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Concrete based on fly ash geopolymers

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.

Experimental Part

Fly ashes from Czech power plants were used for investigation. Their specific surface area ranged from 210 to 300 m^2/kg (Blaine). The chemical composition of the fly ashes is given in the following table.

Wt %	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5
Fly ash	53.7	32.9	5.5	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 ± 5 % (relative). The concrete was prepared by mixing fine-grained and coarse-grained crushed quarry aggregate with the grainsize ranging from 0 to 16 mm, fly ash and other ingredients with the solution of an alkaline activating agent (see Fig. 1).

The SiO_2-to-Na_2O 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 % Na_2O (expressed as percentage of the fly ash weight). The experiments were carried out by using concretes characterized by the water coefficient (the H_2O-to-fly ash ratio) w = 0.30 … 0.40 as well as 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.
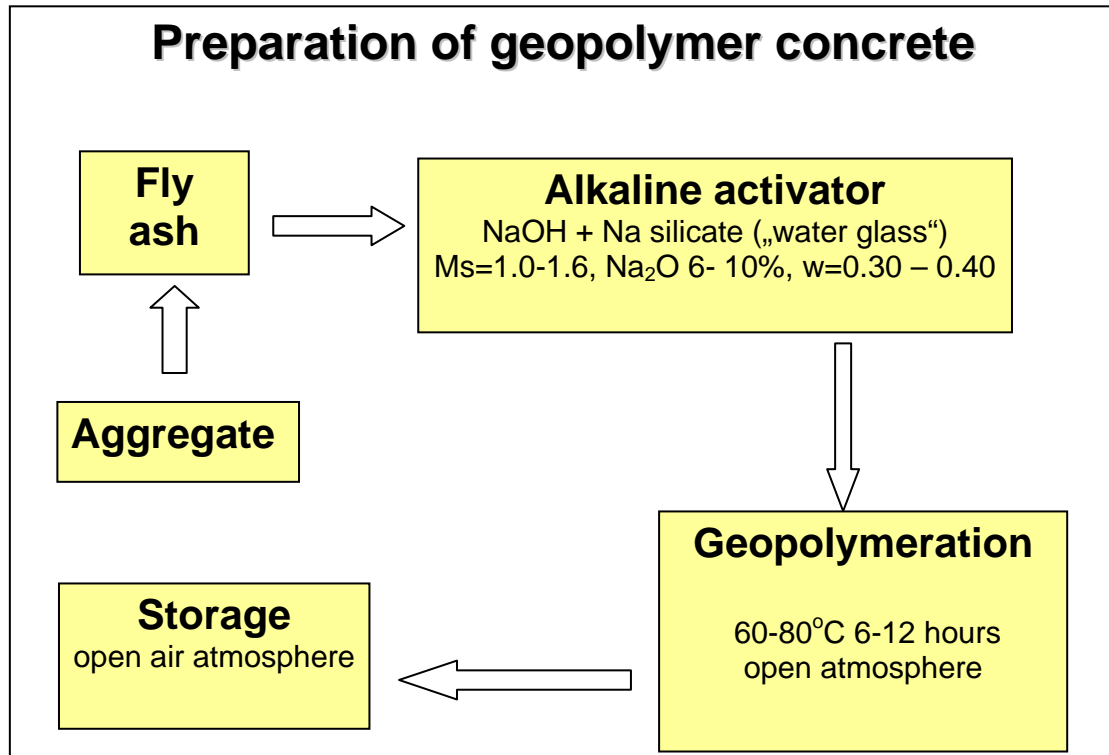

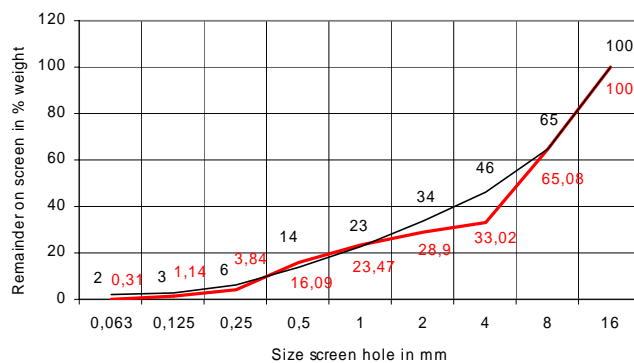Fig. 1 Procedure used for the preparation of geopolymers materials

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

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.

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

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 ^{o}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 ^{o}C were prepared recently (unpublished data [20]).

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.

Results and discussion

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, eg 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 (Fig. 10).

Results and discussion

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.
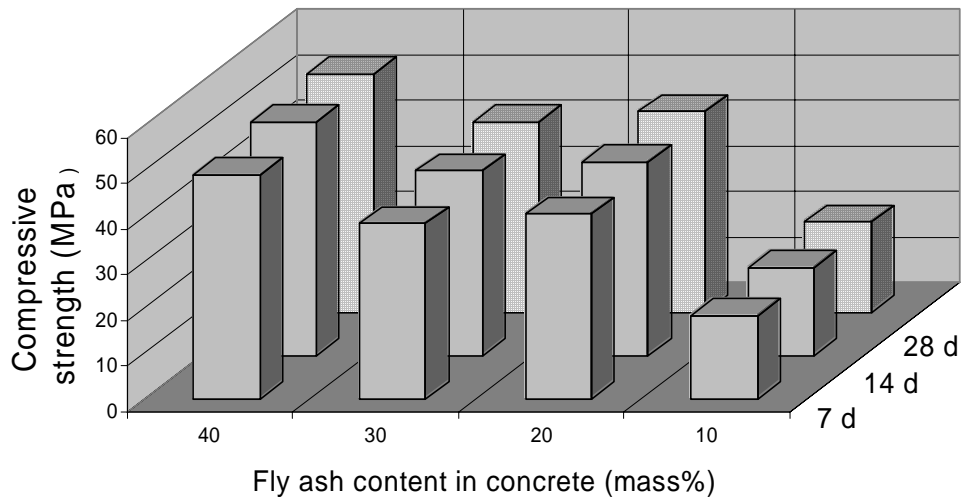

Fig. 5 Evolution of the geopolymers concrete strength in time (12 hours after the preparation at 80 ^{o}C)

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

1. No shrinkage due to hydration takes place in the geopolymers concrete as this phenomenon is typical for cement-based concretes. Therefore, the dimension imparted in the fresh state is preserved as a permanent value. This dimensional property may only be affected by an exceedingly large water coefficient.
2. 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.
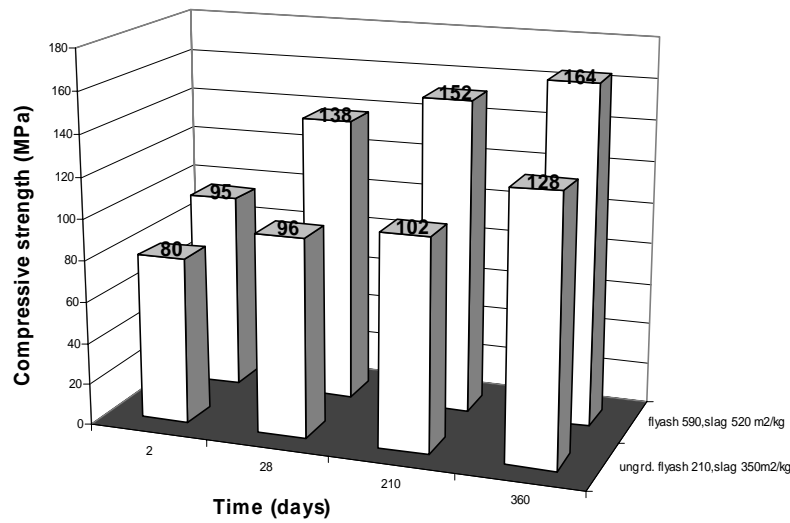
Fig. 6 Evolution of the geopolymers mortar strength in time (fly ash+ slag)

Chemical composition of the geopolymers

Differences due to various conditions of the alkaline activation may be found on the FTIR spectra. The band corresponding to Si-O and Al-O vibrations can be observed in the original fly ash at 1,080 … 1,090 cm^{-1} but this band is displaced towards lower values in the geopolymers. The shift is interpreted as a consequence of the Al penetration into the original structure of the Si-O-Si skeleton (an analogous phenomenon was observed in zeolites). The more pronounced the shift, the greater the extent of the Al penetration from the glassy parts of the fly ash into the $[SiO_4]^{4-}$ skeleton obviously is [10, 11] .

A chemical shift equal to −107.4 ppm attributed to the tetrahedral $[SiO_4]^{4-}$ coordination of $SiQ^4(0Al)$ and identified in ^{29}Si NMR MAS spectra of the original fly ash is regarded as the most important one[14, 15]; also the shifts equal to -95.8, 87.6 and 79.1 ppm corresponding to the $SiQ^4(2-3Al)$ coordination could be found. The latter shift

belongs probably to the mullite phase. The shifts equal to 64.3, 51.9 and 3.5 ppm corresponding to the $AlQ^4(4Si)$ and $AlQ^2(2Si)$ and $AlQ^3(3Si)$coordination were found in the ^{27}Al NMR spectra.
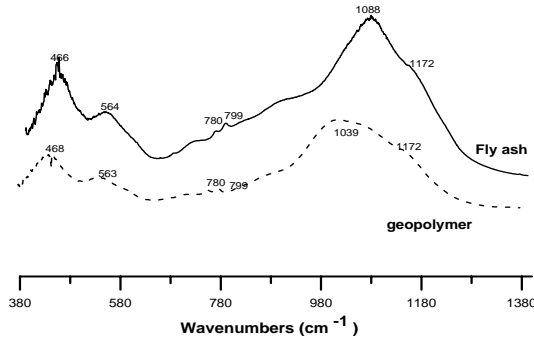

Fig. 7 IR spectra of the fly ash and the geopolymers

A different situation was detected in the geopolymers (pastes). The main shift – the $AlQ^4(4Si)$ coordination – equal to -89.5 ppm and also the shift equal to -97.6 ppm corresponding to the $SiQ^4(2\text{-}3Al)$ were found in the ^{29}Si NMR MAS spectra. The shift equal to -107.6 ppm corresponding to the $Si(0Al)$ coordination was less represented, which points to the Al penetration into the $[SiO_4]^{4-}$ skeleton. This interpretation of the NMR spectra is also shared by other workers[15, 16]. There was a dominant shift equal to -55 ppm in the ^{27}Al NMR MAS spectra as well as a very week shift equal to 3 ppm. The AlQ^4 (4Si) coordination corresponds to these shifts. This interpretation of the NMR spectra is also shared by other workers[14, 15]
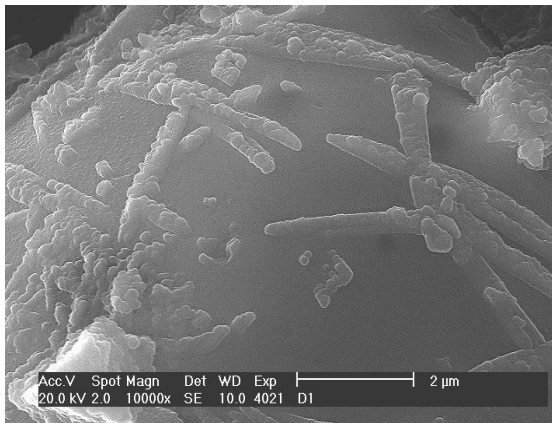

Fig. 8 The beginning of the geopolymers phase development on the surface of the fly ash particle

The geo-polymerization process (alkaline activation of fly ashes in the aqueous environment at pH>12) accompanied by the hardening of the material is different from the hydration processes of inorganic binders (eg Portland cement). This process obviously takes place predominantly "via solution" when, first, the fly ash particles are dissolved and a new geopolymers structure is then formed starting from the solution (Fig. 9).

In addition to the preparation conditions also the presence of Ca atoms entering the Si-O-Al-O skeleton and compensating the charge on Al atoms plays an important role. These charges are usually compensated by Na^+ ions. Nevertheless, Ca^{2+} ions may

probably interconnect individual Si-O-Al-O chains thus giving rise to a stronger structure characterized by higher strength values resulting from the alkaline activation of fly ashes in presence of Ca-containing materials. An important role played by Ca atoms in the geopolymers skeleton is also demonstrated by the results published in the papers [16, 17].
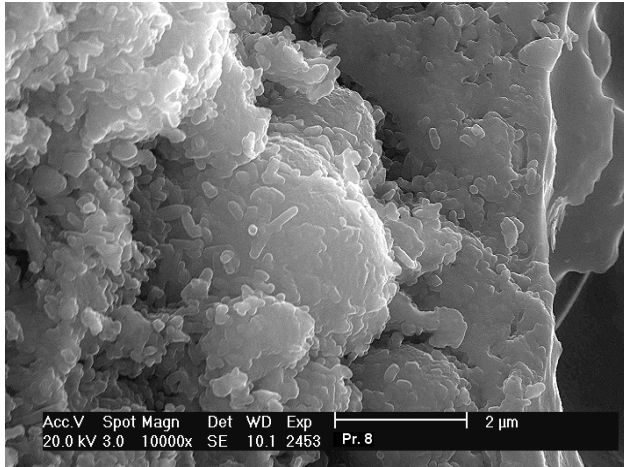

Fig. 9 Detailed character of the geopolymers (the paste w = 0.27, fracture surface, 28 days from the day of preparation)
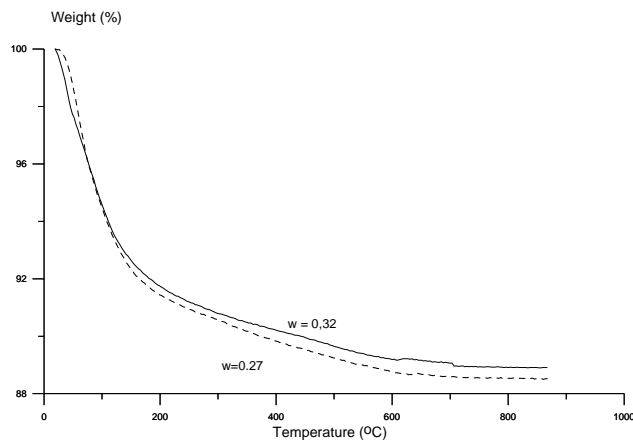

Fig. 10 Variation in the geopolymer mass in dependence on temperature (paste w = 0.27, respectively 0.32)

Water is present in the geopolymers structure as this is revealed by the GTA curves. Water obviously occurs in the form of "free water" but water molecules also exist inside the structure; furthermore, OH$^-$ groups are also present. A prevailing part of water gets lost during the heating at a temperature of 150 … 200 $^\circ$C. No crystalline hydrates could be detected in the geopolymers microstructure.

Therefore, the geopolymer can be characterized as a two- up to three-dimensional inorganic polymer with a summary formula $M_n[-(Si-O)_z -Al-O]_n$. wH_2O.

Porosity of the geopolymer

There are residues of the original fly ash particles present in the geopolymers body on the basis of fly ashes, and the effect of the gradual dissolution is evident on them (Fig.

3). Such geopolymers exhibited a rather high porosity (up to 50 %) regardless of the character of the conditions existing during their preparation. Closed spherical pores formed in result of the dissolution of original fly ash particles, respectively by the air entrained during the preparation are present. The preparation conditions, ie the Na_2O content, respectively the SiO_2–to-Na_2O ratio affect not only the achieved strength values but also the distribution of pore sizes. The porosity of the geopolymers is also influenced substantially by the value of the water coefficient (the H_2O-to-fly ash ratio), see Fig. 13.
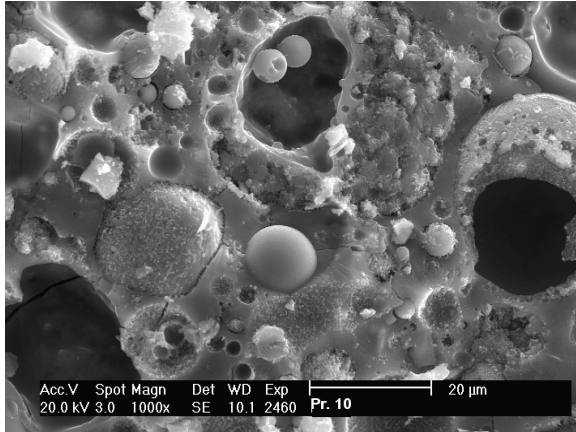

Fig. 11 Porous character of the geopolymer (the paste w = 0.27, fracture surface, 28 days from the day of its preparation)

The porosity of the geopolymers prepared on the basis of a mixture of fly ash with slag was substantially smaller (the overall porosity amounted to 2 … 10 %) and a shift towards smaller pore sizes could be observed (Fig. 6). The compressive strength of such materials amounted to as much as 100 … 160 MPa.
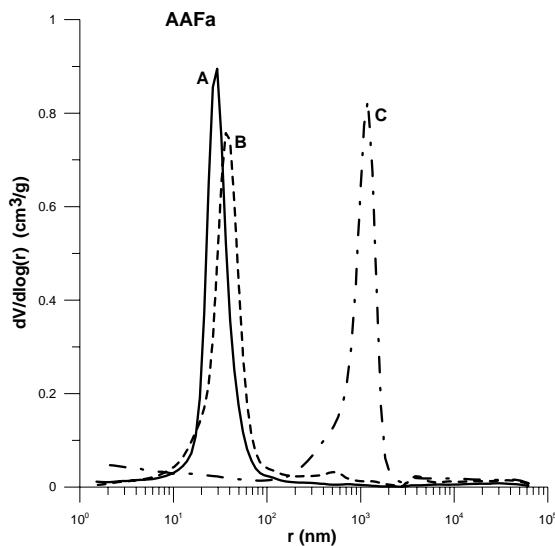

Fig. 12 Influence of the conditions of alkaline activation on the pore size distribution (Hg porosimetry) in a geopolymer, paste w = 0.27 (A … 60 MPa, (9 % Na_2O, B … 40 MPa, 8 % Na_2O, C … 18 MPa, 5 % Na_2O)
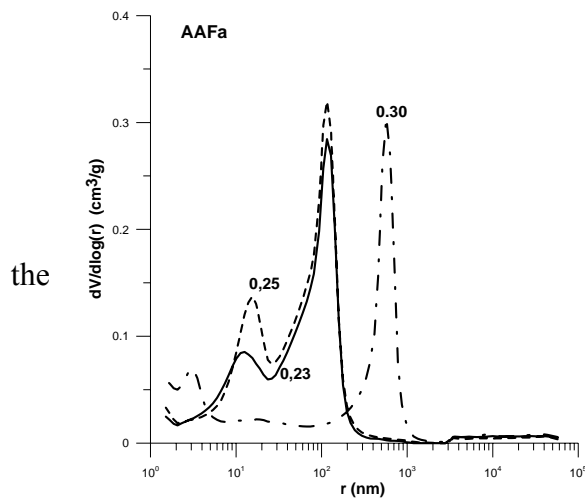
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Fig. 13 Effect of the water coefficient on distribution of pore sizes (Hg porosimetry) in a geopolymer (the paste with a water coefficient ranging from 0.23 to 0.30)
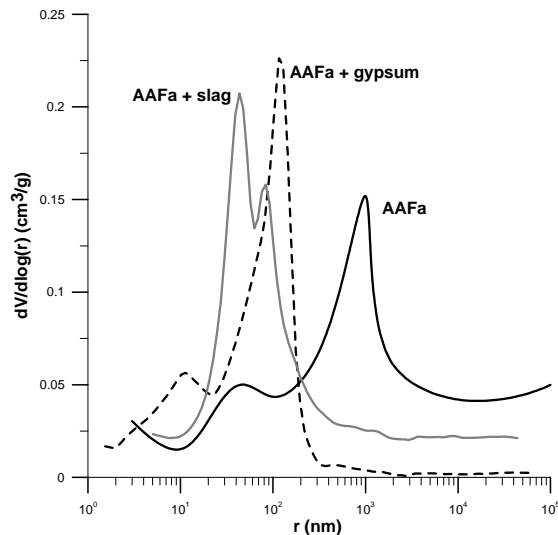

Fig. 14 Influence of the addition of Ca-containing materials on the pore size distribution (Hg porosimetry) in a geopolymer, paste w = 0.27

The addition of Ca-containing materials not only increases the strength but it also reduces the porosity.
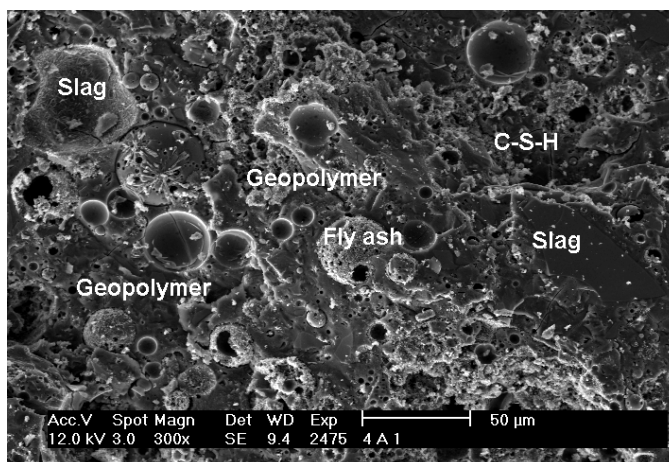

Fig. 15 Co-existence of the geopolymer phase with the C-S-H one in a geopolymers (paste, 60 % of fly ash and 40 % of milled slag), compressive strength after 28 days equal to 120 MPa, fracture surface

However, the high-pressure mercury porosimetry yields only limited information on the character of pores in the nanometric region. More data can be obtained by measuring BET isothermal lines; for instance, Fig.16 shows the distribution of pore sizes in geopolymers prepared under various conditions. It is evident from these results that the geopolymers exhibit – in the nanometric region - a rather similar character that is not particularly dependent on the conditions existing during their preparation. Only the character of the geopolymers samples prepared by using also the slag in addition to the fly ash was different. The porosity of such materials dropped in result of the co-existence of the geopolymers phase with the C-S-H one.
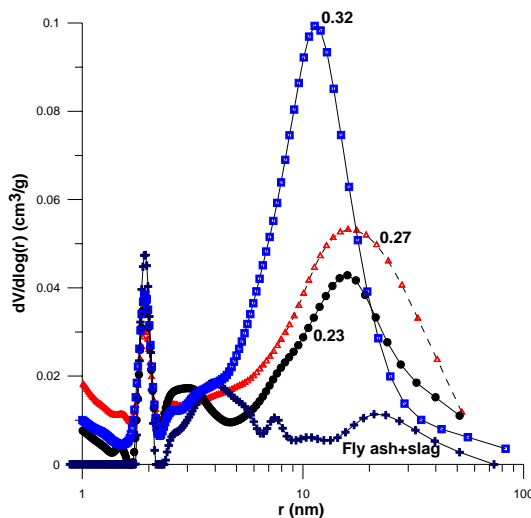

Fig. 16 Pore size distribution (BET) in the geopolymers in dependence on the water coefficient ranging from 0.23 to 0.30 (paste), fly ash + slag, geopolymer prepared on the basis of 60 % of fly ash and 40 % of ground slag

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 $Ca(OH)_2$ and ettringite are higher. There are often $Ca(OH)_2$ 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 [18, 19].

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. 17, 18) in contrast to the concrete made of Portland cement (Fig. 19).
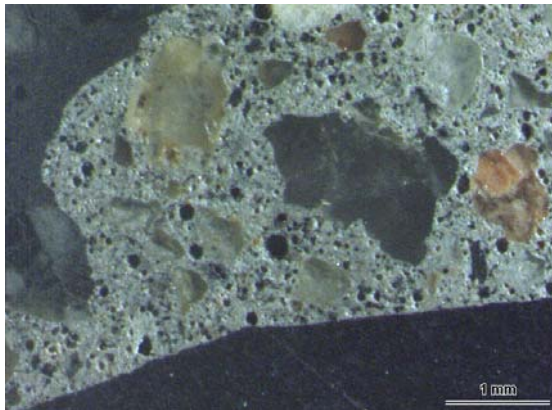
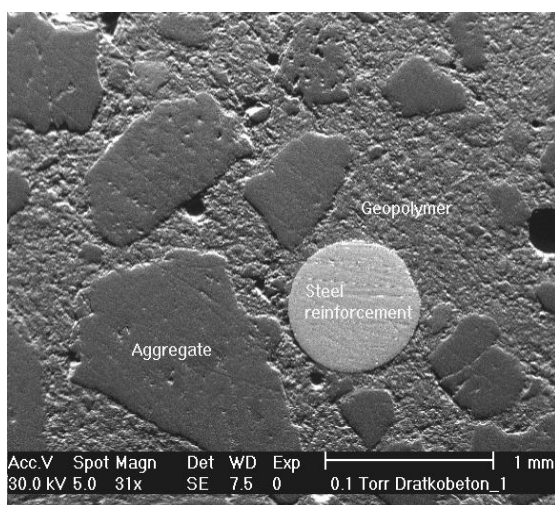Fig. 17 Geopolymer concrete (polished section, optical microscope)

Fig. 18 Boundary between the aggregate (reinforcement) and the geopolymer in the concrete (polished section, BSE representation)
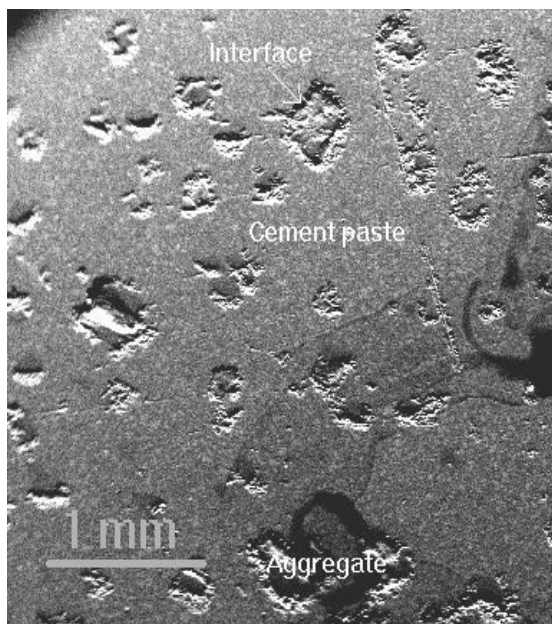

Fig. 19 Boundary between the aggregate and the Portland cement paste in the concrete (polished section, BSE representation)

The Na_2O–to-SiO_2 and Al_2O_3–to-SiO_2 ratios (point analyses) are shown in Fig. 20 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.
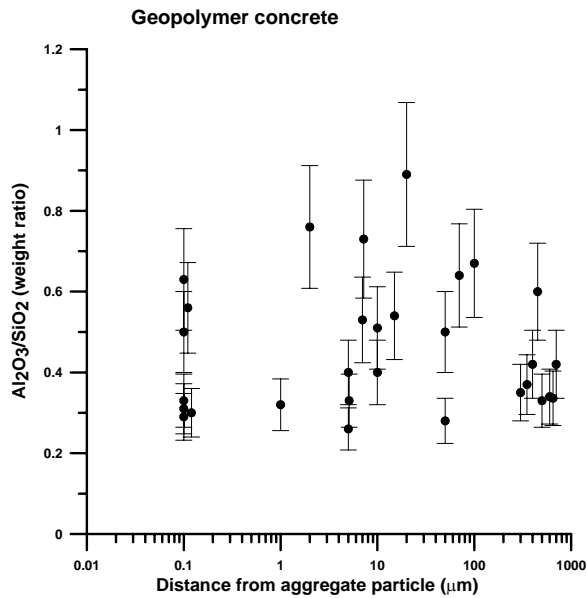

Fig. 20 Dependence of the Al_2O_3–to-SiO_2 ratio on the distance from the aggregate grain in a geopolymer concrete

The character of the boundary between the steel micro-reinforcement and the geopolymers is quite analogous (see Fig. 21 through 23).
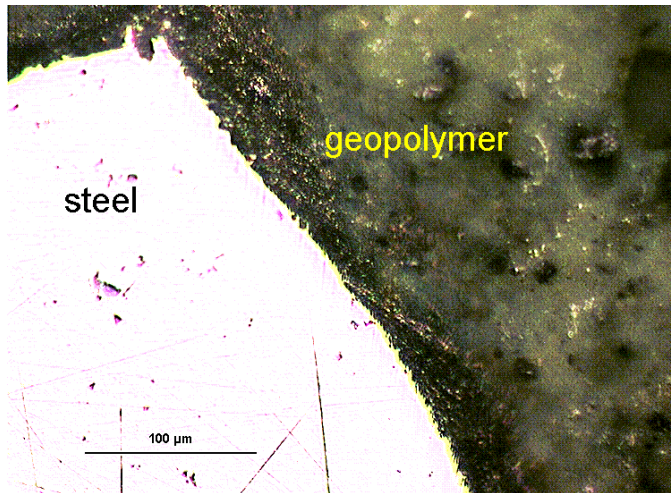

Fig. 21 Character of the boundary between the steel micro-reinforcement and the polymer (polished section, optical microscope)
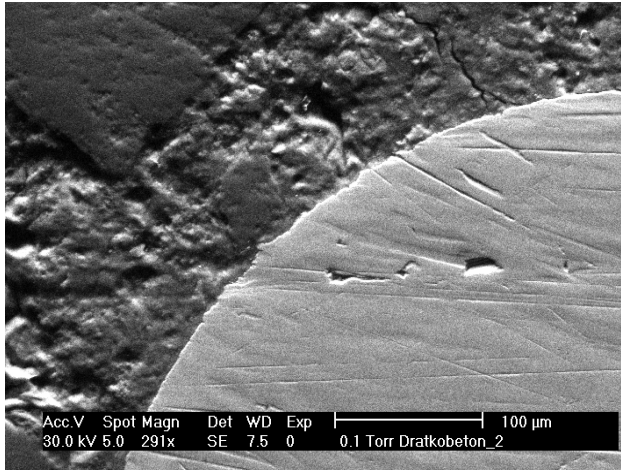
Fig. 22 Character of the boundary between the steel micro-reinforcement and the polymer (polished section, SEM)
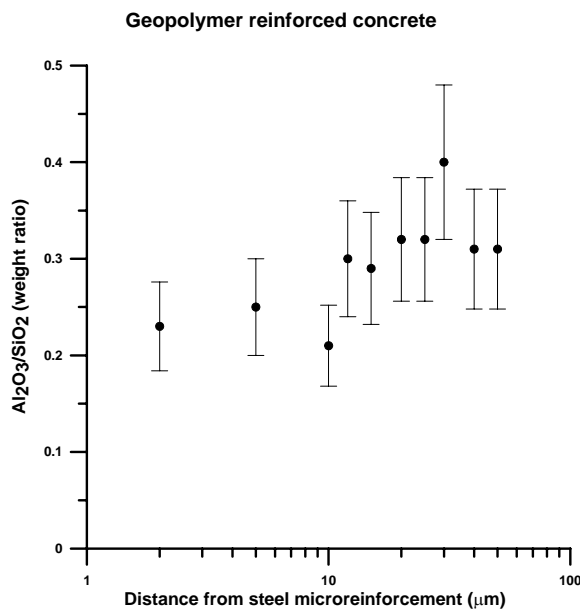

Fig. 23 Dependence of the Al_2O_3–to–SiO_2 ratio on the distance from the steel reinforcement in a geopolymer concrete

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.

Fig. 24 A geopolymer mortar after 150 freezing cycles

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.

Fig. 25 A geopolymers mortar after the 1.5-year exposure to the solutions of NaCl and $MgSO_4$ salts

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_4 $AClH_{11}$) 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 ^{o}C.

Fig. 26 Character of the geopolymers concrete after firing

Fig. 27 Deformation character of the geopolymers mortars during the firing

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 ^{o}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 ^{o}C; they were due to the presence of the melt that 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 ^{o}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. 28 through 31).

Fig. 28 Bone-shaped paving brick

Fig. 29 Paving brick with roughed surface

Fig. 30 Paving brick with ornamental surface

Conclusions

1. The structure of the geopolymers prepared on the basis of fly ashes is predominantly of the $AlQ^4(4Si)$ type and $SiQ^4(4Al)$, $SiQ^4(2\text{-}3Al)$.
2. The geopolymer on the basis of fly ashes is a porous material. The porosity of the geopolymers is very similar in the region of nano-pores regardless of the conditions of their preparation. The geopolymers' strength is affected substantially by macro-pores (10^3 nm and more) formed in result of the air entrained into the geopolymers; these may also be fly ash particles that underwent only partial reaction. The presence of Ca-containing additives (slag, gypsum) reduces considerably the porosity because of the co-existence of the geopolymer phase with the C-S-H one.
3. 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.
4. Rheological properties of concretes differ from those of Portland cement.
5. The geopolymer concrete is resistant to the corrosive environments.
6. 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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