CONCRETE BASED ON FLY ASH GEOPOLYMER

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ABSTRACT: On basis research work basic characteristic geopolymer materials on base electric power station fly-ash was attention assembly on quality concrete with aggregates similar composition which use at production cement concrete. Influence way disposition was following (mixture proportion, composition alkaline activator and temperature) on characteristics concrete. For disposition was using electric power station fly-ash one of largest producer combustion brown coal in Czech republic. Rheological characteristics concrete on base AAFa are different from rheology quality concrete from Portland cement. Concrete mixtures from AAFa require on processing for a longer time than is a common near cement concrete namely regardless of technology processing, as is vibration, tamping or pouring. Flow characteristics concrete from AAFa are in compare with fresh cement concrete when five time slower at of all type processing.

KEYWORDS: Aggregates, cement concrete, composition alkaline activator, concrete mixtures, fly-ash, geopolymer materials, method Kennedy and Bolomey.

1   INTRODUCTION

When exposed to highly alkaline environments (hydroxides, silicates), alumosilicate substances like cement clinker, slags, fly ashes or thermally activated kaolinite substances give rise to new materials - geopolymers, based on 2-3D Si-O-Al structures. These new materials are the subject of considerable interest e.g. at symposiums [1-7], or in articles quoted in databases[8,9]. These publications summarize the results of study of the geopolymers' synthesis, their microstructure (mostly SEM), but also the results of their potential implementation, mainly in the exploitation of inorganic waste materials (particularly power plant fly ash).

These publications predominantly focus on the geopolymer's polymer nature (NMR in the solid phase), its mechanical properties, the effect of aggressive environments, leaching ability and others. The references, however, still lack adequate data on the properties of concretes based on geopolymers. The properties of geopolymer-based concretes are the focus of this study.

2   EXPERIMENTAL PART

The project applied power plant fly ashes (from the Czech Republic) with a surface area of 210-300 m^2/kg (Blaine) whose chemical composition is displayed in the table below.

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Table 1. Chemical composition ash

weight%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5
fly ash	53.79	32.97	5.51	1.84	0.92	0.46	1.76	0.37	2.1	0.15

Differences in the chemical composition of individual fly ash types were ±5% rel. Concrete was prepared by mixing fly ash and other ingredients with the solution of the alkaline activator and aggregates. The SiO_2/Na_2O ratio (M_S module) in the alkaline activator was modified by adding NaOH to water glass to reach values of M_S = 1 - 1.6. The total concentration of the alkaline activator ranged between 6-10 % of Na_2O in the fly ash weight. The experiments mostly consisted in the preparation of concretes with the w/c (H_2O/fly ash) ratio w = 0.30 - 0.40, and also pastes and mortars with w = 0.23. – 0.35. Further on, Ca-containing substances, such as ground water-granulated blast-furnace slag, gypsum, limestone, were added into the concrete mixes.

Rheological properties of the fresh fly ash composition (concrete) rely on the content of fly ash in the mix. Mixtures with higher fly ash contents are of a different rheological nature as compared to fresh cement concrete. Both static and dynamic viscosity of geopolymer concrete is considerably higher. This, in both cases, implies an extended time of vibration or other processing and a very sensitive design of the filler composition, i.e. solid mix components – aggregates. Despite its higher viscosity and a relatively high adhesiveness of the fresh composition, gravitational segregation of coarse and heavier aggregate grains occurs at higher w/c ratios connected with the expulsion of mortar and paste towards the surface of the processed mix of fresh concrete. This situation occurs not only during intensive dynamic processing by vibration, but also by mere placement of the cast composition of fresh geopolymer concrete. In such cases, compact fine-grained admixtures, like ground limestone, ground slag, ground silica powder etc., proved beneficial. The concrete mix was also treated by adding steel micro-reinforcement in the form of steel fibres, or the concrete mix was applied on pre-fitted steel reinforcement (steel rods).

Following the preparation of concrete, the test pieces were exposed to a thermal process under "dry conditions" where they were placed in a drier at temperatures of 60-90 $^{\circ}$C (in open atmosphere) for 6-12 hours. Then, the test pieces were placed in the air in an environment with 40-50 % R.H. until the time when strength values were determined. Compressive strengths were determined after 2, 7 and 28 days or after 90, 360 days respectively. After the strength values were determined, the chips were studied by means of the X-ray diffraction analysis, thermo-gravimetric analysis, high-pressure Hg pore-volume analysis, BET isotherm measurement. Besides, FTIR and NMR MAS (^{29}Si, ^{27}Al) spectrum measurements were performed (Table 2). Following destruction strength measurements, the fracture surfaces of the chips were studied for microstructure by means of the scanning electron microscope where analyses using the ED spectrometer were performed at selected points.

3 RESULTS AND DISCUSSION

3.1 STRENGTH DEVELOPMENT

The strength values of pastes, mortars and concretes prepared on the basis of fly ash geopolymers obtained at periods of 2 – 360 days show a rising trend. Depending on the conditions of preparation and composition, the values of compressive strength for pastes, mortars and concretes range between 15-70 MPa after 28 days. The highest strength values obtained were for geopolymers based on fly ash and blast-furnace slag ranging between 100-160 MPa of compressive strength at 28 days after preparation.
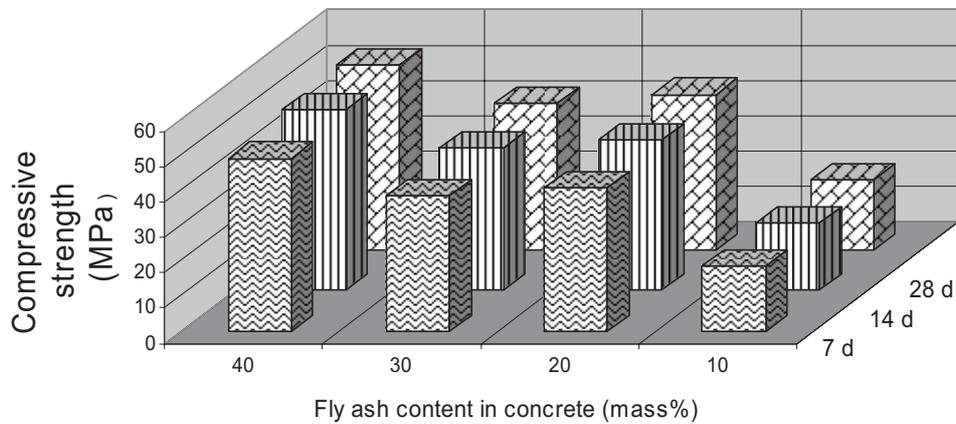
Figure 1. Time pattern of geopoplymer concrete's strength development

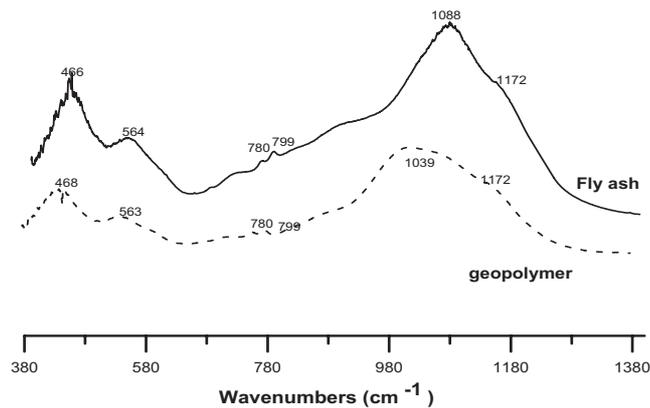## 3.2 CHEMICAL COMPOSITION OF GEOPOLYMER

Figure 2. IR spectra of fly ash and geopolymer

The FTIR spectra (Fig.2) reflect the differences caused by different conditions of alkaline activation. The strip corresponding to Si-O and Al-O vibrations for original fly ash is 1080-1090 cm^{-1}, while for geopolymer it is shifted to lower values. This shift is interpreted as the result of Al penetration into the original structure of the Si-O-Si skeleton, analogically to what was detected in zeolites. The more dramatic the shift, the higher the penetration degree of Al from glasslike fly ash components into the $[SiO_4]^{4-}$ [10,11] network probably is.

In ^{29}Si NMR MAS spectra, the majority signal identified for original fly ash is the signal attributed to tetrahedric $[SiO_4]^{4-}$ (Si(0Al), which belongs to the presence of silica. [12,13] In this spectrum, the coordination Si(2-3Al) was further found, which probably belongs to the mullitic phase. The situation detected for the geopolymer was different. Here, the Si(0Al) coordination was less represented, while the Si(2-3Al) coordination was more represented, which again proves the penetration of Al into the $[SiO_4]^{4-}$ network. This interpretation of NMR spectra is supported by other reference publications. [14,15].

Table 2. Spectrum measurements FTIR and NMR MAS

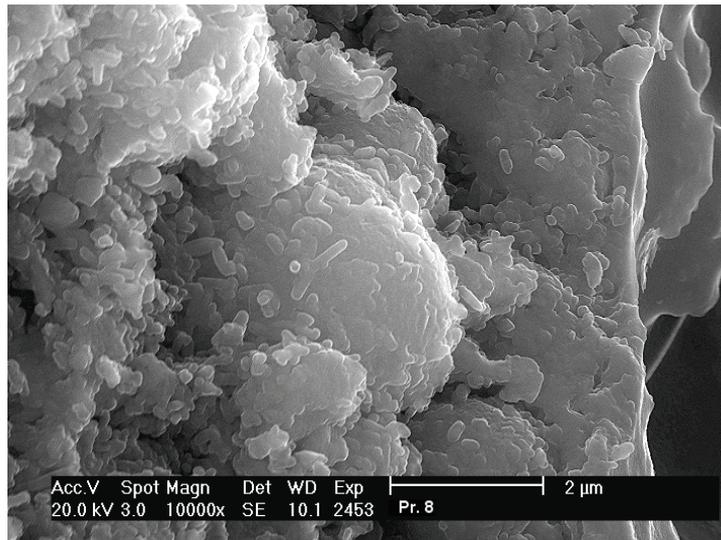| Fly ash geopolymer (paste = 0,27) strength 70 MPa	
^{27}Al NMR	^{29}Si NMR
50.4 ppm 90 % AlQ$_4$(ASi) -4.3 ppm 10 % AlQ$_{2-3}$(2-3Si)	-89.5 ppm 56 % Si(3Al) -97.6 ppm 31 % Si(1Al) -107.6 ppm 13 % Si(0-1Al)

Figure .3. Detailed nature of geopolymer (paste w=0.27, fracture surface, 28 days after preparation)

The geopolymerization process (alkaline activation of fly ashes in a water environment at pH >12) during which material hardening occurs differs from the hydration processes of inorganic binders, e.g. Portland cement. This process seems to follow mostly a mechanism "through a solution" where in a highly alkaline environment fly ash particles are first dissolved, and a new geopolymer structure is formed from the solution, see Fig. 4. A 2D-3D inorganic hydrated polymer (geopolymer) arises with a general formula $M_n\left[-(Si-O)_z-Al-O\right]_n.wH_2O$. A prominent share in this process, apart from preparation conditions, is also that given by the presence of Ca atoms, which enter the Si-O-Al-O skeleton compensating the charge on Al atoms. These charges are usually compensated by Na$^+$ ions. Ca^{2+} ions, however, can probably interconnect individual Si-O-Al-O chains thus forming a more solid structure with higher strengths during alkaline activation of fly ashes with the presence of Ca-containing substances. The prominent role of Ca atoms in the geopolymer skeleton is also testified by the results of reference publications. [16,17]

3.3 POROSITY OF GEOPOLYMER

The mass of fly ash-based geopolymer shows the presence of residues of original fly ash particles on which the effect of gradual dissolution is evident (see Fig. 4). In these geopolymers, relatively high porosity (up to 50%) was determined regardless of the type of conditions of their preparation. Closed spherical pores are present here, which were formed by the dissolution of the original fly ash particles or by air entrainment during preparation.

The effect of preparation conditions, i.e. the content of Na$_2$O or the SiO$_2$/Na$_2$O ratio respectively, is manifested not only by the strength values of the geopolymers reached, but also by the pore size

distribution. The porosity of geopolymers is also significantly affected by the water/cement (H_2O/fly ash) ratio, see Fig.5.
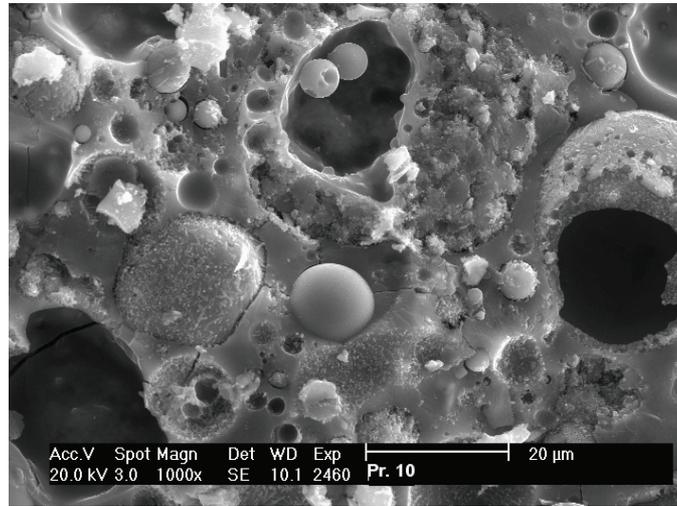

Figure 6. Porous nature of geopolymer (paste w=0.27, fracture surface, 28 days after preparation)
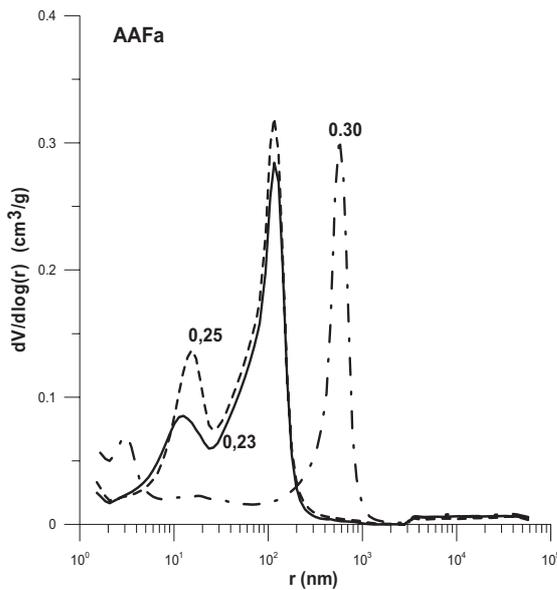

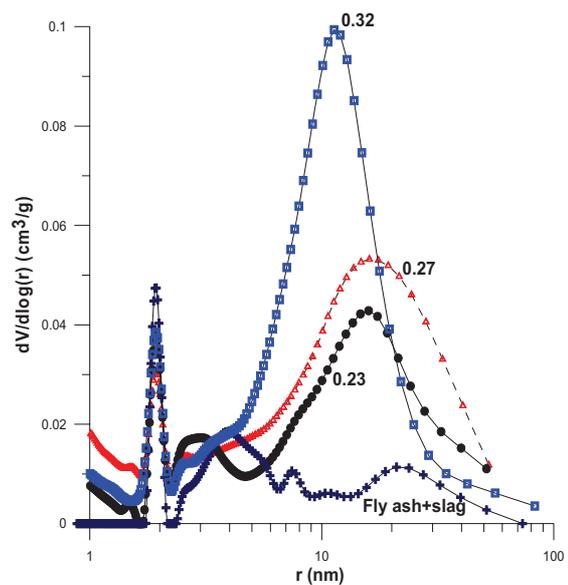| Figure 7. Effect of water/cement ratio on pore size distribution (Hg pore-volume analysis) in geopolymer, paste with w/c ratio | Figure 8. Pore size distribution in geopolymers (BET) |

The effect of adding Ca-containing substances is manifested not only by increased strength, but also by lowered porosity. The considerably lower porosity is obtained in the geopolymers prepared from fly ash and slag mixes, where total porosity amounted to 2-10%, and a shift towards lower pore dimensions was recorded. For these substances, the compressive strength reached was 100-160 MPa. The high-pressure Hg pore-volume analysis, however, provides only limited information on the nature of pores in the nanometric domain. Additional information is obtained through BET isotherm measurement. Fig. 6 displays pore size distribution in geopolymers prepared under different conditions. The results clearly point out the fact that in the nanometric domain geopolymers are of

arelatively similar nature, which does not much depend on the conditions of preparation. Differences occur only in the samples of geopolymers prepared by using slag together with fly ash. These materials show lowered porosity due to the coexistence of the geopolymer and the C-S-H phase.

3.4 GEOPOLYMER – AGGREGATE INTERFACE

In common concrete based on standard Portland cement, there is an intermediate layer between the aggregate grain and hardened cement. This layer is 20-100 μm thick with a microstructure and composition different from hardened concrete. It is richer in the content of $Ca(OH)_2$ and ettringite. $Ca(OH)_2$ particles are often oriented alongside aggregate particles. The porosity of the interface is greater than the porosity of hardened cement, and the porosity gradient established shows a falling trend in the direction towards the aggregate particles. [18]

4 CONCLUSIONS

1. The geopolymer prepared from fly ash contains predominantly structures of the $AlQ_4(4Si)$, $Si(3Al)$ a $Si(2-3Al)$ type.
2. The fly ash-based geopolymer is a porous material. In the nanopore domain, the porosity of geopolymers is very similar, regardless of the conditions of preparation. The strength of geopolymers is significantly affected by macropores (10^3 nm and more), which arise by air entrainment into geopolymers, or they are fly ash particles after partial reaction. With the presence of Ca-containing admixtures (slag, gypsum), porosity is significantly reduced due to the coexistence of the geopolymer and the C-S-H phase.
3. A geopolymer-based binder may serve for the preparation of concrete. Strength characteristics of geopolymer concrete show a long-term rising trend.
4. Rheological properties of such concretes differ from those made with Portland cement.
5. No presence of a transitory layer with a different composition was found on the interface between the geopolymer and aggregates (reinforcement), which exists in concretes made with Portland cement.

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