COMPOSITION AND MICROSTRUCTURE PROPERTIES OF GEOPOLYMER MATERIAL MADE OF ACIDIC FLY-ASH WITH NaOH TREATMENT

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Utilization of industrial and mining wastes is an important issue all over the world, promoted also by the Directive 2006/21/EC (management of wastes from the extractive industry). In Hungary, the lignite-based Visonta thermal power plant generates 160–200 tons of slag and fly ash per year (KOVÁCS, 2001). A viable way of its utilization is the production of construction blocks using geopolymerisation hardening.

The term "geopolymer" was used first by Davidovits in 1972 for three-dimensional Al-silicates that are formed from naturally occurring Al-silicates at low temperature and short time by means of alkali activation (DAVIDOVITS, 1991). Treated by an alkali hydroxide solution, an amorphous poly(sialate) forms from SiO_4 and AlO_4 tetrahedra linked by shared oxygen atoms, while cations (Na^+, K^+ or Ca^{2+}) present in the framework, balancing the negative charges of the AlO_4 tetrahedra. The empirical formula is $M_n(-(SiO_2)_z-AlO_2)_n \cdot wH_2O$, where z is 1, 2 or 3, M is a monovalent cation such as K^+ or Na^+ and n is the degree of polycondensation (KOMNITSAS & ZAHARAKI, 2007). This polymerised gel material acts as an intergranular cementing phase, which consists of zeolitic nanocrystallites bound together by Al-silicate gel. The process of geopolymerisation involves leaching, diffusion, condensation and hardening (DAVIDOVITS, 1991).

Five test bodies treated by geopolymerisation had been produced at the Institute of Raw Material Preparation and Environmental Processing, University of Miskolc. Applied raw material was fly-ash from the Visonta power plant, additionally few percent of FGD gypsum was mixed. The test bodies differ in time of grinding: one was used without grinding, the other four were ground in ball mill for 10, 20, 30, 60 minutes respectively. After grinding the test materials were mixed with NaOH solution for 3 minutes, reaching moisture-saturated conditions and kept in cast for 4 hours, followed by a relaxation period for 16 hours at 20°C. Finally, heat treatment was applied for 4 hours at 150°C. Best average compressive strength (10.66 N/mm^2) was obtained for the test body ground for 30 minutes, however the test body ground for 10 minutes reached 5.15 N/mm^2 compressive strength.

Samples from the five test bodies were observed for microstructure characterisation using optical, SEM, EDS and XRPD methods. EDS element mapping and consecutively image processing was used to characterize the element distribution in the cementing phase and in leached fly-ash grains. Rietveld XRPD refinement has shown that about 88% of the ungrounded sample is X-ray amorphous material. It is justified by optical properties, too. The most abundant detected crystalline phase was mullite (7.5%) which was found also by its optical properties, forming a few aggregates of elongated crystals with 80–100 microns length. Another detected Al-silicate was sillimanite (1.5%). Few quartz (1.7%) and cristobalite (0.8%) grains and iron-oxide spherules present also as crystalline phases.

The chemical composition of the fly-ash grains and matrix was analysed by SEM and EDS. Beside Al, Si and O, five minor elements were detected: Na, Mg, Ca, K and Fe. In the Al-silicate grains the most abundant minor element is Na, most frequently reaching 3–4 at%, but in some grains and in the matrix up to 7.75 at%. The sum of other four minor elements (Mg, Ca, K, Fe) was usually less than 1 at%. Fig. 1. shows the Al vs. Si (+K, Ca, Fe, Mg) composition calculated for 13 oxygen of glassy fly-ash grains, solidified from the Al-silicate melt, from which some mullite and sillimanite crystallizes at higher temperature. Fig. 2. shows the elevated Na-concentration in sample ground for 30 minutes, indicating that Na appears in the intergranular cement and also by diffusion within some grains.

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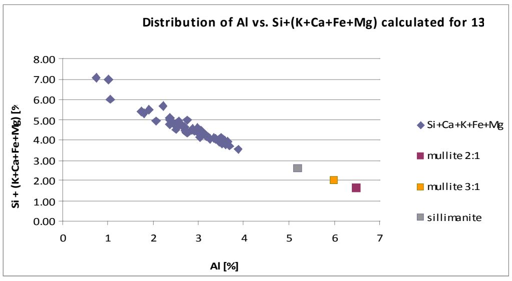

Fig. 1. *Distribution of Al vs. Si (+K, Na, Fe, Mg) in the glassy fly-ash grains.*

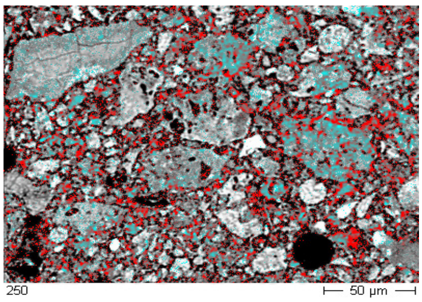

Fig. 2. *Distribution of elevated concentration of Na in the sample ground for 30 minutes. (BSE image combined with element map).*

References

DAVIDOVITS, J. (1991): Journal of Thermal Analysis, 37: 1633–1656.
KOMNITSAS, K. & ZAHARAKI, D. (2007): Minerals Engineering, 20: 1261–1277.
KOVÁCS, F. (2001): Publications of the University of Miskolc, Series A (Mining), 55: 67–76.