuous loss of mass (water loss) at temperatures of up to 400-600°C (Figure 24). The water is probably present in the geopolymer as "free" water in micro-pores as well in gel pores and, finally, as OH groups at the end of Si–O–Si chains. Water in gel pores is bonded as $Na(H_2O)^+$. The heating at temperatures below 200°C is accompanied by a loss of more than 60 % of H_2O. The residual water gets lost or, respectively, the OH groups are eliminated only when the materials are heated to temperatures above 400-600°C.

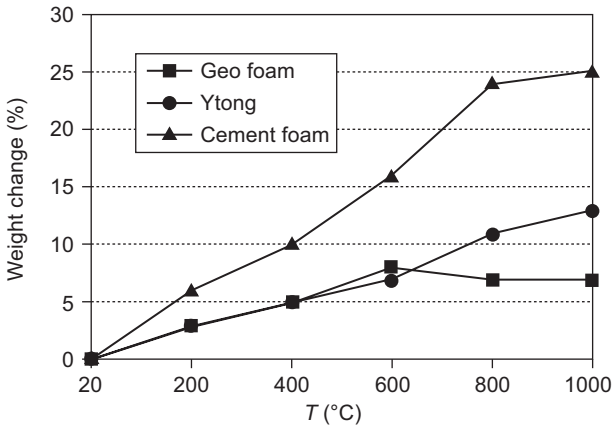


Figure 23. Dependence of the weight change of geopolymer foams on firing temperature.

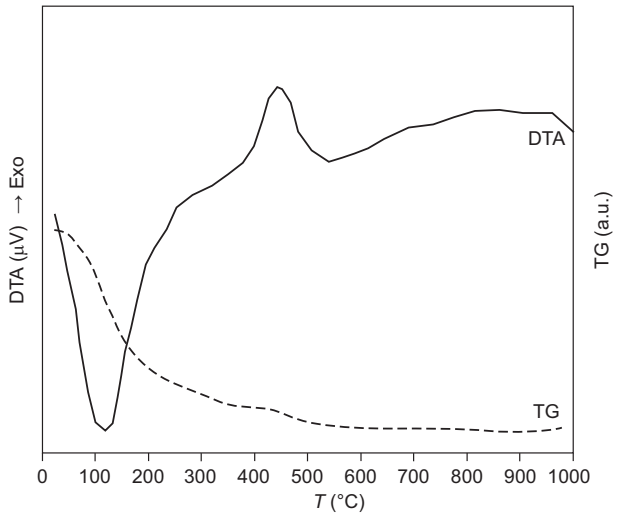


Figure 24. DTA and GTA of a geopolymer foam (Al).

X-ray diffraction spectra of geopolymer foams (Figure 25) after their heat treatment at temperatures ranging from 20 to 1000°C demonstrate that no compositional change occurs at temperatures below 600°C. There are diffractions of residual minerals (remaining after fly ashes), quartz, mullite and hematite as well as amorphous geopolymer phases (a broad peak). A secondary product (the albite $NaAlSi_3O_8$) appears at temperatures above 800°C.

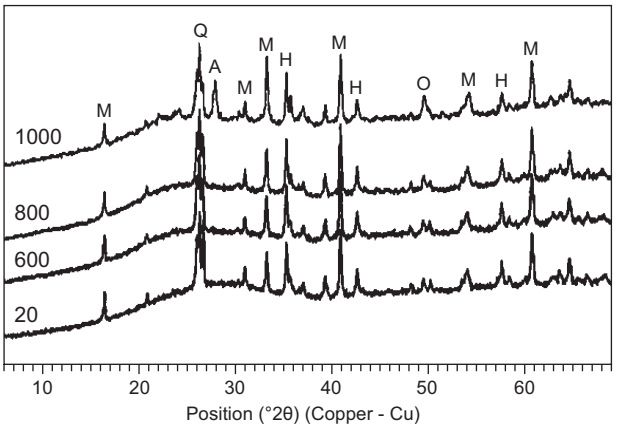


Figure 25. X-ray diffraction spectra of geopolymer foams (Al) in dependence on temperature from 20 to 1000°C.

The structural stability of geopolymers could also be demonstrated by measuring the spectra ^{29}Si, ^{27}Al and ^{23}Na NMR MAS at temperatures below 800°C as mentioned in [14]. The $SiO_4(4Al)$ and $SiO_4(3Al)$ structures predominate, the $Q_4(1\text{-}2Al)$structure is only slightly represented. Structures formed of mullite residues from original fly ash are also represented in the spectra. The Al^{IV} coordination ($AlQ_4(4Si)$) predominates with minor representation of the Al^{VI} coordination formed of mullite residues from the original fly ash. However, the firing temperature affects the character of ^{23}Na NMR MAS spectra. It is evident from ^{29}Na NMR MAS spectra at temperatures below 400°C that Na is present in the structure in the form of $Na(H_2O)_n$ where n = 2 to 8 [see [14]). A shift towards the $Na(H_2O)_2$ structure occurs at higher temperatures. There is a large number of peaks at 600°C which are in relation with the overall structural re-arrangement. A structure corresponding to sodium-silicate glass [16, 17] can be deduced from the spectrum at 800°C.

Changes in the geopolymer morphology occur at firing temperatures above 600-800°C and a gradual sintering can be observed (Figures 26, 27).

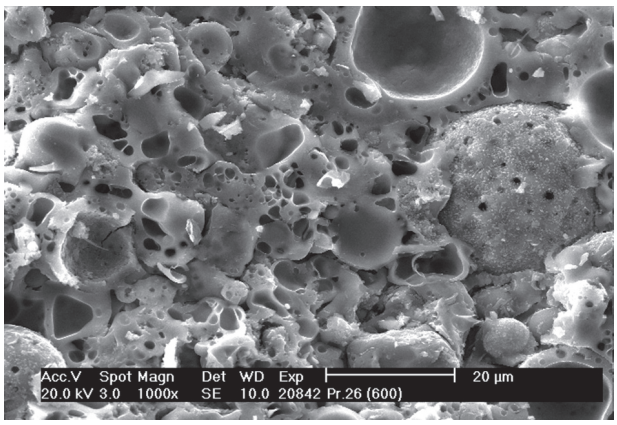


Figure 26. Geopolymer foam (Al) fired at 800°C.

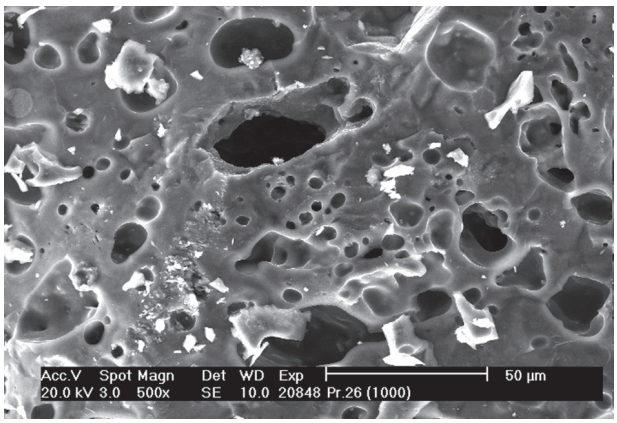


Figure 27. Geopolymer foam (Al) fired at 1,000°C.

The determination of the geopolymer refractoriness under load shows that the $T_{Q.S}$ temperature ranges from 630 to 700°C as found in [14]. An analogous character can also be assumed for geopolymer foams as demonstrated by the dependence of the volume of geopolymer foams on firing temperatures.

As regards the high-temperature behavior, there is a substantial difference between the geopolymer and other inorganic foams. Lime-silicate materials treated

in autoclave lose their mass continuously and first cracks start occurring at a temperature of 800 to 1000°C (Figure 28). The values characterizing the mass loss at temperatures below 1000°C are similar to those observed for alumino-silicate foams. Lime-silicate materials lose their mass at firing temperatures above 800°C. The lime-silicate body becomes friable, which is caused by the disintegration of the phases present in the material (the xonotlite – stable up to 850°C, the tobermorite – stable up to 650°C).

Cement foams (on the basis of portland cement) exhibit pronounced fluctuations in their mass starting from 200°C when free-bound water begins to escape. An ulterior mass loss due to the decomposition of the CSH phase and to the beginning of the portlandite decomposition occurs above 600°C. The cracks become more pronounced and samples start disintegrating during their handling. A melt that strengthens partially the samples starts forming at temperatures of about 1000°C. A spontaneous disintegration of the cement foam exposed to temperatures above 800°C takes place after one-week storing of samples in air; this phenomenon is due to the rehydration of the products originated during the firing (CaO), see Figures 29 and 30.

CONCLUSION

A high-porosity geopolymer material – an incombustible alumino-silica foam – can be prepared by introducing a gas-forming agent (Al, SiO_2 fume) into the mixture composed of the alkaline activator (NaOH + sodium water glass) and fly ash. Aluminium powder or materials containing elemental Si as silica fume, FeSi or SiC can be used as gas-forming agents. The macro-pores are developed thanks to the release of gaseous H_2 in result of the Al (or, respectively, Si) reaction in the strong alkaline environment. The foam formation is more intense if aluminium powder is used as compared with the addition of silica fume. The effect of silica fume becomes apparent at its concentrations ranging from 5 to 10 wt.% because of the low content of elemental Si in this material. The use of FeSi or SiC for the preparation of geopolymer foams is less effective. The formation of the foam starts immediately after the incorporation of the aluminium powder into the mixture but the foam collapse must be prevented by further addition of portland cement or lime. The amount of aluminium powder or, respectively, its grain size exerts a paramount effect on final properties of the geopolymer foam. If silica fume is incorporated, its effect (foam formation) can only be observed after heating to a temperature above 60°C. The Si reaction in the strong alkaline environment is accelerated by the presence of an alumino-silicate material (fly ash). The process of foam formation in the geopolymer slurry is also influenced by the water coefficient that affects the rheological properties of the mixture. The pore size in geopolymer foams prepared by additions of Al and silica fume gas-forming agents is practically the same and it is comparable to that found in lime-silicate materials treated in autoclave. The pores observed in lime-silicate materials are more symmetrical than those present in geopolymer materials where their roundness is poorer. The strength values of geopolymer foams are dependent on their volume weight. The volume weight of geopolymer foams is comparable with that of other inorganic foams. Mechanical properties of geopolymer foams are stable within the investigated period of a year. Geopolymer foams are incombustible and they resist temperatures of up to 1000°C without decomposition. Furthermore, the shape of such materials does not suffer any dimensional changes in the temperature range of 400 – 800°C. In contrast to the lime-silicate and cement foams, the firing of geopolymer foams is not accompanied by any formation of cracks or by additional changes following the firing (rehydration).

Figure 28. Cracks in the lime-silicate material after firing at 1000°C.

Figure 29. Cement foam immediately after firing at 800°C.

Figure 30. Cement foam fired at 800°C and kept one week in air (cracks).

Acknowledgment

The present work could be implemented thanks to the financial support of the Grant agency of the Czech Republic, grant P104/12/0102 and the project "Support for improving teams in research and development and the development of intersectoral mobility at Czech Technical University in Prague" OP VK CZ.1.07/2.3.00/30.0034, which allowed for funding of Dr. Šulc's postdoctoral research.

REFERENCES

1. Schaefer D.W. MRS Bulletin *19*,14 (1994).
2. Narayanan N., Ramamurthy K.: Cem. Concr. Composites *22*, 321 (2000).
3. Homann M., Schlegel E.: *Wärmedämmstoffe für den Wärmeschutz von Gebäuden und Anlagen*, Freiberg 1999.
4. Prud'homme, P. Michaud, E. Joussein, C., Peyratout, Smith A., Arrii-Clasens S., Clasens J.M., Rossignol S.: J.Eur. Ceram.Soc. *30*, 1641 (2010).
5. Henon J., Alzina A., Absi J., Smith D.S., Rossignol S.: Ceramics Intern. *38*, 77 (2012).
6. Henon J., Alzina A., Absi J., Smith D.S., Rossignol S.: J.Porous Mater. *20*, 37 (2013).
7. Medri V., Ruffini A.: J.Eur. Ceram. Soc. *32*, 1907 (2012).
8. Bell J.L., Kriven W.M.: in Developments in Strategic Materials: Ceramic Engineering and Science Proceedings, Vol. 29, 97 (2008).
9. NIS Elements: http://www.nis-elements.cz/.
10. European Silica Fume Committee: http://www.microsilica-fume.eu/web/physico_chemical%20characterization/1011306087/list1187970102/f1.html.
11. Katayamaa S., Yamadab N., Awano M.: Patent US 3150988.
12. Katayamaa S., Yamadab N., Awano M.: J. Eur. Ceramic Soc. *24,* 1957 (2004).
13. Škvára F., Nguyen Anh Duong, Zlámalová Cílová Z.: Ceramics – Silikáty *58*, 12 (2014).
14. Škvára F., Šmilauer V., Hlaváček P., Kopecký L., Zlámalová Cílová Z.: Ceramics – Silikáty 56, 374 (2012).
15. Škvára F., Kopecký L., Myšková L., Šmilauer V., Alberovská L., Vinšová L.: Ceramics – Silikáty *53*, 276 (2009).
16. Tossell J. A.: Phys. Chem. Minerals *27*, 70 (1999).
17. Phair J. W., Van Deventer J. S. J.: Minerals Eng. *14*, 289 (2001).