Aluminosilicate polymers - geopolymers

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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 ASP (paste, mortar)

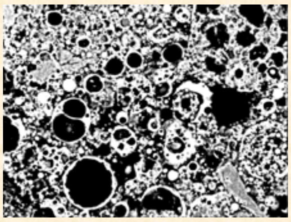
Fly ash + Alkaline activator (NaOH or KOH + Na or K silicate („water glass") Ms=1.0-1.6, Na_2O, K_2O 6- 10%, w = 0.30 – 0.40)

+ Silica sand (+ event. ground limestone)

Homogenization and filling form ⟶ **Geopolymeration** (80°C, 12 hours, open atmosphere)

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

Microstructure

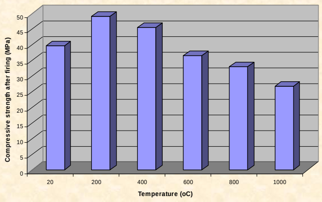


Polished section ASP paste (BSE imaging), Na activator

The ASP prepared by alkaline activation of brown coal fly ash contains:
- a phase of the type $Na_n[-(Si-O)_z – Al – O]_m \cdot wH_2O$,
- parts of unreacted fly ash
- and pores

Mainly amorphous character of geopolymer with a minority phases of quartz, mullite and hematite (X-Ray diffraction)

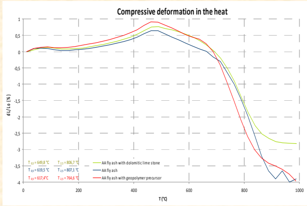
Compressive strength



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

ASP 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.

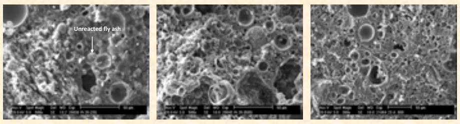
Compressive deformation



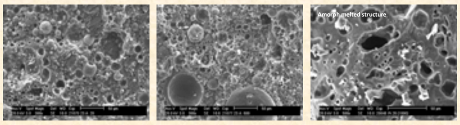
Deformation under load during firing

50x50 mm

SEM

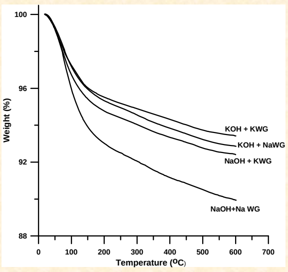


20°C | heated at 600 °C | 800 °C



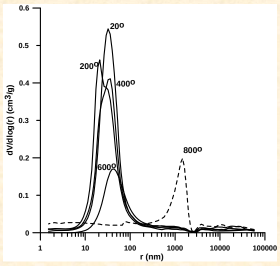
heated at 200°C | 600 °C | 1000 °C

Thermal analysis



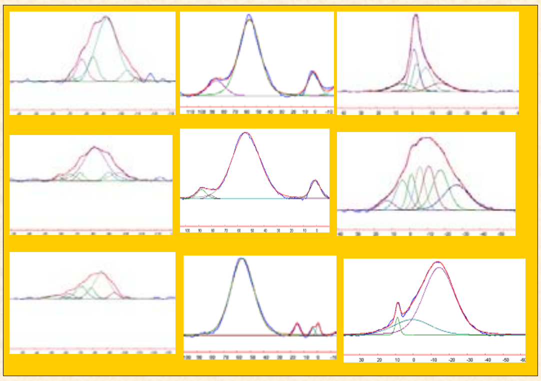
The ASP loses continuously its mass (the water content drops) on heating up to of 400 -600 °C. The water is probably present in the ASP as "free" water in micropores, then in gel pores and as OH^- groups at the end of Si-O-Al chains.

Porosimetry



The porosity of the ASP drops on firing at temperatures below 1000°C and the material density increases.
The microporosity almost disappears at 600°C, new pores at 800°C.

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



20°C

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

600°C

The spectrum at 600°C that correspond to an overall re-arrangement of the structure.

800°C

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

The Na (and K) bond in the ASP structure is weak and this fact explains the tendency o f ASP to efflorescences.

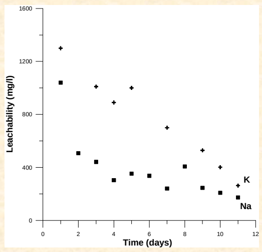
Leachability and efflorescence

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

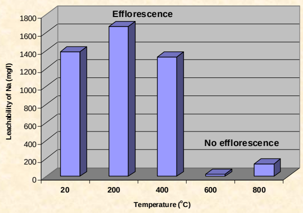
The efflorescences are composed of hydrates of the type $Na_2CO_3 \cdot nH_2O$, $Na_6(SO_4)(CO_3, SO_4) \cdot nH_2O$.

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

Efflorescences on the ASP(K activator) surface kept in a humid environment. The efflorescences are composed of K_2CO_3 .



Leachability of Na, K. ASP mortar with Na and K activator



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

Conclusions

- The aluminosilicate polymer prepared by alkaline activation of brown coal fly ash is a porous body containing an alumino-silicate polymer of the type $M_n[-(Si-O)_z – Al – O]_n \cdot wH_2O$.
- 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 ASP structure as $Na(H_2O)_n$ and not as Na^+. The Na (and K) bond in the ASP structure is weak and this fact explains the tendency of ASP material to the formation of efflorescences in a humid environment.
- The strength values of the ASP fired at temperatures in the range of 200 – 1000 °C attain their maximum at 200 °C; they decline gradually afterwards. The ASP 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.

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