

Geopolymer materials based on fly ash

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Introduction

Alkaline slag cements ^{1, 2}, gypsum-free cement activated by alkalis ^{3,4,5}, Parament-type cements ⁶ or geopolymer binders ⁷ represent new types of inorganic binders which have a common basis, ie the alkali activation of the clinker, respectively that of latently hydraulic bodies (eg slag or fly ash). The action of solutions of alkaline compounds (eg NaOH, Na₂CO₃ or Na₂SiO₃) on hydraulically active bodies results in the disintegration of bonds of the Si-O-Si type and in the subsequent formation – in addition to hydrates of the type C-S-H phase, gehlenite hydrate and hydrogarnets - of hydrates of alkaline calcium aluminosilicates similar to zeolites. In the future, the binders activated by alkalis may offer the possibility to process inorganic wastes because the properties of the bodies on the basis of binders activated by alkalis are often better than those of the materials prepared on the basis of current Portland cements. The presence of the substances of the zeolite type brings about a change in the properties of these binders activated by alkalis ^{10,11,12,13}; for instance, their resistance to acids or the ability to immobilize heavy metals is improved.

Large quantities of power plant fly ash have to be dealt with in the Czech Republic every year (more than 10 million tons a year). The fly ash is added to cements and concretes in this country but, nevertheless, important amounts have to be disposed off in disposal sites (eg in conjunction with rejected gypsum).

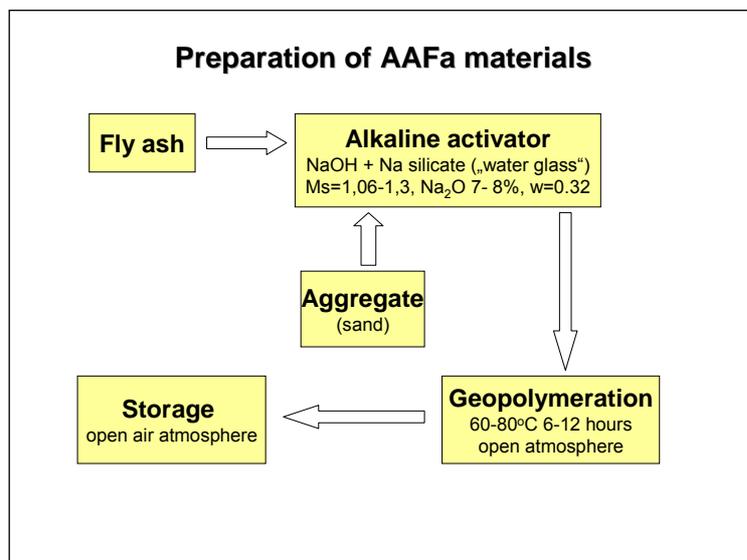
The present paper deals with the properties of new materials ¹⁴ based on the fly ash that has been activated by alkalis.

Experimental Part

The experiments were carried out with a fly ash (Czech Republic) having the specific surface area of 210 m²/kg (Blaine). Its chemical composition is given below.

% by weight	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 binder was prepared by blending the fly ash and other admixtures with a solution of the alkaline activating agent. The SiO₂-to-Na₂O ratio (Ms modulus) in the alkaline activating agent was adjusted by NaOH addition to the soluble glass with a modulus Ms = 1.68 so that the value of the Ms modulus ranging from 1.0 to 1.6 might be achieved. The composition of the soluble glass used for experiments was as follows: 25.9 % SiO₂, 15.5 % Na₂O and 58.6 % H₂O. The overall concentration of the alkaline activating agent ranged from 4 to 10 % Na₂O of the binder mass. The experiments were carried out with slurries and mortars exhibiting mostly the w-to-s ratio ranging from 0.27 to 0.35. Portland slag cement CEM II 42.5, gypsum rejected from desulfurization processes (containing over 95 percent of CaSO₄·2H₂O), ground limestone and dolomitic limestone with the specific surface area of 400 m²/kg were used as admixtures. The mortars were prepared by using silica sand (grain size ranging from zero to 2 mm), respectively crushed limestone (grain size zero to 4 mm) was used.



Small bodies having the dimensions of 20 x 20 x 20 mm were prepared from slurries whereas larger samples with the dimensions of 40 x 40 x 160 mm were made from mortars. The bodies prepared in such a way and ready for testing were subjected to a "dry" thermal process that consisted in placing them in a drier (free atmosphere) at a temperature of 60 to 90 °C

for 4 to 48 hours. Then, the samples were kept in the open air with the relative humidity ranging from 40 to 50 percent till the moment of the strength test. The values of the compressive strength were determined after 2, 7 and 28 days, respectively after 90, 360 and 720 days. The fragments remaining after the strength tests were investigated with the aid of the RTG diffraction analysis, thermal analysis and the high-pressure mercury porosimetry. The FTIR and NMR MAS spectra (²⁹Si, ²⁷Al) were measured too. The microstructure of fraction surfaces originated during the destruction of the samples subjected to strength testing was studied with the aid of a scanning electron microscope and selected spots were subjected to the analysis by ED spectrometer.

A part of the samples prepared from mortar mixes and removed from the mold was kept for 28 days at the laboratory temperature (the relative humidity of the ambient air was 40 %); then, they were placed into solutions of Na₂SO₄, MgSO₄ and NaCl. The concentrations of

these solutions were in agreement with the regulations given in the respective standard (CSN EN 206-1) valid for concrete testing:

- Na_2SO_4 having the concentration of 44 g/dm³,
- MgSO_4 having the concentration of 5 g/dm³,
- NaCl having the concentration of 164 g/dm³.

The solutions were replaced once a month and, on this occasion, the samples were weighed to find out a possible variation in their mass. Mechanical properties of the samples were determined after given periods of time (300, 540 and 720 days). The composition of the layer below the sample surface was investigated with the aid of SEM and ED analyses so that the penetration of sulfates and chlorides into the material might be assessed. The ion penetration into the geopolymer body was investigated by using fragments remaining after the testing of mechanical properties of samples; a localized point analysis was applied to this purpose and the ion concentration was determined in dependence on the distance from the sample surface.

Another part of samples was exposed to the action of temperature in the range from 100 to 1,100 °C; the temperature was increased at a rate of 5 °C/minute and the soak at the maximum temperature lasted for 2 hours. The heat-treated samples were left to cool down till the next day when the tests aimed at determining the compressive strength of samples were carried out at the room temperature.

The refractoriness under load was also determined according to the Czech standard CSN 993-8. This test was carried out with a hollow cylinder having the dimensions of 5 x 5 cm. There was a circular hole with a diameter of 12 mm in the center of the cylindrical sample. The temperature increased at a rate of 5 °C/minute and the loading applied on the sample amounted to 0.2 MPa.

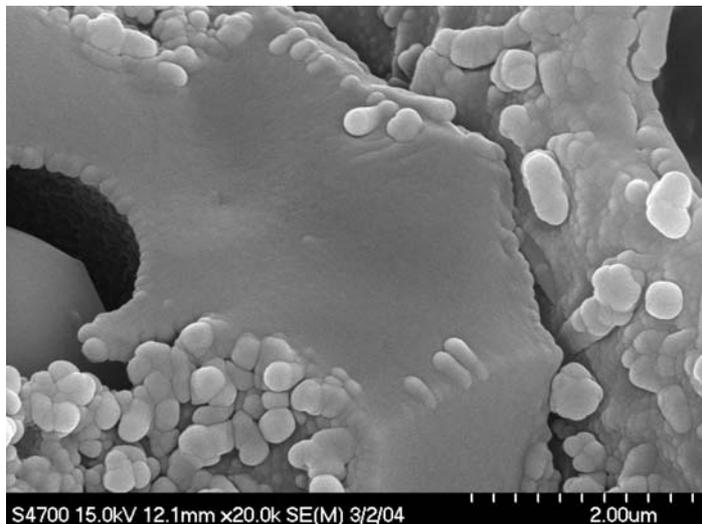
Furthermore, the geopolymer samples were also subjected to alternating freezing and defrosting cycles according to the Czech standard CSN 72 2452. The samples with the dimensions of 4 x 4 x 16 cm were kept for 28 days at a laboratory temperature in the ambient air with the relative humidity of 40 percent. Their frost resistance was then determined.

Results and Their Discussion

We can say in general that the properties of fly ashes activated by alkalis (AAFa) as the setting point, the rheological properties and the strength values are influenced by the water coefficient, the M_s modulus and the Na_2O concentration in the alkaline activating agent. The beginning of the body setting and the setting period (AAFa) are difficult to determine because these mixes often lose slowly their consistency. In some cases, the setting point may be rather delayed in time (by up to 3 days) but, on the other hand, it may

be extremely short (a few minutes). The strength values are affected substantially by the temperature and the duration of the alkaline activation (“geopolymerization”) when the maximum values of strength could be achieved after 6-12 hours at a temperature of 60-80 °C. Local peaks and local minima could be observed on the curve characterizing the dependence of the strength on the heating time. Maximum strength values were also obtained after a long-term heating lasting for about 42 hours; substantially smaller values of strength were observed after the heating lasting 18-24 hours. Optimum values of strength were obtained if the Na₂O concentration ranged from 7 to 10 % and the Ms value varied from 1.0 to 1.4 (Fig. 2). The values of the AAFa strength after 24 hours are superior to those typical for standard Portland cements after 28 days of hydration, and they were increasing even further in the time horizon of 90 to 720 days.

An important influence on the strength of AA fly ashes is exerted by the present of Ca-containing materials, eg cement, limestone, dolomitic limestone and gypsum ¹⁵. Such

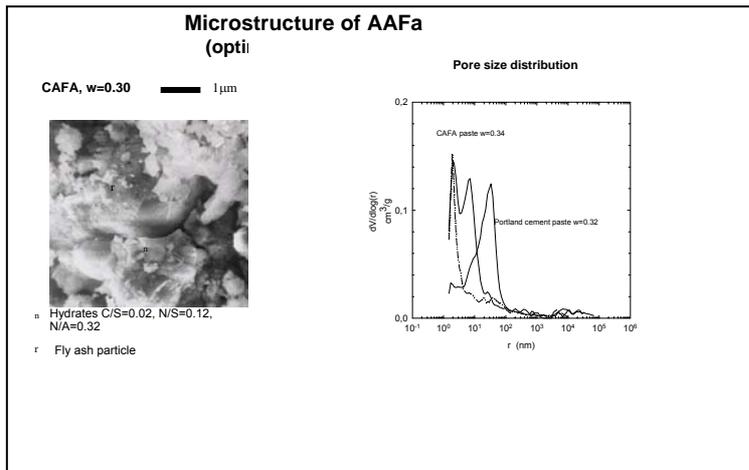
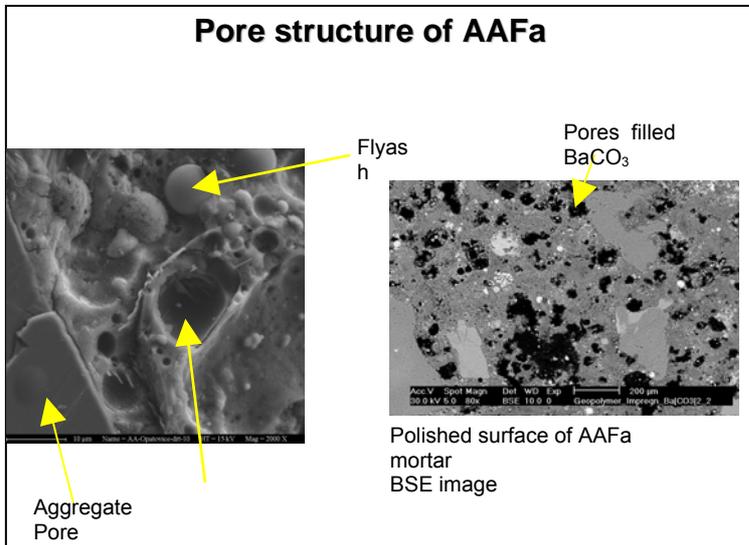
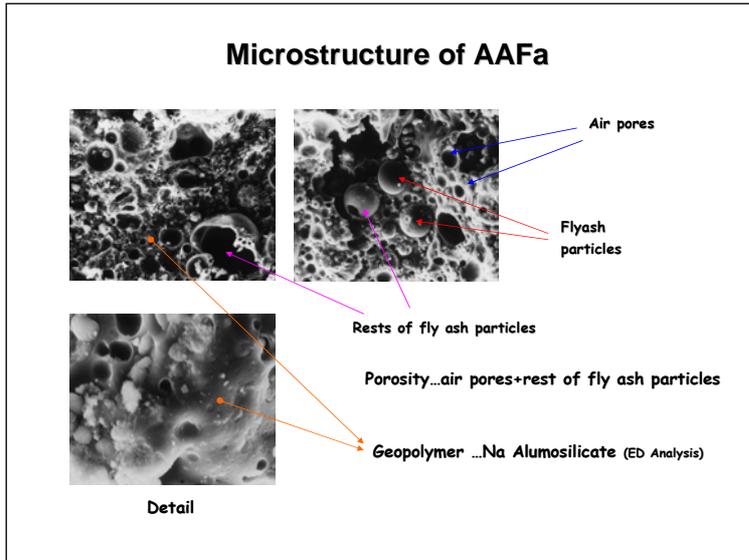


admixtures exert an unambiguously favorable effect on the strength development in time. The mixes in which crushed limestone was used as aggregate instead of silica sand were characterized by substantially higher values of strength as compared to the mixes to which traditional “standard” sand was added. Also the use of a “real” construction sand was accompanied

by higher values of strength as compared to the values achieved with silica sand.

The AAFa geopolymerization (setting and hardening) represents a complex process that has not been described completely yet. The geopolymerization is an exothermic process even when the setting takes places at higher temperatures.

The character of the products obtained by the alkaline activation of fly ashes is predominantly amorphous and residues of the original material (mullite, quartz) may be identified in these products. Also the data obtained by thermal analysis point to the occurrence of hydrated amorphous (gel-like) products and the H₂O content decreases continuously in dependence on temperature. This behavior could be observed even in samples analyzed after 360-720 days elapsed from their preparation. The main body of hydrates (regardless of the hydration conditions) has an explicitly amorphous glassy character – acicular minority aggregates occur only sporadically. The data obtained by means of ED spectrometer analyses on fracture surfaces after sample destruction



demonstrated that the main part of hydrate was formed by Na-alumosilicate hydrates. Only a minor part of hydrates was formed by probably polymerized soluble glass and a partial substitution of Si for Al took place here. There are residues of original fly ash particles present in the hydrate body. The effect of a gradual dissolution on these particles is evident. We can see closed spherical pores remaining after the original fly ash particles or caused by air entrapped during the sample preparation.

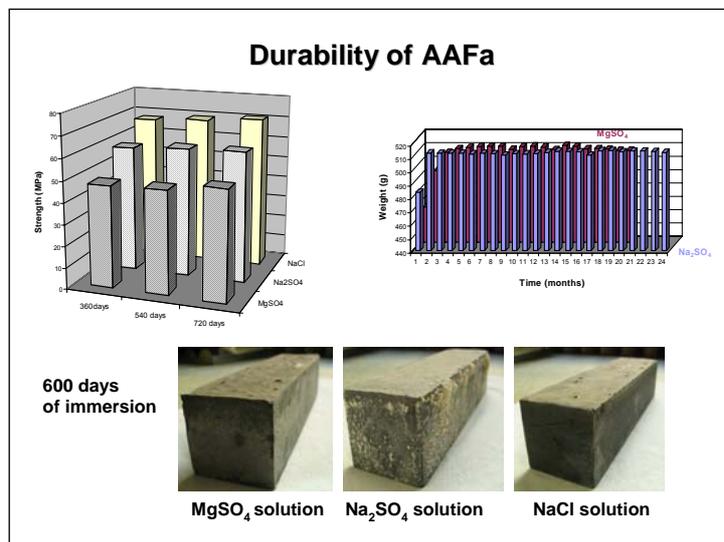
The optimal composition of initial mixture of sourced components results in the AAFa materials with compressive strength of 100 up to 150 MPa.

The alkaline activation of fly ashes in aqueous environment at $\text{pH} > 12$ at which the setting of the material occurs is different from the processes of inorganic binder hydration, eg Portland cement. This process obviously takes place predominantly by a mechanism called “via solution” when, first, the particles of fly ash are dissolved in a strong alkaline environment and the dissolution process is then followed by the formation of a new geopolymer structure. A 2D-3D inorganic hydrated polymer (geopolymer) having a general formula of $M_n[-(\text{Si}-\text{O})_z - \text{Al}-\text{O}]_n \cdot w\text{H}_2\text{O}$ is formed.

A higher temperature of 40-95 °C is necessary for the formation of a sufficiently interconnected network of bonds within the geopolymer (on the basis of fly ashes). In addition to the conditions of preparation, also the presence of Ca ions plays an important role. The Ca ions enter the Si-O-Al-O structure where they compensate the charge on Al atoms. These charges are usually compensated by Na^+ ions. It is quite probable, however, that Ca^{2+} ions may interconnect the individual Si-O-Al-O chains thus giving rise to a stronger structure characterized by higher strength values achieved thanks to the alkaline activation of fly ashes in presence of Ca-containing materials. Also the data published in the papers^{22, 23} corroborate the important role played by the Ca atoms in the geopolymer skeleton.

AAFa Durability

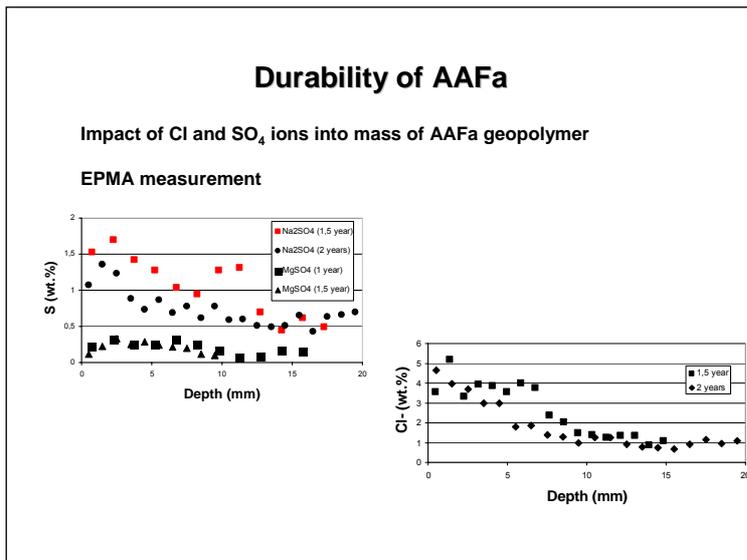
The materials prepared on the AAFa basis kept in the solutions of (Na, Mg) sulfates for long periods of time are resistant to the corrosion. No signs of sample deterioration were



observed. In contrast to Portland cement, no visible damage of samples occurred even if they were kept in corrosive solutions continuously for 720 days.

The values of compressive strength of AAFa geopolymer materials exposed to the action of sulfate solutions increased over the whole period of measurement (720 days). The same behavior was also observed for materials kept at the

laboratory temperature out of the corrosive environment. The mass of samples kept in sulfate solutions changed by 2 rel. % at the maximum. The dimensions of the samples did not vary over the whole testing period and no signs of any expansion as those accompanying the exposure of materials based on Portland cement to the action of sulfate could be observed.

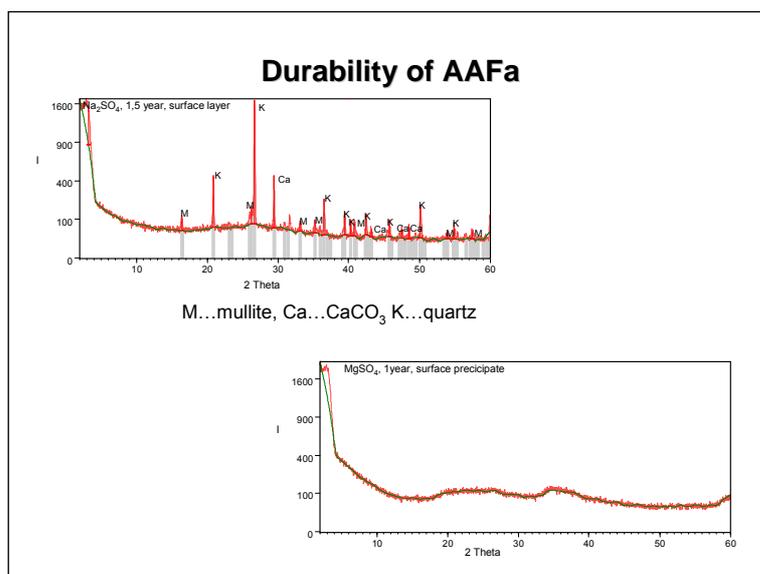


The penetration of sulfate ions into the AAFa body (measured perpendicularly from the surface in contact with the sulfate solution) showed a decreasing tendency; the sulfate concentration in the body was very low. The concentration of sulfate ions during the exposure of the material to the corrosion by MgSO₄ solution was smaller than during its exposure to Na₂SO₄,

which is in relation to the selected concentration of corrosive solutions. A white reaction product having an amorphous character could only be found when the sample was exposed to the corrosion by MgSO₄ solution. The product in question is probably magnesium aluminosilicate.

The basic difference in the corrosion of AAFa geopolymer materials and those on the basis of Portland cement by sulfate solutions is obvious from the data obtained.

The AAFa materials kept in the environment of NaCl solution for long periods of time are resistant to the corrosion and do not exhibit any sign of deterioration. The values of compressive strength of AAFa geopolymer materials exposed to the NaCl solution increased over the whole period of measurement (720 days) and achieved as much as 70 MPa. The mass of samples kept in the NaCl solution increased during the 1st year (by about 3 rel. %)



and remained stable afterwards. The penetration of chloride ions into the AAFa body (measured perpendicularly in the direction from the surface in contact with the chloride solution) showed a decreasing tendency and the chloride concentration in the body was low. The penetration of chloride ions was greater than

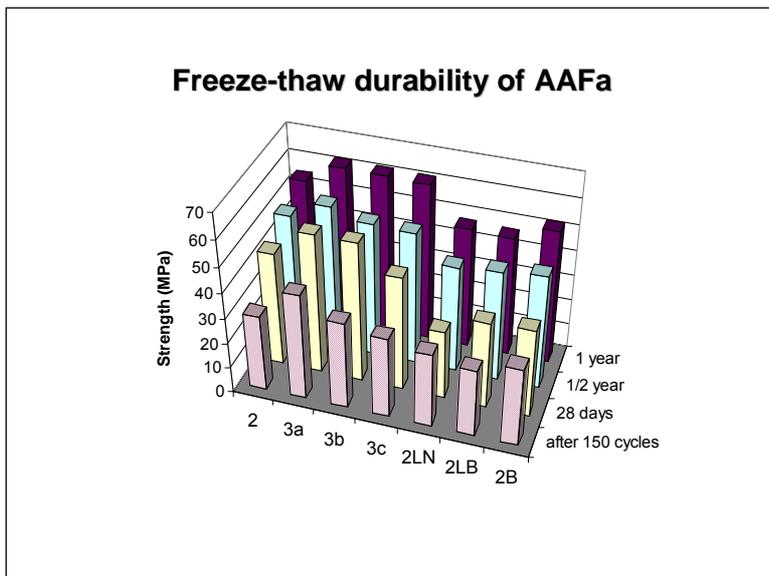
that of sulfates; this fact is probably due to the smaller size of chloride ions. Practically no

corrosion products were observed on the surface of AAFa geopolymer materials kept in the NaCl solution.

No new crystalline phases formed when the AAFa materials were kept in sulfate and NaCl solutions. The RTG diffraction analysis only confirmed the occurrence of original crystalline phases of fly ash. The absence of expansion products as the ettringite ($C_6A\bar{S}_3H_{32}$) or the Friedel salt (C_4ACIH_{11}) in samples kept in salt solutions for 2 years is an important finding.

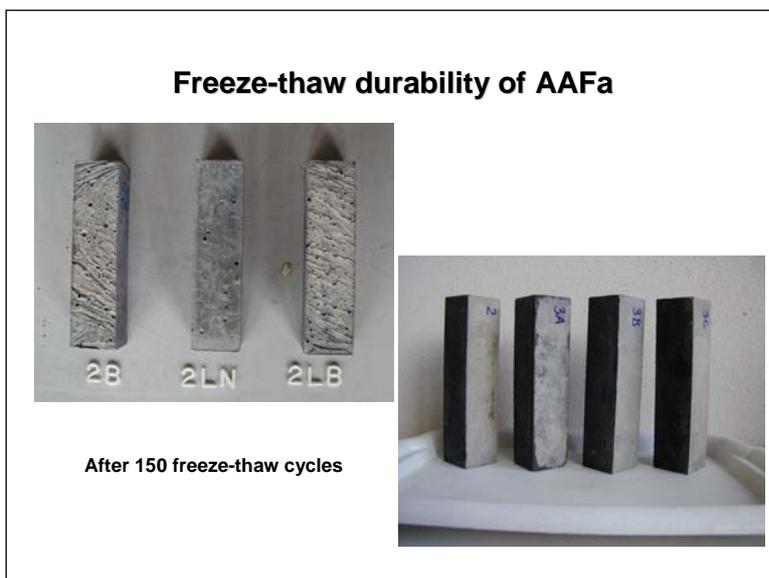
The resistance of AAFa materials to salt solutions is very good as compared with that of the cement-based concrete in which crystalline ettringite or the Friedel salt is formed thus giving rise to the body disintegration in result of the crystallization force.

The frost resistance of AAFa geopolymer materials was investigated by using 150



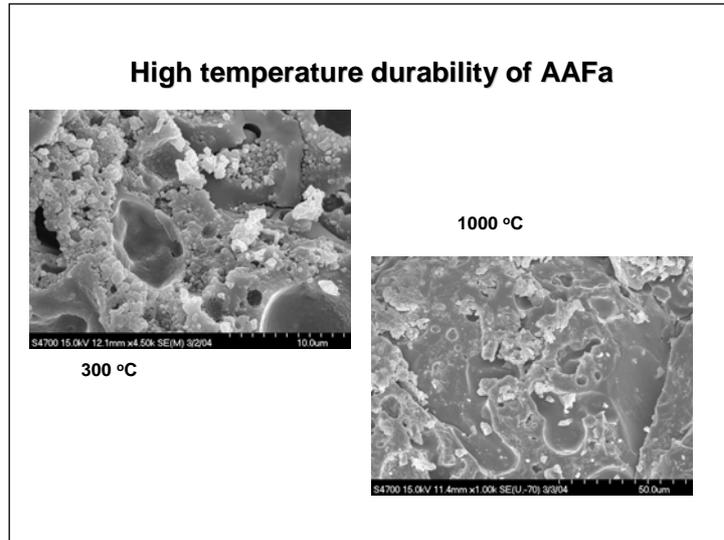
freezing and defrosting cycles in aqueous environment. The mass of the samples did not change (no body disintegration occurred) during the freezing and defrosting cycles in aqueous environment. The values of the compressive strength of samples were smaller after defrosting cycles as compared with the values obtained for the samples after 28 days without any frost resistance

testing. No damage or deformation could be detected after 150 cycles. The strength of the samples after 150 freezing cycles dropped to about 70 percent of that determined after the same period of time.



It is evident from the results obtained that the investigated geopolymer AAFa materials possess an excellent frost resistance.

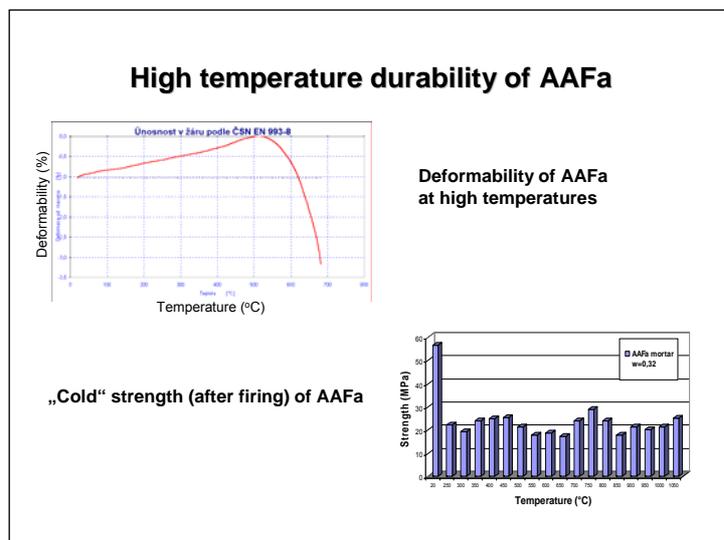
The influence of high temperatures on the properties of AAFa materials was investigated in the temperature range of 250 to 1100 °C. The geopolymer AAFa material exposed to the effect of high temperatures loses a substantial part of its strength which



dropped to 40 percent of its original value. The loss of compressive strength becomes already obvious at a temperature of 250 °C and the firing at higher temperatures does not practically affect this parameter. The minimal values of the residual compressive strength were observed in the temperature range of 600 to 700 °C; they were caused by the occurrence of the melt that

began to form. The values of compressive strength (measured on cold samples after their firing) of AAFa materials subjected to the effect of higher temperatures showed a growing tendency; however, this behavior is due to the solidifying melt. Nevertheless, the residual strength of AAFa bodies after their heat treatment is relatively higher than that of the materials on the basis of Portland cement .

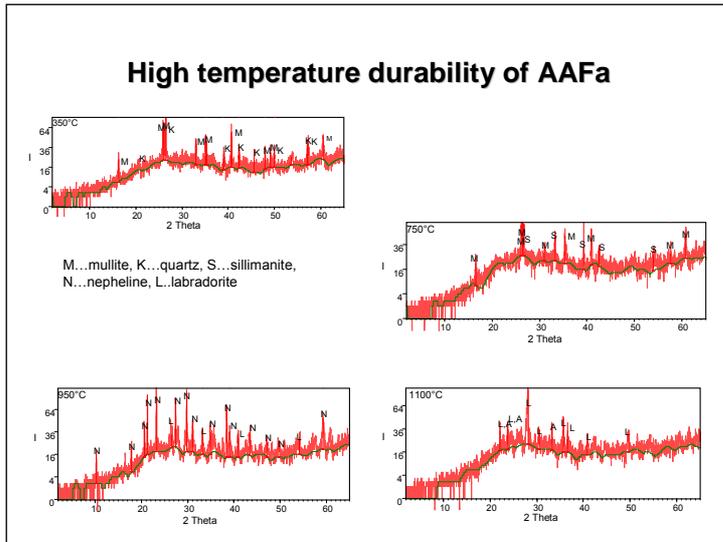
The tests of the refractoriness under load of AAFa materials permitted to determine the



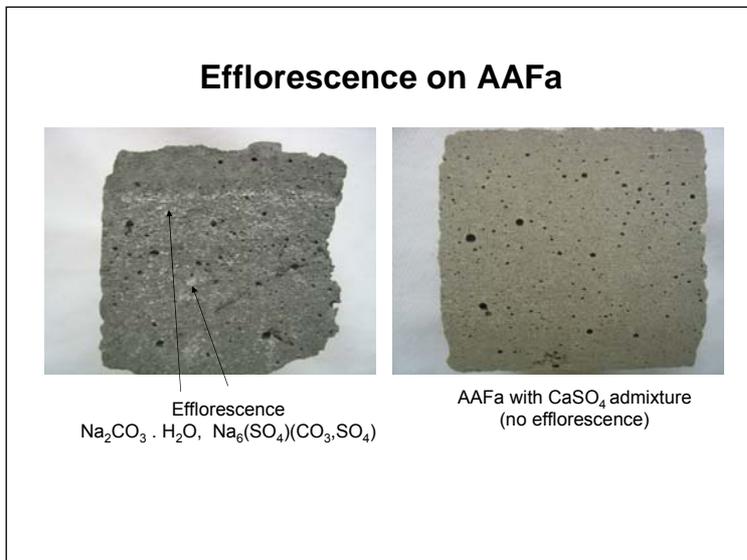
temperature range in which the AAFa body starts softening and the sample dimension subjected to the load force begins to decrease. The $T_{0.5}$ value was obtained for temperatures ranging from 576 to 589 °C. Therefore, AAFa bodies can not be characterized as purely refractory material.

The occurrence of the melt in AAFa bodies under the action of

temperature superior to 600 °C was also corroborated by micrographs. The RTG diffraction analysis of fired samples demonstrated the formation of new crystalline phases (probably albite, sillimanite, nepheline, labradorite). The amount of crystalline phases dropped at temperatures above



1100 °C because of the melt dissolution and the sample expansion. No significant changes in the composition of the samples subjected to the effect of temperatures in the range from 250 to 1100 °C could be observed on IR spectra.



Efflorescences often occurred on the surface of AAFa samples. However, no efflorescences could be seen on fired samples kept (after firing) at the laboratory temperature for 720 days. The efflorescences did not occur on samples treated in this way before their exposure to the aqueous environment. A white coating on the surface of AAFa

bodies could be observed after their subsequent drying.

Conclusions

There is no doubt that the investigated materials on the basis of alkali-activated latently hydraulically active substances (fly ash, slag) belong among bodies that – because of their high values of strength and predominantly amorphous character – represent a transition between the traditional inorganic binders and the ceramics; they can be included into the group called “chemically bonded ceramics”. These materials on the basis of AA fly ashes can be characterized as inorganic polymers similar to zeolite precursors. The character of AA fly ashes is similar to that of geopolymers formed by the alkaline activation of kaolinitic materials^{5, 6, 7}. They can also be described as low-temperature hydrated aluminosilicate glasses²⁴.

The products resulting from the alkaline activation of fly ashes exhibit an amorphous character with minority crystalline phases. The FTIR spectra reveal the differences between the non-hydrated fly ash the alkali-activated one when the main band corresponding to Si-O and Al-O vibrations is displaced towards lower values. In the ^{29}Si MAS NMR spectrum, these products exhibit a three-dimensional glassy structure with prevailing Q4(2Al) arrangement. The Al atoms penetrate into the original silicate structure of the fly ash during its alkaline activation and a new phase is formed.

The materials on the basis of alkali-activated fly ashes possess an excellent durability in the corrosive environment of salt solutions, they exhibit very good frost resistance and can resist the effect of temperatures of up to about 600 °C. There is a fundamental difference between the corrosion of geopolymer AAFa materials by sulfate solutions and that of the materials on the basis of Portland cement.

The alkali-activated binders give the possibility to utilize rejected inorganic wastes; the properties of such binders are often better than those of standard Portland cement.

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