

# GEOPOLYMER MATERIALS ON THE FLYASH BASIS – LONG-TERM PROPERTIES

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*The influence of the external environment on the properties of geopolymers on the basis of fly ashes exposed to various conditions (environments of different humidity levels, autoclave, dry conditions at 80°C, immersed in water) has been investigated for two years. The strength values of geopolymers kept under various conditions do not drop during the period of two years. The maximum values could be achieved if the geopolymers were kept under dry conditions at 80°C and in the air at a relative humidity ranging from 40 to 50 percent. The strength values do not change practically if the geopolymers are kept in water, in an autoclave or in an environment with the relative humidity of 95 percent. The long-term exposure of fly ash-based geopolymers does not result in any change in their microstructure and practically no new phases arise. The exposure to water is accompanied by a gradual leaching of sodium until its almost complete transition to water. The exposure of geopolymers to alternating humid and dry conditions gives rise to efflorescences. The NMR <sup>23</sup>Na, <sup>27</sup>Al and <sup>29</sup>Si spectra of fly ash-based geopolymers revealed a practically unchanged occurrence of structures in samples after their long-term exposure to various conditions as compared with the initial structures. Practically no evidence (X-ray diffraction and IR analyses) of any formation of new phases after various exposure conditions. No significant morphological changes (the formation of crystalline phases) in samples kept under above mentioned conditions could be identified after two years as compared to the initial state; hence, the original amorphous character of the geopolymers is preserved. The structure of man-made geopolymers can probably be deduced rather from the amorphous mineral allophane than from crystalline zeolites. Therefore, thanks to a comprehensive long-term investigation, the fly ash-based geopolymers can be regarded as stable hydraulic binders.*

## INTRODUCTION

The reaction of alumino-silicate materials (fly ash, metakaolin and other materials) suspended in a strong aqueous alkaline environment (obtained by alkaline hydroxides or, respectively, by alkaline silicates) gives rise to a new solid – a man-made alumino-silicate polymer – the geopolymer. This product is composed of an almost amorphous alumino-silicate gel. The gel contains a 2D to 3D inorganic polymer of the type  $M_n[-(Si-O)_z - Al - O]_n \cdot wH_2O$ , where M ... Na, K or even also Ca, Mg. Considerable attention has been paid to this new type of material.

A large number of papers pinpointing potential possibilities of this binder as a compound suitable for the manufacture of building materials were published. However, the papers dealing with geopolymer materials contain only sporadic data on their long-term properties

over periods lasting a couple of years (Provis [1], Davidovits [2, 3], Duxson [4], Hardjito, Wallah [5, 6, 7]). There is no doubt that any practical application of geopolymers can not be envisaged without good knowledge of their long-term properties.

Therefore, the present work focused on the investigation of long-term properties of geopolymers (pastes, mortars) based on fly ashes rejected from Czech power plants fired by brown coal. The periods lasted for 2 years and more.

## EXPERIMENTAL

### Material

Fly ash rejected at the browncoal-fired Opatovice power plant was used for experiments. Its composition is given in Table 1.

Table 1. Composition of the Opatovice fly ash (percent by weight).

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI
52.85	31.84	7.34	2.12	1.14	0.41	1.69	0.36	1.51	0.21	0.74

## Sample preparation

Pastes and mortars were prepared on the basis of the above fly ash. The fly ash was mixed with the solution of an alkaline activating agent (NaOH + water glass). The compositions of individual combinations of the activating agent are given in Table 2. A predominant number of experiments was carried out with the alkaline activating agent containing 8 % by weight of Na<sub>2</sub>O; the SiO<sub>2</sub>/Na<sub>2</sub>O ratio was equal to 1.0. The geopolymer pastes and mortars exhibited optimum rheological properties at this composition of the activating agent, their period of workability was acceptable and the strength attained maximum values [8]. The mortars were prepared by using 3 grainsize fractions of silica sand (in a ratio of 1:1:1). The fly ash-to-sand ratio was equal to 1:1. The alkaline activating agent containing 7.5 % K<sub>2</sub>O and characterized by the SiO<sub>2</sub>/K<sub>2</sub>O ratio equal to 1.0 was used in some other experiments.

Table 2. Composition range of the alkaline activating agents used for experiments.

SiO <sub>2</sub> /Na <sub>2</sub> O; % Na <sub>2</sub> O			
0.8 ; 5	1.0 ; 5	1.2 ; 5	1.5 ; 5
0.8 ; 8	1.0 ; 8	1.2 ; 8	1.5 ; 8
0.8 ; 10	1.0 ; 10	1.2 ; 10	–
0.8 ; 12	1.0 ; 12	–	–

Ready pastes and mortars were kept in open steel molds (4 × 4 × 16 cm) at a temperature of 80°C for 12 hours (in a dryer). Geopolymers possessing maximum strength values [8] could be prepared under such conditions. Demolded pastes and mortars were then kept in air for 14 days followed by an exposure to different types of environment:

- Environment with a relative humidity ranging from 40 to 50 % and a temperature of 20 to 22°C (air).
- In water at a temperature of 20 to 22°C (water).
- In a moisture cabinet (humidifier) at a relative humidity of 95 % (wet).
- Under hydrothermal conditions in an autoclave at a temperature of 95°C (autoclave).
- Dry environment at a temperature of 80°C (dry).

The samples were kept permanently under the above conditions for a period lasting 2 years. Their mechanical properties (compressive strength, tensile strength under flexure) were determined after 7, 28, 120, 360, 540 and 720 days. X-ray diffraction spectra (PANalytical X'Pert PRO Philips), IR spectra (Nicolet 740 Nexus) and NMR MAS <sup>29</sup>Si, <sup>27</sup>Al, <sup>23</sup>Na spectra (BrukerAvance 500WB/US) were also recorded after the same periods of time. The morphology of fraction surfaces after the destruction tests was studied with the aid of the SEM method (Hitachi S4700) as well as by the point and surface analysis.

## RESULTS AND DISCUSSION

## Mechanical properties

Mechanical properties of geopolymer mortars with specific compositions after 7 to 720 days are given in Figures 1 and 2. All types of selected exposures of geopolymer mortars are accompanied by the stabilization of their strength values. Small variations in the strength could only be observed in the initial stages. No exposure mode resulted in the deterioration of the strength values (within the framework of experimental errors).

The values of strength obtained for individual exposure modes are different. The strength continues to grow after the exposure of the samples to dry conditions

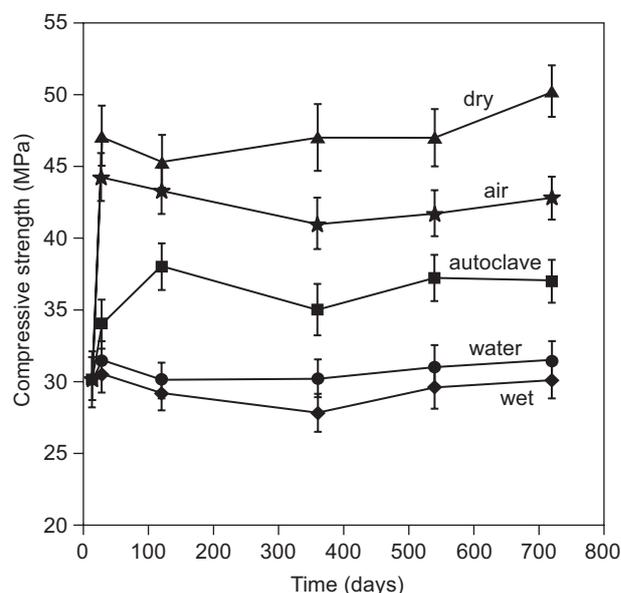


Figure 1. Time dependence of the compressive strength.

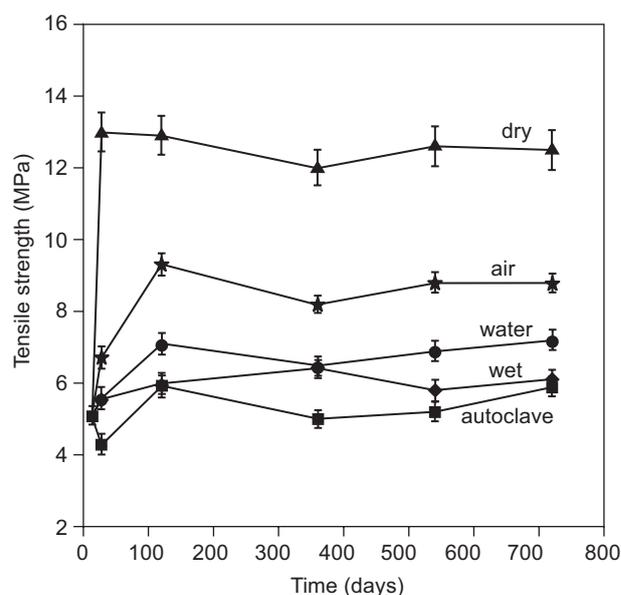


Figure 2. Time dependence of the tensile strength under flexure.

and a higher temperature as well as to the air, which is probably due to the continuation of the geopolymerization process.

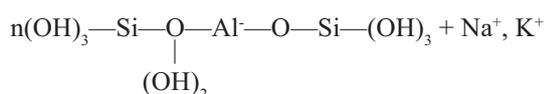
The strength of samples kept in water, in the wet environment or, respectively, under hydrothermal conditions does not vary owing to the adverse effect of the aqueous environment on further progress of geopolymerization. The results obtained for samples kept in water agree with the previous data [9] found during the long-term exposure of geopolymer mortars to salt solutions (Na<sub>2</sub>SO<sub>4</sub>, NaCl a MgSO<sub>4</sub>): the strength values do not vary or grow slightly in the period ranging from 90 to 720 days elapsed from the moment of their preparation. A high value of resistance of geopolymer materials to the action of acid was found in an earlier work [15].

The alkali-silicate reaction taking place in geopolymer concretes containing aggregates with the so-called „active SiO<sub>2</sub>“ represents another long-term property. The potential possibility of the occurrence of such a reaction is due to the presence of „free“ alkalinity in the geopolymer body (see below). The alkali-silicate reaction in fly ash-based geopolymer concretes was not studied within the framework of the present paper.

According to Kupwade-Patil [10] the mechanism of the alkali reaction in geopolymer concretes containing aggregates with „active SiO<sub>2</sub>“ is completely different from that occurring in PC-containing concretes. Other geopolymer phases are formed in the geopolymer concrete containing „active SiO<sub>2</sub>“ and no expansion-prone Na-Ca-S-H gels occur.

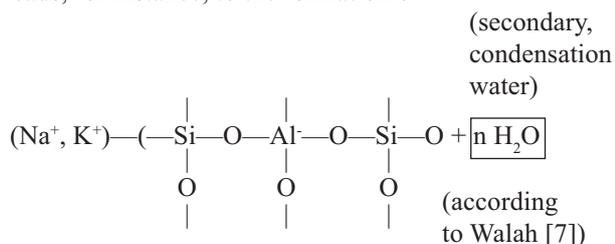
#### Geopolymerization vs. hydration

Silanolates –Si–OH and alumolates –Al–OH of the type, for instance,



form during the reaction of alumino-silicates (fly ashes) in a strong alkaline environment.

This product further condenses in the strong alkaline environment by giving rise to a Si–O–Al–O polymer. The reactions accompanied by the elimination of water leads, for instance, to the formation of



The condensation gives rise to e 2D up to 3D polymer and the material hardens. The polycondensation reaches only a certain point or stops completely if the

proces takes place in an aqueous environment with a high relative humidity or under hydrothermal conditions hampered by a more difficult removal of H<sub>2</sub>O molecules. However, the polymerization proceeds in the environment with a decreased humidity when the H<sub>2</sub>O content drops. Maximum strength values could be achieved during the preparation of the geopolymer under „dry“ conditions (80°C, dryer) in contrast to the preparation in the environment characterized by a high relative humidity or under hydrothermal conditions when the strength values were up to 10 times smaller [8].

The proces of geopolymer hardening and further development of its strength can be characterized as polymerization in the aqueous alkaline environment with the possibility of the polymerization deceleration or of its complete stopping in the presence of excess water. This proces is accompanied by the formation of secondary H<sub>2</sub>O, a part of water evaporates while some water remains entrapped in capillary and gel pores.

In contrast to the geopolymer hardening, the Portland cement hardens in result of the hydration of clinker minerals when C–S–H products, C–A–H phases and Ca(OH)<sub>2</sub> are formed. The water present in the suspension of Portland cement is used up by the hydration reaction. The water that has not been used for the hydration gives rise to a network of capillary pores while another part of water is contained in the gel of the C–S–H phase. The achievement of the maximum strength of Portland cement requires the exposure of cement bodies to humid conditions. The strength drops substantially if the bodies are kept in „dry“ conditions, see, for instance [11].

The hardening proces of Portland cement is controlled by the hydration when the insufficient quantity of H<sub>2</sub>O (evaporation, „dry“ curing conditions) results in the proces deceleration or its discontinuation.

#### Efflorescence

The exposure of geopolymer pastes, mortars (or even concretes) to alternating wetting and drying is accompanied by the formation of efflorescences as shown in [12]. The efflorescences are composed of hydrates (Na<sub>2</sub>CO<sub>3</sub>·nH<sub>2</sub>O, respectively NaHCO<sub>3</sub>·nH<sub>2</sub>O, Figure 3).

The efflorescences occurring on the geopolymer surface are regarded as an unpleasant beauty flaw; nevertheless, the duration of the phenomenon is limited in time, Figure 4. The efflorescences do not affect mechanical properties of geopolymers. Sodium (potassium) is bound weakly in the geopolymer body and, therefore, it can be leached easily as NaOH. NaOH reacts with CO<sub>2</sub> present in the air by giving rise to easily soluble Na<sub>2</sub>CO<sub>3</sub>. Soluble Na<sub>2</sub>CO<sub>3</sub> does not form any „protecting“ insoluble layer on the geopolymer surface but it gives rise to efflorescences. Sodium is replaced consequently by H<sub>3</sub>O<sup>+</sup> cation compensating the negative charge of aluminium.

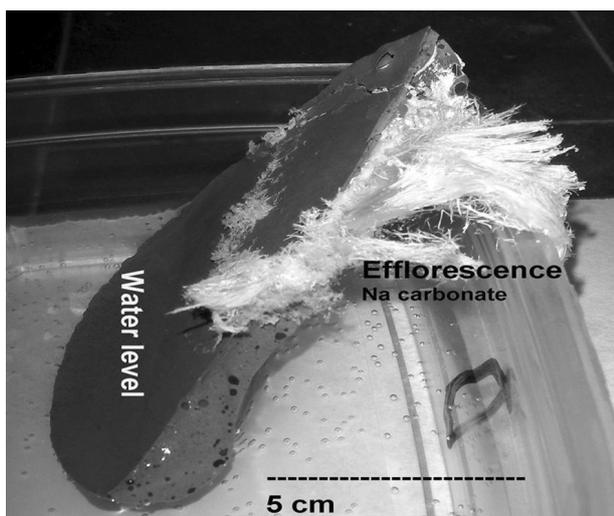


Figure 3.  $\text{Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$  efflorescences after 50 days of a partial immersion of the geopolymer in water.

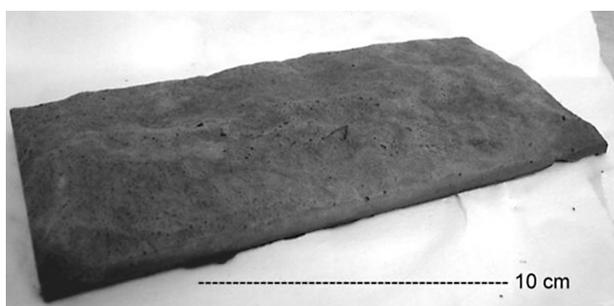


Figure 4. Geopolymer slab after 6 years in open air. The slab was subjected to rain, snow, sunshine, etc. First, the efflorescences could be found but, later, no such phenomena were observed. The slab does not exhibit any signs of deterioration, cracks, etc.

In contrast to hardened Portland cement, the geopolymers do not contain phases of the C-S-H type,  $\text{Ca}(\text{OH})_2$  and a phase of the C-A-H type (calcium hydro-aluminates, the ettringite). Hydrated Portland cement contains the C-S-H phase in the thermodynamic equilibrium with  $\text{Ca}(\text{OH})_2$ .  $\text{Ca}(\text{OH})_2$  reacts with  $\text{CO}_2$  present in the air by giving rise to insoluble  $\text{CaCO}_3$ . Insoluble  $\text{CaCO}_3$  is thus formed on the surface of hydrated Portland cement. This layer prevents further reaction of  $\text{Ca}(\text{OH})_2$  with  $\text{CO}_2$  present in the air. Therefore, the  $\text{Ca}(\text{OH})_2$  leaching from Portland cement is much slower because of the formation of the  $\text{CaCO}_3$  layer on its surface as compared to the  $\text{NaOH}$  leaching from the geopolymer.

#### X-ray and infrared spectroscopic analysis

X-ray diffraction spectra of geopolymers (irrespective of the composition of the alkaline activating agent and the reaction conditions) exhibit broad diffusion peaks (with one or even two tops) as demonstrated by

numerous citations (eg Provis [1], Davidovits [2]), Figure 5. The peaks (broad amorphous peak „halo“) correspond predominantly to the amorphous character of geopolymers. The estimated peak position is 3.25, that of the weak one can be attributed to 2.25 nm. There are also distinct diffractions in the X-ray spectra of fly ash-based polymers corresponding to residual minerals from the fly ash (quartz, mullite, hematite).

Practically no change in the character of X-ray diffraction spectra occurred in result of different curing conditions, see the respective Figures. No diffractions corresponding to the formation of new crystalline phases, eg zeolites, see Figure 5, could be detected in the spectra (within the framework of experimental error). No change in the character of the spectra was found either when the composition of the alkaline activating agent changed (within the range mentioned in Table 2). Provis [1], Duxson [4], Fernández-Jiménez [13] observed weak diffractions of analcime ( $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ ), Na-P1 zeolite ( $\text{Na}_{1.4}\text{Al}_2\text{Si}_{3.9}\text{O}_{11.5} \cdot \text{H}_2\text{O}$ ), faujasite ( $\text{Na}_2\text{Al}_2\text{Si}_{2.4}\text{O}_{8.8} \cdot 6.7\text{H}_2\text{O}$ ), etc. in fly ash-based geopolymers. The occurrence of crystalline zeolites could be observed particularly in geopolymers prepared by using metakaolin (Provis [1]).

IR spectra of fly ash-based the geopolymer exhibit characteristic bands with peaks at 455, 561, 690, 779, 1015 a 1641  $\text{cm}^{-1}$ . The character of IR spectra does not vary in dependence on the geopolymer curing conditions. No bands corresponding to newly formed crystalline phases could be detected in the spectra, see Figure 6.

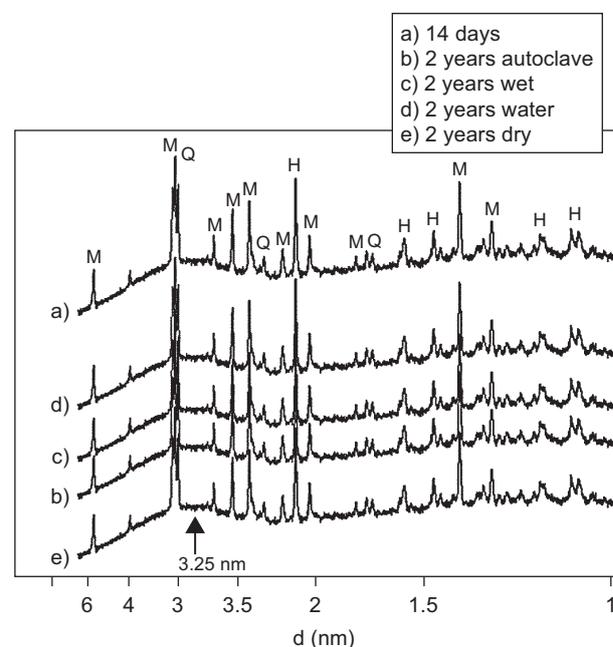


Figure 5. X-ray diffraction spectra of the geopolymer: 14 days from the date of its preparation, 2 years in water, 2 years in the autoclave at 95°C. A broad diffusion peak of the amorphous geopolymer is evident in the spectrum. The individual diffractions correspond to residual phases from the fly ash: M - mullite, Q - quartz, H - hematite.

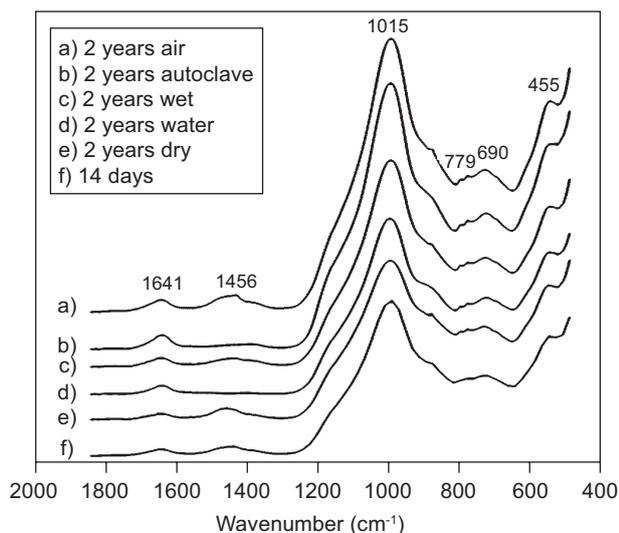


Figure 6. IR absorption spectra of the geopolymer: 14 days from the date of its preparation, 2 years in water, 2 years in the autoclave at 95°C.

### NMR spectroscopy

NMR  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  spectra were determined at various time periods elapsed from the very moment of preparation as well as after the 2-year exposure to various curing conditions, see Figure 7. The spectra were subjected to deconvolution, always in the same way so that the qualitative comparison of the results obtained for individual types of exposure is possible. The results obtained by the deconvolution are given in Figures 8 and 9.

There is a variety of peaks at -80, -85, -89, -96, -101, -108 ppm in the NMR  $^{29}\text{Si}$  spectrum of the geopolymer. The spectra correspond to a series of  $\text{Q}^3$ ,  $\text{Q}^4$  (0-4Al) structures with dominant  $\text{Q}^4$ (3-4Al) structures, see Figure 8. The NMR  $^{27}\text{Al}$  spectrum of the geopolymer exhibits a peak at 55 ppm corresponding predominantly

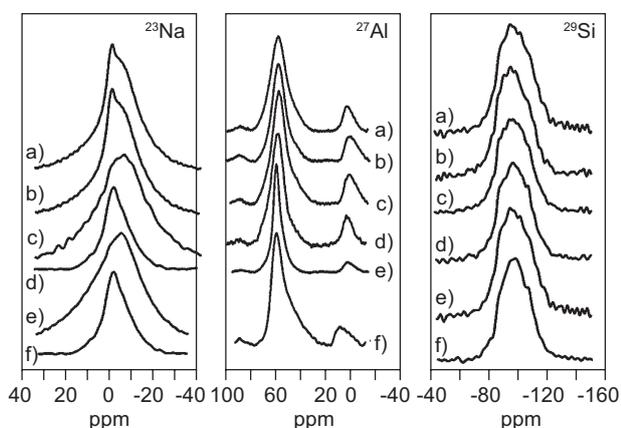


Figure 7. MAS NMR  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ,  $^{23}\text{Na}$  spectra after 14 days from the date of preparation and after the curing lasting 2 years. a) 2 years air, b) 2 years autoclave, c) 2 years wet, d) 2 years water, e) 2 years dry, f) 14 days.

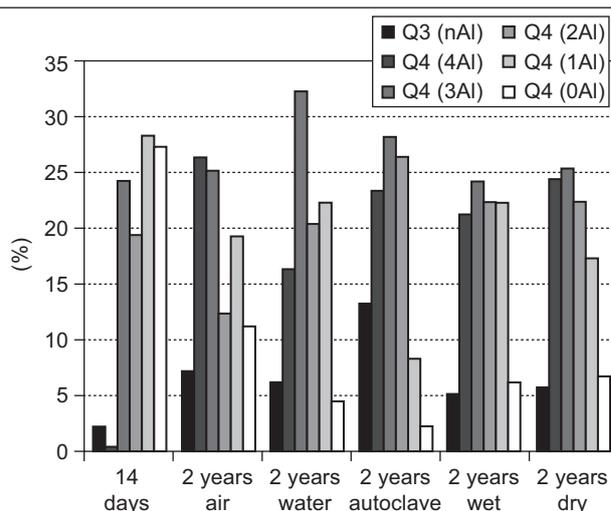
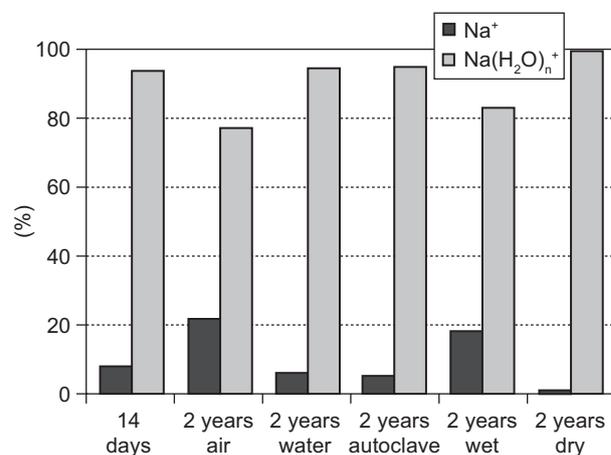
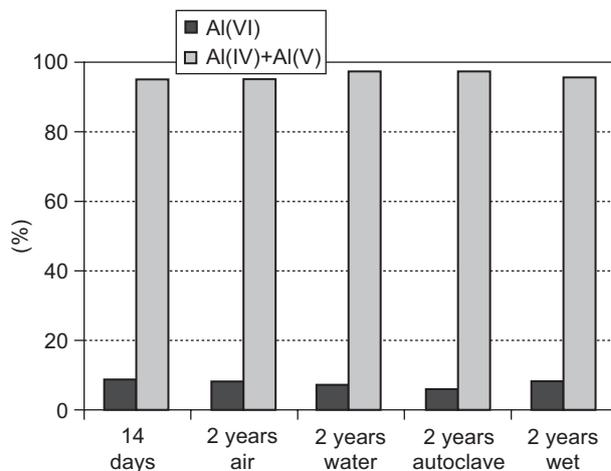


Figure 8. Distribution of individual structures deduced from  $^{29}\text{Si}$  spectra 14 days from the date of preparation and after the curing lasting 2 years.



a)  $^{27}\text{Al}$



b)  $^{23}\text{Na}$

Figure 9. Distribution of individual structures deduced from  $^{27}\text{Al}$  and  $^{23}\text{Na}$  recorded immediately after the preparation and two-year curing.

to the tetrahedral coordination of aluminium as well as another weak peak at 0 to -5 ppm corresponding to Al(VI) coordination, see Figure 9. Also the presence of a minor Al (V) structure could be detected in the spectra. The occurrence of the octahedral Al coordination is due either to the presence of the residual mullite or it belongs to Al(VI) in the AS polymer.  $^{23}\text{Na}$  spectrum points to the presence of Na in the dominant  $\text{Na}(\text{H}_2\text{O})_n^+$  form in addition to a minor  $\text{Na}^+$  form, see Figure 9.

Practically the same occurrence rate of the structure could be detected in the NMR  $^{23}\text{Na}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  spectra of fly ash-based geopolymers exposed to various curing conditions as compared to the structures observed 14 days from the preparation date. The results indicate that the long-term curing does not cause any pronounced structural changes.

### SEM

No pronounced morphological changes (the formation of crystalline phases) could be detected in the geopolymer after a two-year exposure to various conditions (air, a very dry environment, water, autoclave, wet environment) as compared with the sample after 14 days from the date of its preparation, see Figures 10, 15. An amorphous character of the geopolymer with residues of unreacted fly ash is obvious was typical for all exposure modes.

The exposure to water is accompanied by a gradual leaching of sodium until the moment when the leaching is almost complete. The diffusion character of sodium leaching from the geopolymer was observed during the exposure to water. The sodium concentration in samples kept in water for two years was very low even deep in the sample bodies ( $4 \times 4 \times 16$  cm), see Figures 10, 16 as well as [12].

No decrease in the strength of the geopolymer was observed despite the leaching of sodium from its body. It seems that sodium does not take part in the strength

of the geopolymer structure and that its bond in the geopolymer body is weak [10]. An easy leaching of sodium is a cause of the efflorescence formation that takes place particularly during the alternating wetting and drying (Figures 3 and 4). The character of the Na(K) bond in geopolymer materials is described in detail in [12]. No efflorescences form during the exposure to air (in the laboratory) and even the samples from previous experiments kept in the laboratory for 10 to 12 years did not suffer from any efflorescence. No changes in prepared geopolymers or formation of new crystalline phases were observed when the materials were kept in a very dry atmosphere (the dryer,  $80^\circ\text{C}$ ).

Portland cement-based materials disintegrate under the effect of intense water penetration (eg under pressure) because of the  $\text{Ca}(\text{OH})_2$  leaching, and amorphous hydrates of  $\text{SiO}_2$  are formed. Even a partial leaching of  $\text{Ca}(\text{OH})_2$  (20 - 30 %) from the cement concrete may result in a substantial decrease in the strength [14, 15]. The leaching of sodium (NaOH) from the geopolymer body does not result in the degradation of its structure (Figures 10 and 11) in contrast to the C-S-H phase.

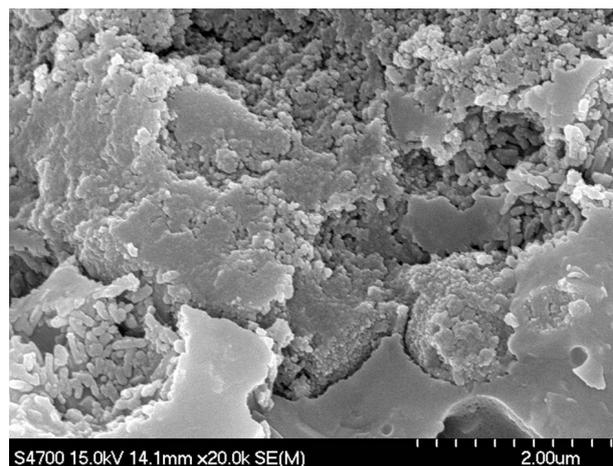


Figure 11. Geopolymer, paste, leaching for 3 years in water, fraction surface,  $\text{Na}_2\text{O}$  content amounting to 0,1 %.

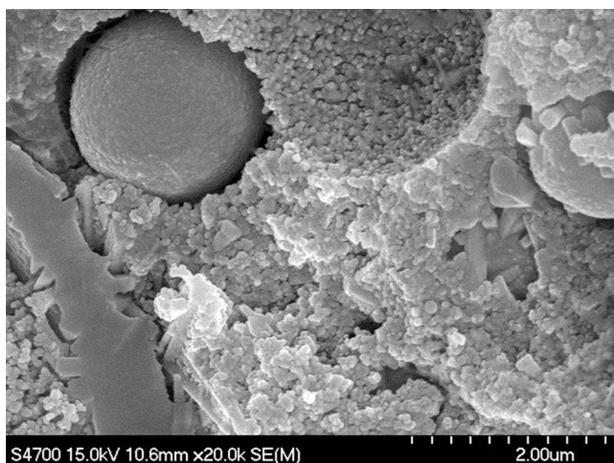


Figure 10. Geopolymer, paste, no leaching, fraction surface,  $\text{Na}_2\text{O}$  content equal to 8 %.

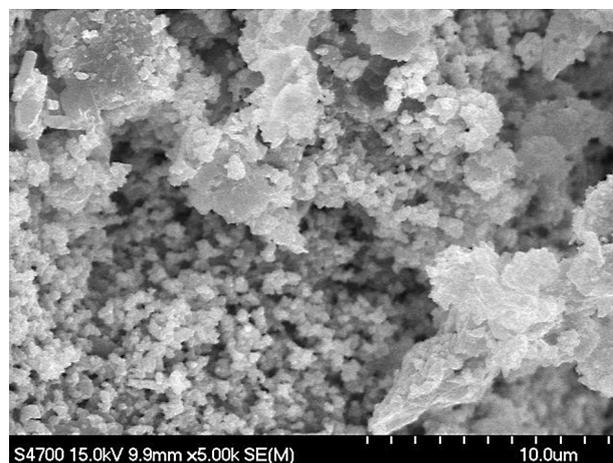


Figure 12. Geopolymer, 2 years in the autoclave, fraction surface.

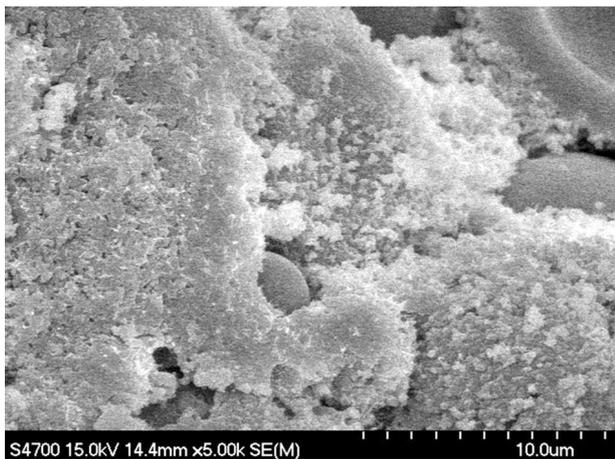


Figure 13. Geopolymer, 2 years in an environment with a relative humidity equal to 95 %, fraction surface.

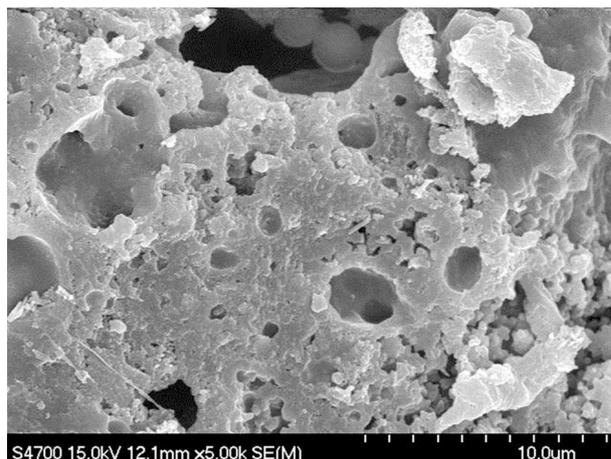


Figure 15. Geopolymer, two-year exposure to 80°C (dryer), fraction surface.

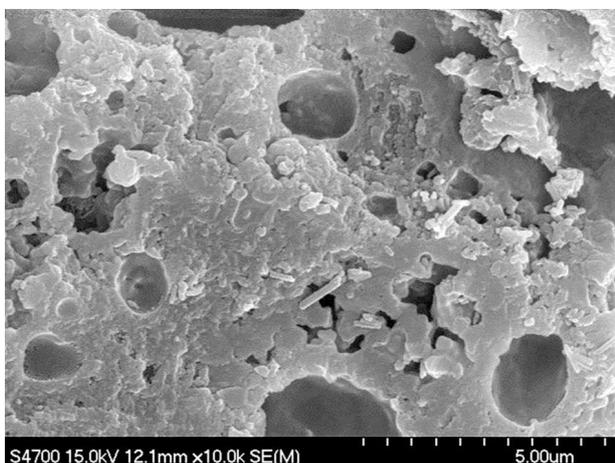


Figure 14. Geopolymer, two-year exposure to an environment with a relative humidity ranging from 40 to 50 %, fraction.

A possible similarity between the geopolymers and the mineral allophane?

In conjunction with the long-term stability of geopolymer the question arises whether there are minerals occurring in the nature that would be similar to geopolymers. So far, the geopolymers have been put in relation with crystalline zeolites as mentioned by Davidovits [2, 3], Provis and others [18]. The workers in question assume that the geopolymer structure is composed of nano-crystalline zeolites.

Man-made geopolymers exhibit a morphological similarity with a natural amorphous hydrated aluminosilicate mineral – the allophane, see Figures 17 and 18.

The allophane mineral (as well as the man-made one) is characterized by an assembly of hollow spheres as indicated by Wada, Henmi [19-22], Montarges-Pelletier [23]. The composition of the mineral allophane is  $0,85\text{-}2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot y\text{H}_2\text{O}$  ( $y > 2,5$ ), the alkali content (Na, K) ranges from zero to 5 percent in dependence on

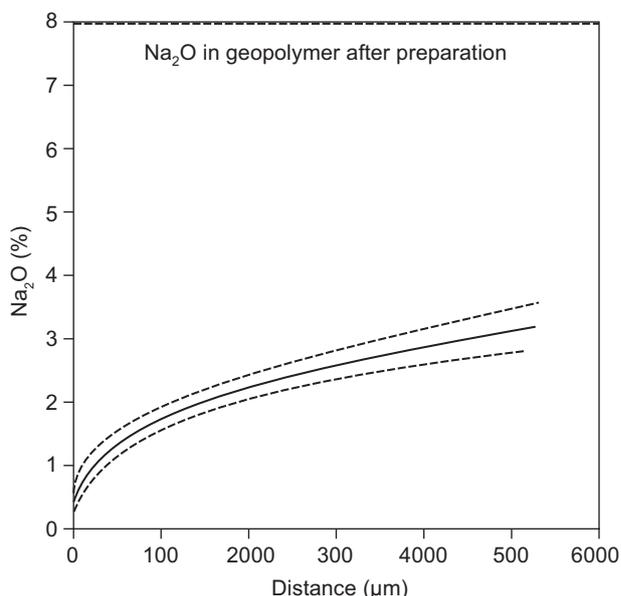


Figure 16. Sodium concentration profile, sample body 4 × 4 × 16 cm, 120 days in water.

the Si-to-Al ratio, Wada [21]. *See also the note\**. Also the amorphous geopolymer phase exhibits the character of mutually communicating spherical particles (Figure 16) measuring a couple of nano-meters as mentioned by Kriven [17], Provis [18]. Kaufhold [27] found spherical nano-particles in the allophane from an Ecuador deposit; in this case, the determined diameter of allophane particles ranged from 5 to 10 nm (similar values were also determined for man-made allophane). X-ray diffraction and IR spectra of the allophane mineral, see Wilson [24] also show a similarity with the geopolymer spectra. NMR spectra of the allophane mineral (Wilson [24],

\*A large deposit of the allophane mineral has been discovered recently in Ecuador in a layer about 5 m thick (extension about 5 000 km<sup>2</sup>, Fe<sub>2</sub>O<sub>3</sub> up to 8 percent). *Clay and Clay Minerals* 2009; 57: 72-81

Hos [25], Henmi [26]) point – analogously to geopolymers – to the presence of a variety of  $Q^3$ ,  $Q^4(0-4Al)$  structures. However, aluminium in the allophane is present in the octahedral coordination in contrast to the geopolymers where this element is predominantly present in the tetrahedral coordination. The absence of a regular large-scale arrangement is characteristic for the allophane whereas a regular small-scale arrangement composed of  $SiO_4$  tetrahedra and  $AlO_6$  octahedra, Wada [24], is typical. It is evident from the above facts that the structure of man-made geopolymers may be rather derived from the amorphous allophane mineral than from the crystalline zeolites.

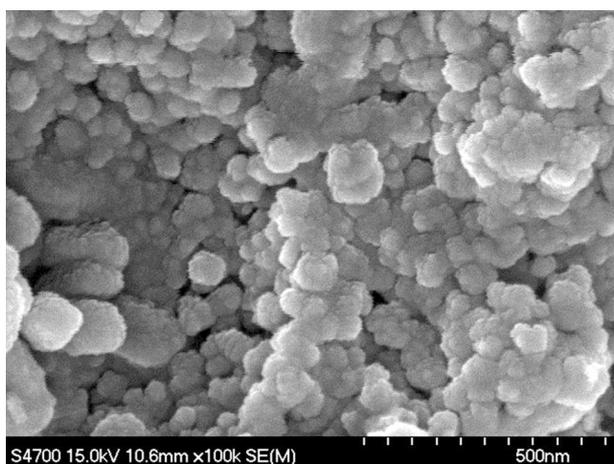


Figure 17. Fly ash-based geopolymer (detail).

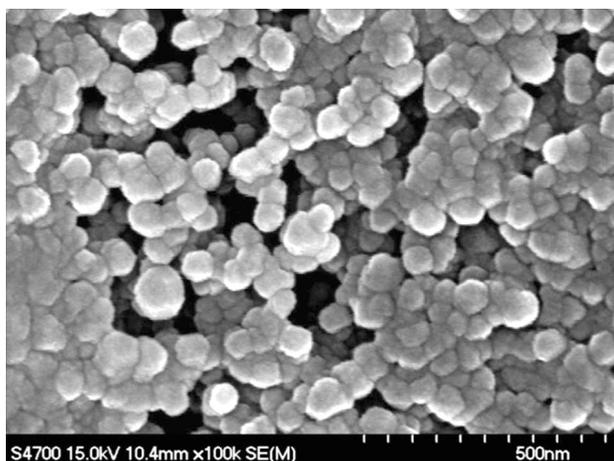


Figure 18. Allophane, Schöller coal mine, Kladno, Czech Republic.

## CONCLUSIONS

The results of a long-term investigation into the properties of fly ash-based geopolymers subjected to various curing conditions demonstrate that such materials can be regarded as a stable hydraulic binder. Nevertheless, the properties of geopolymer materials

(and, particularly, those of concretes) should be monitored even in the future as this is usually performed for traditional concretes based on Portland cement.

The (even temporary) formation of massive efflorescences in an environment characterized by alternating wetting and drying can be regarded as a negative feature of fly ash-based geopolymers.

The values of the compressive and tensile strength of geopolymers do not drop over a short-term horizon of time (2 years). All types of selected curing conditions of geopolymers are accompanied by a stabilization of strength values; small variations in the strength could only be observed at the beginning. The strength values are dependent on the type of the exposure to which the geopolymers are subjected. The values continue to grow under dry curing conditions and in the air, which is a consequence of the continued geopolymeration process. The values stagnate for materials exposed to water, wet conditions or, respectively, to hydrothermal conditions when the adverse effect of aqueous environment on the progress of the geopolymeration process makes itself felt.

The spectroscopic investigation of fly ash-based geopolymers exposed to various curing conditions demonstrated a good stability of their structure because no evidence pointing to the formation of new phases could be detected.

No pronounced morphological changes (the formation of new crystalline phases) could be found in the geopolymer after its long-term (two-year) exposure to various curing conditions (air, very dry environment, water, autoclave, wet environment) as compared with a sample investigated 14 days after the date of its preparation. The amorphous character of the geopolymer containing residues of unreacted fly ash is preserved after the exposure to all the types of curing conditions. The character of the geopolymer phase exhibits some similarity with the amorphous alumino-silicate allophane mineral. Hence, the structure of man-made geopolymers may rather be derived from the amorphous allophane mineral than from crystalline zeolites.

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