High-temperature properties of geopolymers based on waste fly ash

František Škvára, Simona Pawlasová, Lenka Myšková, Lucie Alberovská
Department of Glass and Ceramics, ICT Prague, CZ-166 28 Prague 6, Technická 5, Czech Republic
skvaraf@vscht.cz

Raw materials

Brown coal fly ash (class F) - Czech Republic
Mineralogical composition: amorphous (glassy) phase, mullite, quartz, hematite

Oxide	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2
%	53,52	32,87	0,33	2,05	1,80	0,85	5,89	1,89

Silica sand (0 - 4, 4 - 8, 8 - 16), ground limestone, dolomitic limestone

Preparation of geopolymer (paste, mortar)

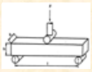
Fly ash (+ground limestone) **+ Alkaline activator** (NaOH + Na silicate („water glass“) Ms=1.0-1.6, Na2O 6- 10%, w=0.30 – 0.40) **(+ Silica sand)**

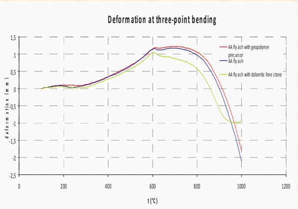
Homogenization and filling form on the vibration exciter → **Geopolymeration** (80°C, 12 hours, open atmosphere)

Storage at temperature of 20 °C and R.H. 35-40%

Mechanical properties

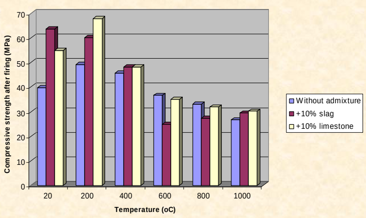
Deformation at 3 point bending





Plastic deformation begins over 700 °C

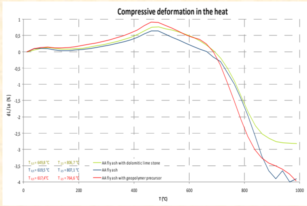
Compressive strength



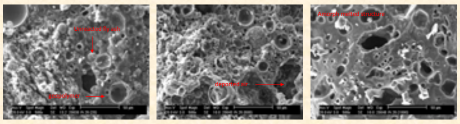
Strength values of the geopolymer (mortar) after firing (determined at 20 °C)

Geopolymer on the basis of Czech brown fly ash without further addition attains the maximum of compressive strength after the heating on 200 °C, at higher temperature attends to continuous decreasing of strength up to the 1000 °C. Ground dolomitic limestone increases compressive strength of unburned samples, compressive strength after burning up to 400 °C as well.

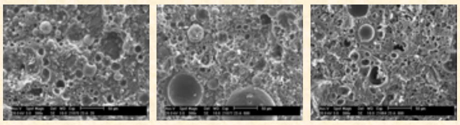
Compressive deformation



SEM

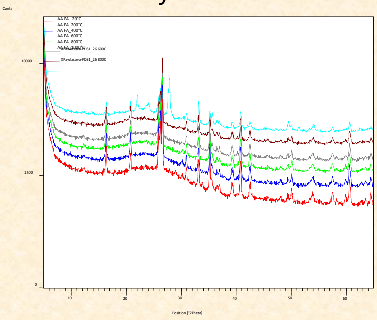


20°C fired at 600 °C 1000 °C



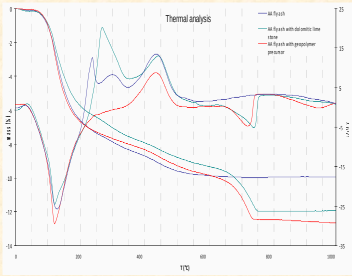
admixture 10% of ground dolomite
20°C fired at 600 °C 800 °C

X-Ray diffraction



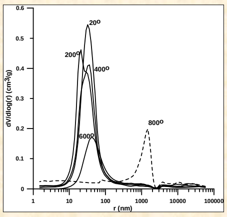
Mainly amorphous character of geopolymer with a minority phases of quartz, mullite and hematite. No formation of new compounds at the temperatures to 1000 °C.

Thermal analysis



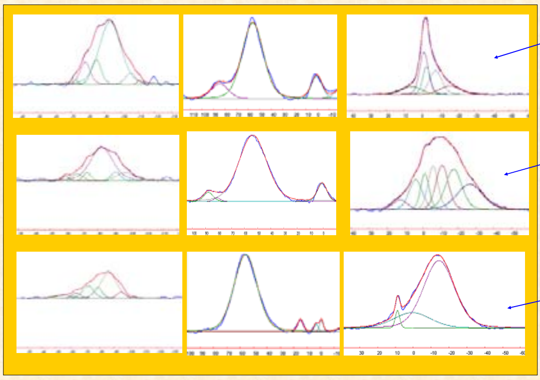
The geopolymer loses continuously its mass (the water content drops) on heating up to of 400-600 °C. The water is probably present in the geopolymer as “free” water in micro-pores, then in gel pores and as OH groups at the end of Si-O-Al chains.

Porosimetry



The porosity of the geopolymer drops on firing at temperatures below 1000°C and the material density increases. The micro-porosity almost disappears at 600°C; new pores form at 800°C.

NMR ^{29}Si ^{27}Al ^{29}Na



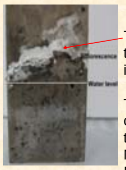
20°C
600°C
800°C

Below 400°C Na occurs in the structure in the form of $Na(H_2O)_n$ where n= 2 – 8

There is a series of peaks in the spectrum at 600°C that correspond to an overall re-arrangement of the structure.

At 800 °C, there is adominant -14 ppm peak in the spectrum that corresponds to the structure of a sodium silicate glass.

Leachability and efflorescence

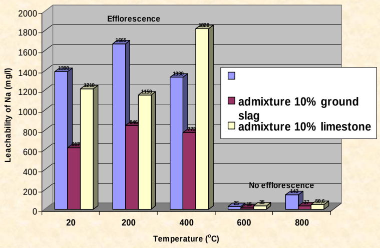


Typical efflorescences on the geopolymer surface kept in a humid environment.

The efflorescences are composed of hydrates of the type $Na_2CO_3 . nH_2O$, $Na_6(SO_4)(CO_3, SO_4).nH_2O$.

Geopolymer after firing at 800°C. Without any efflorescences formed in a humid environment

Na leaching from a geopolymer (mortar) vs. firing temperature



The Na bond in the geopolymer structure is weak and this fact explains the tendency of geopolymer to efflorescences. The K leaching from the geopolymer structure is comparable or even larger than that of Na (MacKenzie 2006).

Conclusions

- The geopolymer prepared by alkaline activation of brown coal fly ash is a porous body containing an alumino-silicate polymer of the type $M_n[-(Si-O)_z – Al – O]_n . wH_2O$.
- Si(3Al) could be identified as the main coordination in the ^{29}Si NMR MAS spectra; the Si(2-3Al) coordination was less represented. The Si(0Al) coordination is characterized by a minor representation, which demonstrates an Al penetration into the $[SiO_4]^{4-}$ network.
- The $AlQ^4(4Si)$ coordination was identified in the ^{27}Al NMR MAS spectra as predominant.
- Na is obviously bonded in the geopolymer structure as $Na(H_2O)_n$ and not as Na^+. The Na bond in the geopolymer structure is weak and this fact explains the tendency of geopolymer material to the formation of efflorescences in a humid environment.
- The strength values of the geopolymer fired at temperatures in the range of 200 – 1000 °C attain their maximum at 200 °C; they decline gradually afterwards. The geopolymer strength after firing is substantially higher than the residual strength of Portland cement. The firing at temperatures below 1000 °C results in structural changes typical for vitreous materials.
- The Na bond in the structure suffers a fundamental change and, starting from 600 °C, the character of the Na bond is the same as that in glassy materials. The Na leaching declines in a very significant way after firing at temperatures above 600 °C and the tendency to the formation of efflorescences disappears.
- The addition of Ca-containing agents improves thermal properties of geopolymers.

This study was part of the of research projects Czech Science Foundation Grant 103/08/1639 ***„Microstructure of inorganic alumosilicate polymers“*** and CEZ:MSM 6046137302 ***“Preparation and research of functional materials and material technologies using micro - and nanoscopic methods”***