ALUMINOSILICATE SYSTEM BASED ON ALKALI ACTIVATION OF INDUSTRIAL BY-PRODUCTS REINFORCED WITH WOLLASTONITE MICROFIBERS

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ABSTRACT

Portland cement-based products are the most commonly used building materials. However, it is well known that the production of OPC not only consumes significant amount of natural resources and energy but also releases high quantity of carbon dioxide (CO_2) to the atmosphere. Purpose of this work is to develop material similar to Portland cement-based concrete, which would be convenient both in terms of energy and environmental friendliness. This article presents preparation, composition and properties of inorganic aluminosilicate polymer, called geopolymer, synthesized from an alkali activation of fly ash/slag mixtures. In the research, effects of different kinds of fly ash from Czech power plants and different dosage of slag and alkali activators that influence compressive strength of hardened geopolymer pastes were discussed. Relatively small flexural strength after 28 days was enhanced with wollastonite microfibers. The study of the microstructure was based on XRD and SEM-EDX analyses.

KEYWORDS:

Geopolymer; fly ash; slag; wollastonite microfibers.

INTRODUCTION

Blast furnace slag and fly ash are well-known materials in construction, used for producing blended cements and concretes. However, only amounts of 20-30 % of slags and fly ashes are used in these terms and the excess is stored in large waste dumps. The utilization of these excesses in the manufacturing of other building materials would contribute to the elimination of an environmental problem (Puertas, 2000). One of the efforts to make environmentally friendly concrete is the development of inorganic aluminosilicate polymer, called geopolymer, synthesized from materials of geological origin or by-product materials that are rich in silicon and aluminium (Sumajouw, 2006). According to Davidovits, geopolymerization involves a chemical reaction of Al–Si materials under highly alkaline conditions, yielding polymeric Si–O–Al–O bonds. Its chemical structure can be described by $M_n\{-(Si\text{-}O)_z\text{-}Al\text{-}O\}_n \cdot wH_2O$, where "M" is a cation such as potassium, sodium or calcium; "n" is a degree of polymerization; and "z" is ratio of SiO_2 and Al_2O_3 (1, 2 or 3) (Davidovits, 1994). The reaction mechanism (Fig. 1) shows the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate (Duxon, 2006).

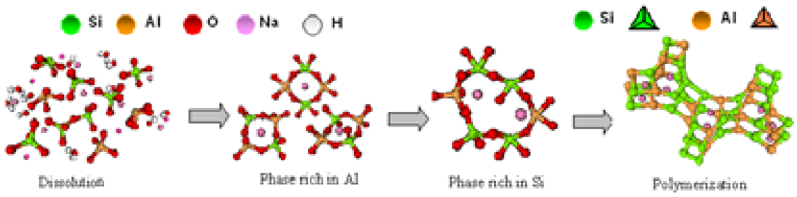

Figure 1 – Conceptual model for geopolymerization

EXPERIMENTAL

In this research, low calcium fly ashes (LCFA) obtained from Czech power plants and different kinds of finely blast furnace slag (BFS) and steel slag, were used as the base material. Chemical composition of by-products was determined by X-ray Fluorescence (XRF). The most widely used raw materials are given in Table 1. Alkali activators used in this study were potassium hydroxide in flake form dissolved in water to form 16M water solution and potassium water glass (K_2O=8.2 %, SiO_2=19.8 % and water=72.0 %). Both of the solutions were mixed together and then poured into a solid fly ash/slag mixture. Time of the mixing takes 3 minutes. The wollastonite (Fig. 9) obtained from Ankerpoort NV: The Mineral Company (Netherlands) in different weight addition was added. Material was elaborated into steel molds of 2×2×10cm. Specimens were cured at laboratory temperature for 24 hours.

Table 1 – Composition of LCFA Počerady 4B and BFS Štramberk as determined by XRF

Oxides (wt. %)	SiO_2	Al_2O_3	CaO	Na_2O	K_2O	MgO	SO_3	Fe_2O_3	TiO_2	P_2O_5
LCFA Počerady 4B	53.9	29.8	2.1	0.2	2.7	0.9	0.8	7.2	1.8	0.1
BFS Štramberk	34.6	8.4	41.9	0.6	0.6	10.0	1.6	0.2	1.1	–

RESULTS AND DISCUSSION

Mechanical properties

Compressive strength evolutions of the pastes are shown in Fig. 2-5. Samples prepared from low calcium fly ash Počerady and BFS exhibit the best mechanical properties (Fig. 2, 3). Fig. 4 indicates that when the slag content increases in pastes, compressive strength increases as well. Strength development is also related to the weight ratio of 16M KOH and potassium water glass in alkali activator, although the weight ratio 3.7 and higher leads to creation of efflorescence (Fig. 5).

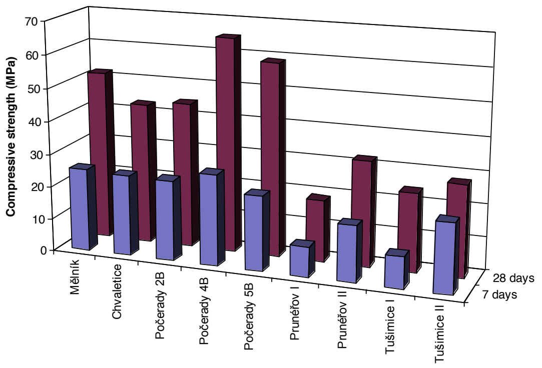

Figure 2 – Alkali activated fly ashes with the same addition of BFS Štramberk

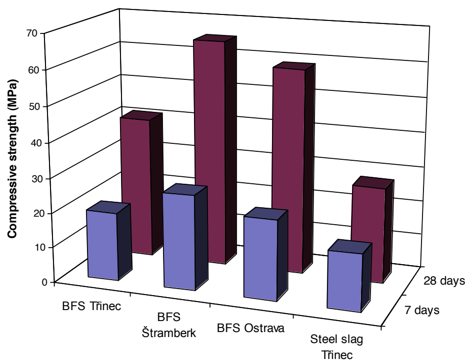

Figure 3 – Alkali activated slags with the same addition of LCFA Počerady 4B

Binder with 60 wt. % of LCFA Počerady 4B and 20 wt. % of blended BFS Štramberk with the weight ratio of 16M KOH/K-water glass 2.5 shows very good compressive strength and also economic factor both of which depend on the increasing price of BFS. The flexural strength was consequently measured only with the samples from this kind of matrix.

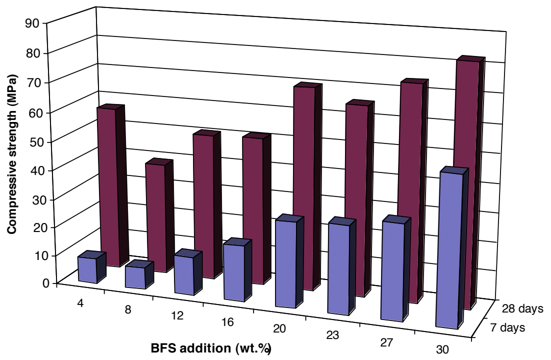

Figure 4 – Alkali activated FA Počerady 4B with the different dosage of blended BFS Štramberk

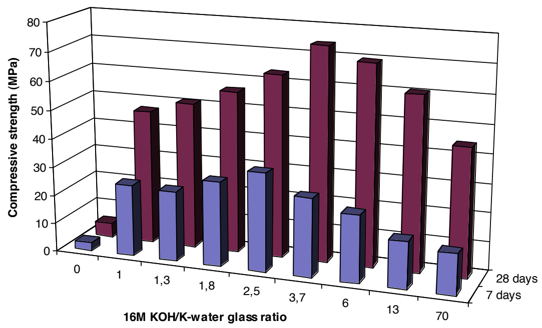

Figure 5 – Alkali activated FA/BFS with the different weight ratio of 16M KOH/K-water glass

The flexural failure tests were carried out by means of a bending strength tester of Michaelis. Surprisingly, the results show decrease of flexural strength after 7 days. For that reason the addition of wollastonite microfibers was used. Figure 6 demonstrates that the content of fibers from 7.5 wt. % has favourable influence on the flexural strength. The addition of fibers has also a positive effect on compressive strength (Fig. 7) because wollastonite serves as the microfiller.

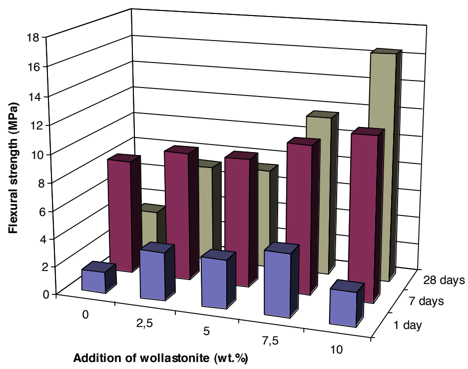

Figure 6 – Flexural strength of alkali activated FA/BFS with the different weight ratio of wollastonite microfibers

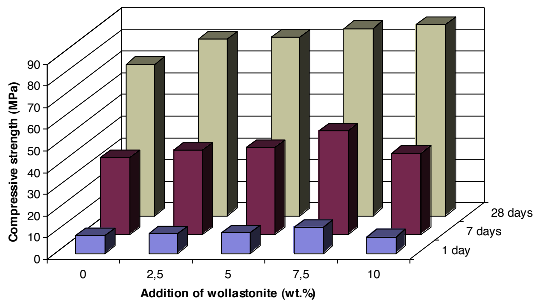

Figure 7 – Compressive strength of alkali activated FA/BFS with the different weight ratio of wollastonite microfibers

Microstructure analysis

Microstructure was observed by SEM-EDX under a Philips XL 30 electron microscope (Fig. 8) equipped with an energy dispersive analyzer (EDX). Figure 8 shows the SEM micrograph of geopolymer binder with wollastonite microfibers. The first area indicates the incorporation of wollastonite into geopolymer matrix. Result of EDX analysis in the amorphous matrix shows the ratio of Al/K~1. This fact demonstrates that the negative charge of aluminum tetrahedron is compensated by the presence of cation K^+ in order to maintain electric neutrality in the matrix. Main reaction products formed in the samples are two types of gels: alkali alumino-silicate-hydrate (place 2) and Al-containing CSH gel with K ion in structure forming around the slag particles (place 3).

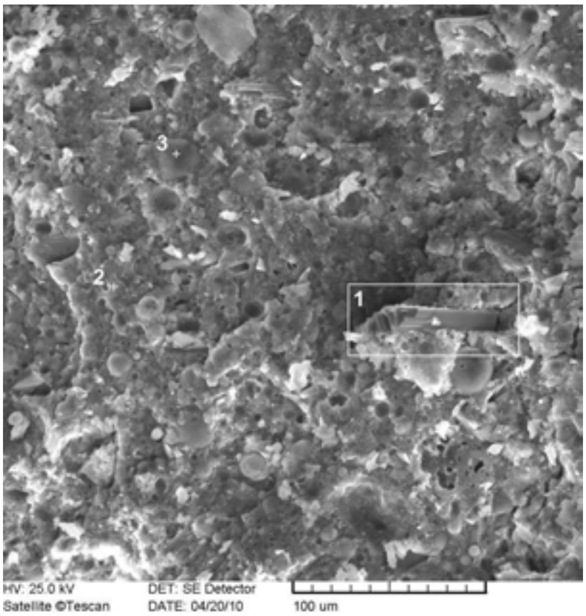

Figure 8 – Morphology of fracture area of alkali-activated fly ash/slag sample with wollastonite microfibers

Figure 9 – SEM picture of fibrous wollastonite particles

The XRD analysis (Siemens D-5005) of geopolymer matrix shows main peaks of crystalline quartz and mullite phases, which come from fly ash. Both of the samples indicate the presence of a big amount of amorphous phase (hump from 15 to 40 °2θ). The XRD diffractogram in Fig. 10 is a geopolymeric binder 1 day after synthesis. The creation of new crystalline phases such as carbonates (ankerite, calcite, tilleyite...), feldspar anorthite and some amount of silicate species (hydrogen silicate and foshagite) were detected. After 28 days the amount of carbonates and hydrotalcite increases but the quantity of silica species decrease based on formation of large amorphous networks by condensation. The alkali activation after 28 days also gave rise to the formation of crystalline phases identified as chabazite, type of zeolite (Fig. 11).

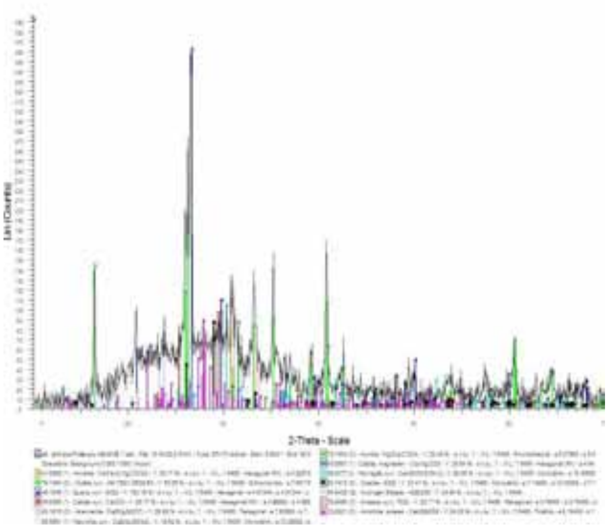

Figure 10 – XRD diffractogram of alkali-activated fly ash/slag matrix 1 day after synthesis

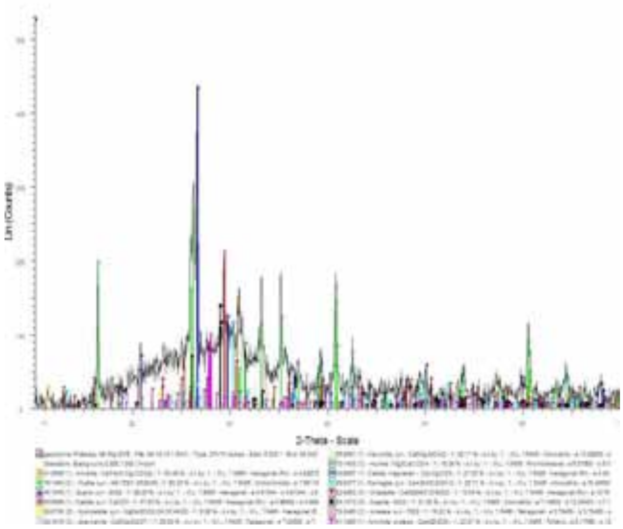

Figure 11 – XRD diffractogram of alkali-activated fly ash/slag matrix 28 days after synthesis

CONCLUSION

Main conclusions extracted from this work are:

- compressive strength development of alkali-activated LCFA/BFS system is dependent on both the slag content and the weight ratio of 16M KOH/K-water glass
- the content of wollastonite microfibers from 7.5 wt. % has favourable influence on the flexural strength and also a positive effect on compressive strength
- SEM-EDX demonstrated that the main hydration products informing the binder are alkaline silicoaluminate and Al-containing CSH gel with K ion in structure
- XRD analysis proved the increasing formation of carbonates via air CO_2 that has negative effect on flexural strength. This negative aspect was suppressed with the addition of wollastonite microfibers.

Results presented in this work demonstrate that LCFA/BFS-based geopolymer with wollastonite microfibers has very good potential for its application in building industry.

ACKNOWLEDGEMENTS

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