

CONCRETE BASED ON FLY ASH GEOPOLYMERS

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Abstracts. Rheological characteristics concrete on base fly ash geopolymer are different from rheology quality concrete from Portland cement. Concrete mixtures from fly ash geopolymer 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. Concrete based on fly ash geopolymer is the porous material. In the area of nanopores the geopolymer porosity is very similar without any regards to preparing conditions. The way how to prepare geopolymers (water coefficient, composition of alkali activator) influences the geopolymer porosity in the area (10^2 nm and more), which develop themselves by bringing the air to the geopolymers or these are partly reacted (hollow) fly ash parts. These pores have closed character. Any presence of the temporary phase with different composition was not found between geopolymer and aggregate as it is at the concretes from Portland cement. Geopolymer composition is almost the same in the close nearness even in the geopolymer mass. Geopolymer's concretes based on fly ash are obvious to have increasing character within 2–360 days. In the presence of Ca contained ingredients as a result of geopolymer co-existence and C-S-H phase and maximal geopolymer strength was reached.

Keywords. *Geopolymer, alkali activated, concrete*

1 Introduction

The exposure of aluminosilicate bodies of the type cement clinker, slag, fly ash or thermally activated substances to very alkaline environments



(hydroxides, silicates) gives rise to the formation of new materials – geopolymers characterized by a two- to three-dimensional Si-O-Al structure. Substantial attention has been given to these new materials, for instance, at symposia [1]-[7] or in papers mentioned in databases [8], [9]. Such contributions deal not only with the results obtained during the investigation into the synthesis of geopolymers and their microstructure (by using predominantly SEM) but also with their possible applications particularly in conjunction with the valorization of inorganic rejects (first of all, fly ashes). The above contributions pay special attention to the polymer character of the geopolymer (solid phase NMR), to its mechanical properties and to the effect of aggressive (corrosive) environments as well as to its leaching behavior, etc. There are only few published data dealing with the properties of concretes on the basis of geopolymers. Therefore, the present paper deals with the investigation into the properties of the concretes on the basis of geopolymers.

2 Experimental part

Fly ashes from Czech power plants were used for investigation. Their specific surface area ranged from 210 to 300 m²/kg (Blaine). The chemical composition of the fly ashes is given in the following table.

| wt% | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | K ₂ O | Na ₂ O | TiO ₂ | P ₂ O ₅ |
|---------|------------------|--------------------------------|--------------------------------|------|------|-----------------|------------------|-------------------|------------------|-------------------------------|
| Fly ash | 53.79 | 32.97 | 5.51 | 1.84 | 0.92 | 0.46 | 1.76 | 0.37 | 2.1 | 0.15 |

The differences in the compositions of individual fly ashes fluctuated by $\pm 5\%$ (relative). The concrete was prepared by mixing fine-grained and coarse-grained crushed quarry aggregate with the size ranging from 0 to 16 mm, fly ash and other ingredients with the solution of an alkaline activating agent (see Fig. 1).

The SiO₂-to-Na₂O ratio (M_s modulus) in the alkaline activating agent was adjusted by adding NaOH to soluble glass in order to obtain M_s values ranging from 1 to 1.6. The overall concentration of the alkaline activating agent varied in the range of 6 to 10% Na₂O (expressed as percentage of the fly ash weight). The experiments were carried out by using concretes characterized by the water coefficient (the H₂O-to-fly ash ratio) $w = 0.30 - 0.40$ as Fig. 1. Procedure used for the preparation of geopolymers materials as well the pastes and mortars with $w=0.23-0.35$. In some cases, also calcium-containing materials (eg ground pelletized blast-oven slag, gypsum, limestone) were added to the concrete mixes.



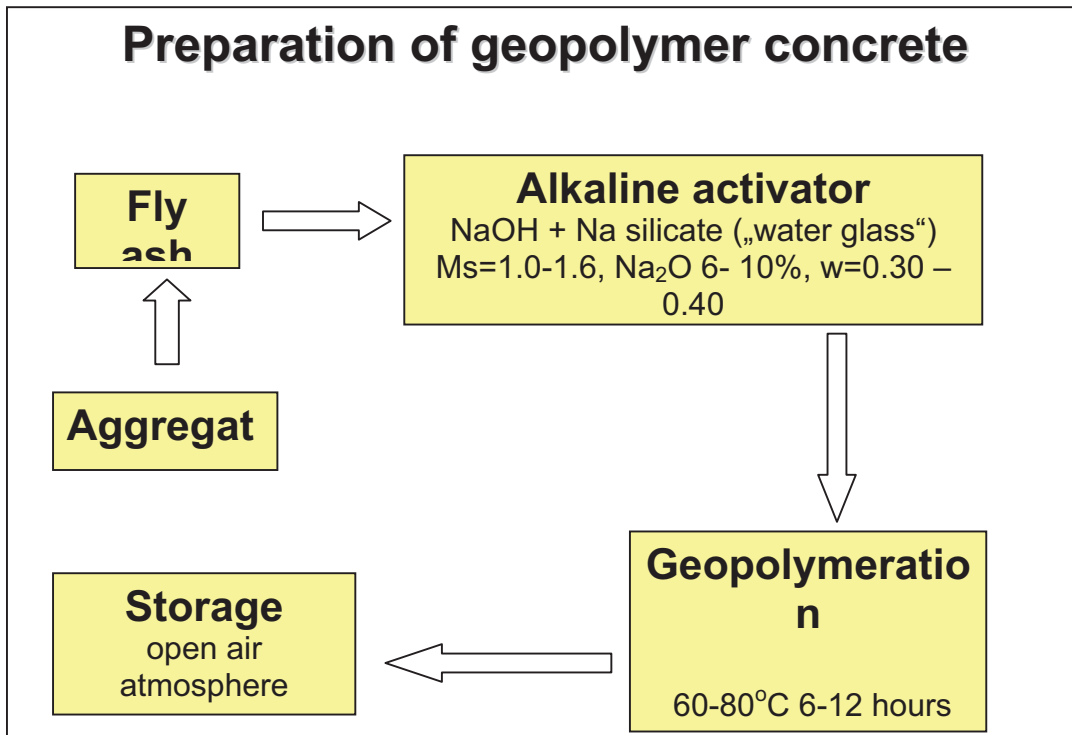


Fig. 1.

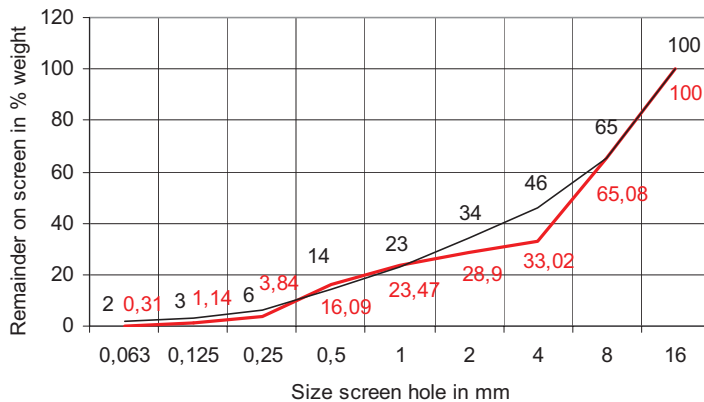


Fig. 2. Spline aggregate gradation 0/4, 4/8, 8/16 in comparing to exemplary spline.

The aggregate was composed of three fractions; the main goal was to approach - as much as possible - the exemplary spline cumulative grain size curve recommended in the standard DIN/ISO 3310-1. The curve was modified partially to suit the geopolymers concretes. A part of the samples of mortar mix samples taken out of the mold was maintained at the laboratory temperature in an environment with the relative humidity of 40% for 28 days. The samples were then kept in the solutions of Na_2SO_4 , MgSO_4 and NaCl in accordance with the instructions (CSN EN 206-1 standard) for the testing of concretes.





Fig. 3. Character of the fresh geopolymers concrete.



Fig. 4. Incorrect mix, aggregate segregation and the mortar displaced towards the surface.



Fig. 5. Correctly composed mix, uniform distribution of the aggregate.

The geopolymers samples were also subjected to the tests consisting of alternating freezing and defrosting in accordance with the CSN 72 2452 standard. The bodies with the dimensions of 4 x 4 x 16 cm were kept at the laboratory temperature in the environment with the relative humidity of 40% for 28 days; their frost resistance was then determined. Micro-reinforcement (dispersed fine steel wires) was added to the concrete mix too. Also the effects of other types of reinforcement were studied (sized fiberglass of various dimensions, fiberglass mats and various sizes of man-made fibers and cords). The attention also focused on the verification of the function performed by the concrete reinforcing steel rods especially as regards the adhesion and the interaction in the contact zone with the geopolymers concrete.

The concrete samples obtained in the above way were subjected to a heat treatment process under “dry conditions”: the samples were kept



in a dryer at a temperature ranging from 40 to 90°C (in the open atmosphere) for 6 to 24 hours. The samples were then kept in air with the relative humidity of 40 to 50% till the moment of determination of their strength. The compressive strength of the samples was determined after 2, 7 and 28 days, respectively after 90 and 360 days. Geopolymer concrete mixes that do not require the application of the heat treatment and which harden at a temperature of 20°C were prepared recently (unpublished data [12]).

Fragments remaining after the strength determination were investigated with the aid of the RTG diffraction analysis, thermal analysis, high-pressure HG porosimetry and by measuring BET isothermal lines. Also FTIR and NMR MAS (^{29}Si , ^{27}Al) spectra were measured. A scanning electron microscope was used for the investigation of the microstructure on the fracture surfaces of the fragments remaining after the destruction tests. Selected spots were analyzed with the aid of an ED spectrometer.

3 Results and discussion

3.1 Rheological properties

Rheological properties of the fresh fly-composition are dependent on the fly ash content in the mixture. In comparison with the fresh cement concretes, the mixtures containing higher percentages of fly ash exhibit a different rheological behavior. Both the static and dynamic viscosity of the geopolymers concrete are substantially higher. Therefore, longer treatments by vibration or by other techniques are required in both cases and the aggregate setup (ie the solid components of the mixture) must be selected with great care. Despite the higher viscosity and a rather pronounced adhesion ability of the fresh composition coarser and heavier grains of the aggregate start settling at higher values of the water coefficient; this process is accompanied by the displacement of the mortar and the paste towards the surface of the processed fresh concrete mix. This situation occurs not only during an intense dynamic treatment by vibration but also during a simple free deposition of the cast composition of the fresh geopolymers concrete. Solid fine-grained additives, e.g. ground limestone, ground slag, milled silica powder, etc. yielded good results in this case. The mixing process of all the components of the geopolymers concrete results in the absolutely perfect coating of even the smallest grains of the aggregate. However, a faster mixing of the geopolymers concrete is accompanied by the entrainment



of a considerable amount of air into the fresh geopolymer concrete. This air which is concentrated in small bubbles in the whole volume of the composition is not able to leave the composition within a reasonable period of time because of the low mobility of the binder component; hence, its substantial part remains enclosed in the processed mix. It is evident from the microscopic pictures the air occurs in the form of closed air pores that are not accessible to water; therefore, such pores are harmless from the viewpoint of the water absorption of the geopolymer concrete.

3.2 Strength evolution

The strength values of pastes, mortars and concretes of the geopolymers on the basis of fly ashes show an increasing trend after 2-360 days from the moment of their preparation; the respective values range from 15 to 70 MPa after 28 days in dependence on the conditions of their preparation and on the composition. The highest strength values were obtained for the geopolymers on the basis of fly ash and blast-oven slag; in this case, the compressive strength measured after 28 days elapsed from the moment of their preparation ranged from 100 to 160 MPa.

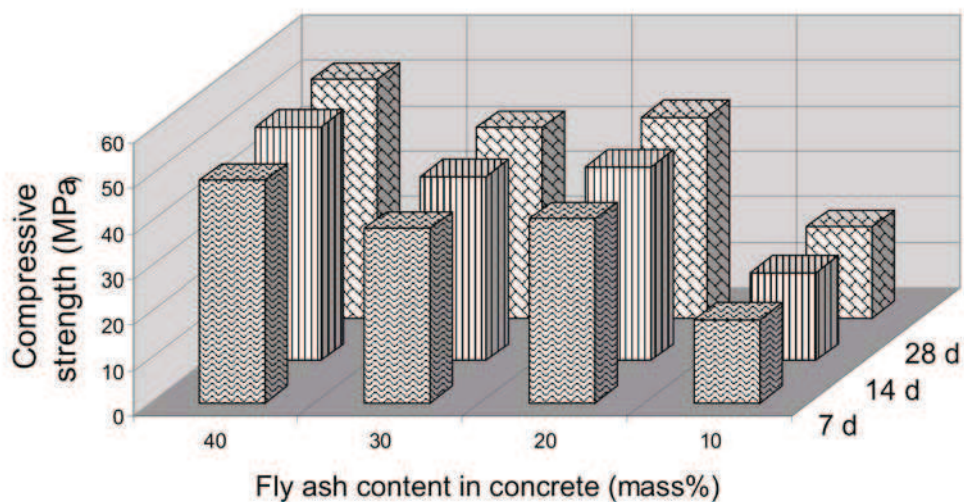


Fig. 6. Evolution of the geopolymers concrete strength in time (12 hours after the preparation at 80°C).

The facts may be regarded as remarkable from the viewpoint of the application in the building industry:

The ratio of the compressive strength to the tensile strength under bending varies in the range of 10.0:5.5 (the ratio for cement-based



concrete ranges from 10.0:1.0 to 10.0:1.5) which means that a higher tensile strength of the geopolymer concrete gives the possibility to reduce the quantity of the reinforcement in the structural elements.

3.3 Geopolymer – aggregate interface

There is a transition layer between the aggregate grain and hardened cement in the ordinary concrete on the basis of the standard Portland cement. The thickness of the layer ranges from 20 to 100 μm ; the layer microstructure and composition differ from that of hardened cement. The contents of $\text{Ca}(\text{OH})_2$ and ettringite are higher. There are often $\text{Ca}(\text{OH})_2$ particles oriented along the aggregate particles. The porosity of the transition layer is larger than that of the hardened cement and a porosity gradient with the decreasing character in the direction away from the aggregate particles could be observed [10], [11].

The character of the geopolymer – aggregate boundary is quite different. No transition zone could be detected either morphologically or by a direct measurement of the geopolymer compositions in the proximity of the aggregate itself (Fig. 7, 8) in contrast to the concrete made of Portland cement (Fig. 9).

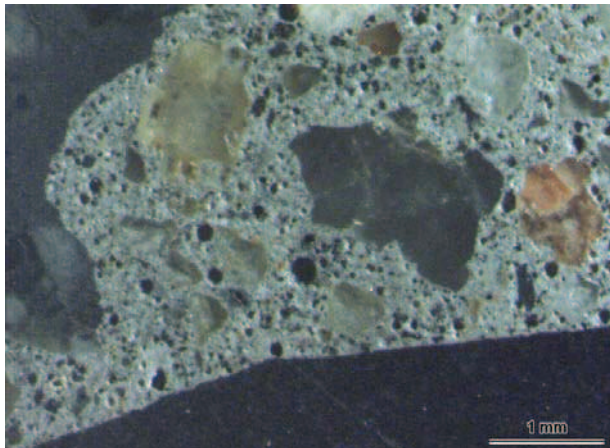


Fig. 7. Geopolymer concrete (polished section, optical microscope).

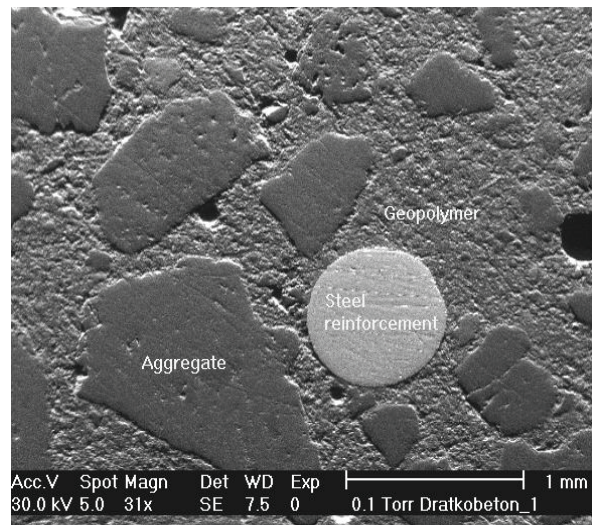


Fig. 8. Boundary between the aggregate (reinforcement) and the geopolymer in the concrete (polished section, BSE representation).



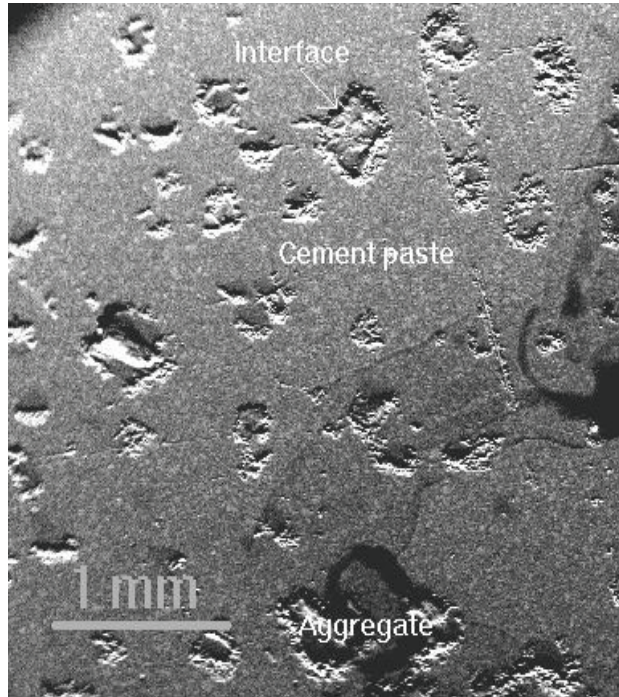


Fig. 9. Boundary between the aggregate and the Portland cement paste in the concrete (polished section, BSE representation).

The Na_2O -to- SiO_2 and Al_2O_3 -to- SiO_2 ratios (point analyses) are shown in Fig. 10 and 21 in dependence on the distance from the aggregate particle. We can say that – within the range of experimental error (heterogeneous character of geopolymers) - no important changes in the geopolymers compositions take place in the close proximity of the aggregate as this is usually the case of Portland cement.

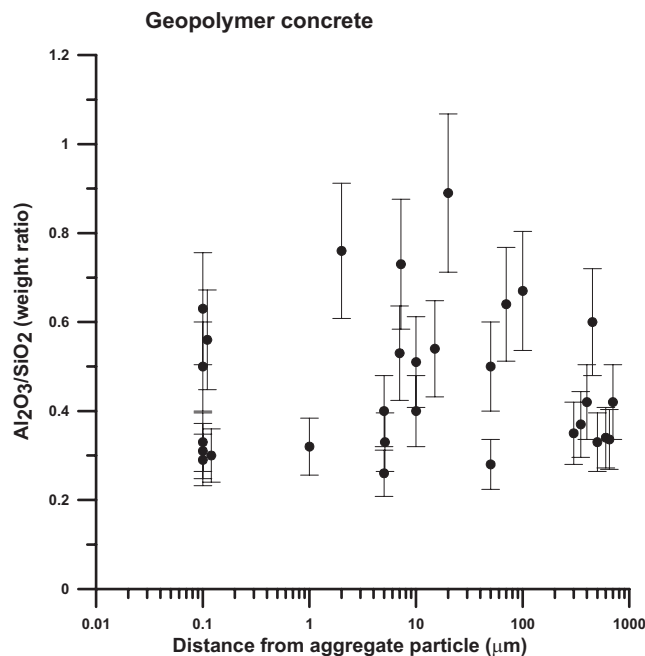


Fig. 10. Dependence of the Al_2O_3 -to- SiO_2 ratio on the distance from the aggregate grain in a geopolymer concrete.



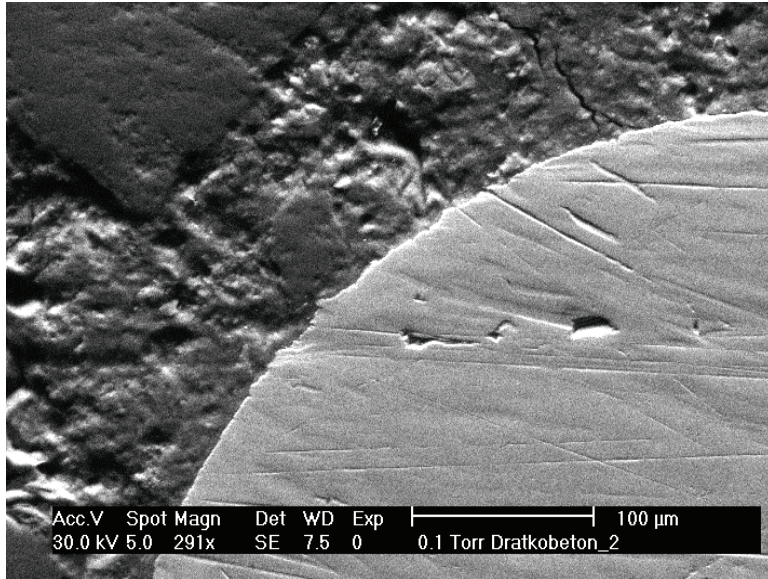


Fig. 11. Character of the boundary between the steel micro-reinforcement and the polymer (polished section, SEM).

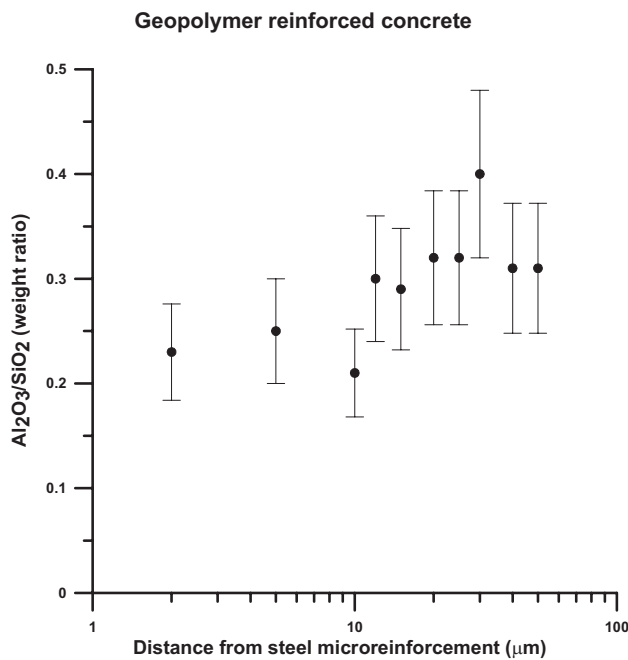


Fig. 12. Dependence of the Al₂O₃-to-SiO₂ ratio on the distance from the steel reinforcement in a geopolymer concrete.

The character of the boundary between the steel micro-reinforcement and the geopolymers is quite analogous (see Fig. 10-12).

3.4 Durability of the geopolymers concrete

The mass of the sample bodies did not change practically during the freezing and defrosting cycles taking place in the aqueous environment (no disintegration of the samples took place). The compressive strength of the sample bodies after the freezing cycles were lower as compared



with those obtained for the samples after 28 days without any frost resistance tests. No visible defects or deformation could be observed after 150 cycles. After 150 freezing cycles, the strength values dropped to about 70% of the strength measured in the same period of time. It is obvious from the results obtained that the geopolymers materials on the basis of the fly ash possess an excellent frost resistance.

Geopolymer mortars and concretes kept in the NaCl solution for long periods of time resist to corrosion without showing any signs of sample damage. The exposure of the geopolymers materials to the NaCl solution resulted in the consistent increase in the compressive strength during the whole period of measurement (720 days) and the values were as high as 70 MPa. The mass of the samples kept in the NaCl solution grew during the 1st year (by about 3% relative) to become stable afterwards. The penetration of chloride ions into the body of the geopolymers materials (point analyses, the measurement was carried out in the direction perpendicular to the surface in contact with the NaCl solution) shows a decreasing trend and the chloride concentration in the body is low. Almost no corrosion products could be found on the surface of the geopolymer materials while they were kept in the NaCl solution.

The exposure of geopolymers materials to the solutions of sulfates and NaCl did not result in the formation of new crystalline phases. The RTG diffraction analysis only confirmed the occurrence of original crystalline phases present in the fly ash. The absence of expansive products as, for instance, the ettringite ($C_6AS_3H_{32}$) or Friedel salt (C_4AClH_{11}) in the samples after the two-year exposure to the salt solution is an important finding.

The resistance of geopolymer concretes to the action of salt solutions is better than that of the cement-based concrete in which the crystalline ettringite or the Friedel salt are formed; eventually, the body disintegrates in result of the crystallization stress.

The effect of high temperatures on the properties of geopolymer mortars was investigated in the temperature range of 150 to 1100°C.

A geopolymer material exposed to the action of high temperatures loses a substantial part of its strength that drops to 40 % of its original value. The strength already starts dropping at a temperature of 250 °C and it remains practically the same at higher firing temperatures. The lowest values of the residual strength were observed in the temperature range of 600 to 700°C; they were due to the presence of the melt that





Fig. 13. Character of the geopolymers concrete after firing.

started forming. The values of the residual strength after the firing were rather higher than those characterizing the materials on the basis of Portland cement. The test aimed at determining the resistance of the concrete on the basis of fly ash to the action of higher temperatures was carried out by the 3-point loading of the bodies while the tensile strength under bending was determined. Of course, the selection of the aggregate plays an important role in this case; nevertheless, no initial deformation but a fragile fracture characterized the behavior of cement-based concrete at temperatures of about 600 °C. On the contrary, a pronounced plastic deformation and a gradual rupture of the drawn section of the body profile took place at the same temperature in the concrete activated with the fly ash.

Examples of geopolymer concretes (Fig. 14,15).



Fig. 14. Bone-shaped paving brick.

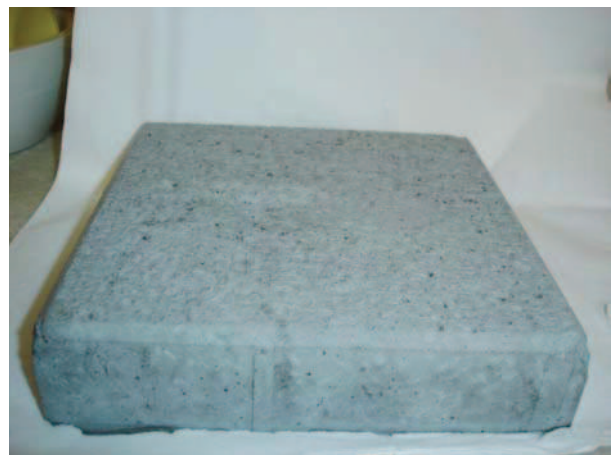


Fig. 15. Paving brick with roughed surface.



4 Conclusions

1. A concrete can be prepared by using the geopolymer binder. No shrinkage due to hydration (typical for the cement-based concretes) takes place in the concrete. The ratio of the compressive strength to the tensile strength under bending varies in the range of 10.0 : 5.5 (this ratio changes in the cement-based concrete from 10:1. to 10:1.5). The strength values of the geopolymer concrete increase in the long run.
2. Rheological properties of concretes differ from those of Portland cement.
3. The geopolymer concrete is resistant to the corrosive environments.
4. No transition phase with a different composition as this is typical for concretes on the basis of Portland cement was found between the geopolymers and the aggregate (reinforcement).

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References

- [1] Proc. 1st, 2nd, 3rd conference “Slagalkaline cements and concrete”, Kew (1978, 1985, 1989)
- [2] Proc. 1st Intern. Conf. “Alkaline cements and concretes”, Kiew (1994)
- [3] Proc. 2nd Intern. Conf. “Alkaline cements and concretes”, Kiew (1999)
- [4] Proc. 1st European Conf. of Soft Mineralurgy “Geopolymer ‘88”, Compiègne (1988)
- [5] Proc. 2nd Intern. Conf. “Geopolymere ‘99”, St. Quentin (1999)
- [6] Proc. World Congress “Geopolymer 2005” St. Quentin (2005)
- [7] Proc. GGC2005 Intern. Workshop on Geopolymers and Geopolymer Concrete, Perth (2005)



- [8] Reference from SciFinder Database (Chemical Abstracts), keyword “geopolymers”
- [9] Reference from Web of science database, keyword “geopolymers”
- [10] Diamond S.: The microstructure of cement paste in concrete. Proc. 8th Int. Congr. Chem. Cement, Rio de Janeiro, 1986, p. 122-147
- [11] Maso J.C.: The bond between aggregate and hydrated cement paste. Proc. 8th Int. Congr. Chem. Cement, Rio de Janeiro, 1986, p. 378-380
- [12] Project “*Mechanical and Engineering Properties of Geopolymer Materials Based on Alkali-Activated Ashes*” ICT Prague, Czech TU Prague, unpublished results (2006)

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