

FIXATION OF HEAVY METALS IN GEOPOLYMERIC MATERIALS BASED ON BROWN COAL FLY ASH

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Submitted January 17, 2006; accepted March 15, 2006

Keywords: Geopolymer, Fly ash, Leachability, Fixation

The alkali-activated brown coal fly ash - geopolymer - can be used as a matrix for the fixation of heavy metals. The addition of heavy metals does not result in any substantial extension of the setting time as this happens in the case of Portland cement. The materials prepared by the alkali activation of fly ashes exhibit measurable properties in contrast to some cement mixes containing heavy metals. In contrast to the Portland cement mixes, the strength values of AA fly ashes containing metal admixtures (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} and Pb^{2+}) do not drop in the time horizon of 180-520 days. The IR and NMR spectroscopy corroborate the penetration of aluminium ions into the original Si-O-Si structure (AlQ_4 (4Si), $AlQ_{2.3}$ (2-3Si) and $Si(3Al)$ units). The salts of heavy metals are distributed uniformly within the geopolymer body. The leaching values characterizing the mixes containing salts of heavy metals are not the same for the individual investigated metals (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} and Pb^{2+}) and they vary within the ranges of the 1st-3rd class of durability (as per regulations valid in the Czech Republic). The best results could be achieved for the zinc fixation when the solidification in Portland cement was practically impossible. The resistance of AA fly ashes to leaching is influenced significantly by the presence of calcium ions in the geopolymer matrix.

INTRODUCTION

New inorganic materials - geopolymers - can be prepared by alkaline activation of aluminosilicate materials as blast-furnace slags, fly ashes, activated kaolinitic materials, etc. The term "geopolymer" was first coined by Davidovits [1-15] who used it to describe a group of inorganic binders similar to man-made zeolites. The structure of these materials is composed of the Si-O-Si polymer system that also occurs in zeolites. In contrast to the zeolite materials, the geopolymers are almost amorphous bodies. The alkaline activation of inorganic wastes (fly ashes, slags, flue dust, etc.) gives the possibility to synthesize low-cost and environmentally friendly structural materials similar to cement.

The goal of the present work was to contribute to the state of knowledge of the effect played by heavy metals (Zn, Cu, Cr, Cd and Pb) in the matrix of geopolymers based on alkali-activated fly ashes. The existing data dealing with the fixation of heavy metals in the geopolymer matrix were mostly related to the geopolymers based on kaolinitic materials of extra-European provenience [16, 17]. Our research projects have paid the attention to the synthesis of geopolymer materials from brown coal fly ashes because they are rejected in large quantities (more than 10 million tons annually) in the Czech Republic.

The present paper was devoted to the investigation into the influence of the concentration and the type of heavy metal compounds on the properties and microstructure of synthesized geopolymer materials as well as into the resistance of heavy metals to leaching from the matrix of geopolymer materials [24].

EXPERIMENTAL

Unground brown coal fly ash occurring in the Czech power plant at Opatovice was used for the preparation of geopolymers. Its chemical composition is given in table 1. Its specific surface area was 258 m²/kg. We also used standard CEMI 42.5 Portland cement with the specific surface area of 316 m²/kg. The geopolymers were prepared using two types of soluble glass: soda water glass characterized by the silica modulus $M_s = 2.86$ and potash water glass with the silica modulus $M_s = 2.43$; to obtain soluble glass with the required chemical composition we further modified it with an addition of sodium hydroxide or potassium hydroxide. The SiO₂-to-Na₂O ratio (M_s modulus) in the alkaline activating agent was adjusted by NaOH addition to the soluble glass so that the value of the M_s modulus 1.2 might be achieved. The overall concentration of the

alkaline activating agent was 7.5 % Na₂O of the binder mass. In some cases, also CaSO₄·2H₂O (98% pure) was added.

Slurries of geopolymer based on alkali-activated fly ashes (indicated further on as AA) characterized by $w = 0.29$ (and possessing acceptable rheological properties) were prepared for investigation. The slurries contained various concentrations of heavy metals (Zn²⁺, Cu²⁺, Cr³⁺, Cd²⁺ and Pb²⁺) introduced as powdered salts. The concentrations of Zn, Cu, Cr and Cd in the mixtures were 0.5 and 1.0 % by weight (related to the quantity of fly ash). Homogenized slurries were placed into a dryer where they were kept at a temperature of 80°C for 12 hours. The bodies with the dimensions of 2×2×2 cm were taken out of the molds after 24 hours and kept in air at a temperature of 20°C.

To be able to compare the results we also prepared cement slurries possessing about the same rheological properties as those of AA slurries. Slurries containing the same amounts of heavy metals were prepared for further experiments. Bodies with the dimensions of 2×2×2 cm were made using the cement slurries ($w = 0.30$, acceptable rheological properties) and they were placed into an air-conditioned cabinet with a temperature of 20-22°C and a relative humidity of 98 percent. The samples were always taken out of the mold after 24 hours when the slurry containing additions of heavy metals had already hardened. The samples were maintained in an environment characterized by the relative humidity of 98 percent till the 28th day and then they were kept in air at a temperature of 20°C and a relative humidity of 30-40 % until the compressive strength tests started (2-180 days).

The composition of the products was determined with the aid of the RTG diffraction, infrared spectroscopy, scanning electron microscope with ED spectrometer, high-pressure mercury porosimetry as well as by ²⁹Si and ²⁷Al MAS NMR spectroscopy in the solid phase. Their resistance to leaching was determined by using a standardized procedure (Czech Ministry of Environment): the samples were ground and leached in deionized water. The concentration of heavy metals in the leaching liquid was determined by means of the AA spectroscopy.

Table 1. Chemical compositions of brown coal fly ash and CEM I Portland cement.

Oxide (wt.%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	As ₂ O ₃
Fly ash	52.94	33.04	6.27	2.24	0.93	0.04
Cement	19.36	4.44	2.49	65.3	1.71	~
Oxide (wt.%)	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	V ₂ O ₅
Fly ash	0.25	1.75	0.25	1.75	0.13	0.059
Cement	4.98	1.26	0.09	0.24	0.10	<0.01

RESULTS AND DISCUSSION

The rheological properties of AA fly ash slurries - geopolymers - were assessed only visually. The AA fly ashes activated by potash water glass and the solution of potassium hydroxide are characterized by a better fluidity and a shorter setting time than those activated by soda water glass and the solution of sodium hydroxide. Such phenomenon can be explained by a lower solubility of aluminosilicates (fly ashes) in KOH [18]. The addition of heavy metal results in the deteriorated workability of slurries; this regards particularly water-soluble salts (zinc sulfate, copper sulfate) when the visual workability of the slurry started deteriorating gradually already after the addition of 0.5 % by weight of CaSO₄·2H₂O to the mix. The visual workability of the slurries did not grow worse if salts characterized by a poor solubility in water were used. The addition of 3.5 % by weight of CaSO₄·2H₂O not only improved the rheological properties but it also shortened the setting time by several hours.

This phenomenon can be explained by the possibility of calcium ion penetration into the geopolymer structure.

The occurrence of heavy metals in Portland cement slurries gives rise to a substantial shift in the beginning of the setting time, which is not acceptable in the technical practice; this regards in particular the slurries containing ZnO, PbO and ZnO flue dust. The beginning of the setting time of slurries containing 0.5-2.0 % by weight of zinc (ZnO) shifted to the 4th day. The slurries containing 0.5 % by weight of lead (PbO) started setting after 2 days and the setting of the slurries containing 1.0 % by weight of lead (PbO) could be observed after as many as 5 days. A variety of workers [19-22] studied the slowdown in the hydration of cements containing specifically zinc and lead; it was found that the hydration of the C₃S phase resulted in the formation of an amorphous layer of Zn(OH)₂ in presence of zinc, which slows down the hydration of this phase. The C₃A hydration in presence of zinc is influenced by the sulfate concentration in the cement. The hydration slows down if the sulfate concentration is higher (above 2.5 %). It can be said that zinc gives rise to an amorphous gel-like layer at the surface of cement grains in slurries containing zinc as ZnO. No substantial shift in the beginning of the setting time of slurries containing zinc sulfate could be observed. Also the influence of lead on hydration was studied. Lead slows down the cement setting by giving rise to compounds coating the silicate phases.

The compressive strength of fly ashes activated by potash water glass and the KOH solution did not exceed 17 MPa even if they had been left to age for 520 days. On the contrary, the compressive strength of fly ashes activated by soda water glass and NaOH solution

reached the value of 43 MPa after 14 days already and it did not decrease significantly afterwards (within the range of experimental errors). However, the compressive strength dropped again if the mix composed of fly ashes and gypsum had been activated with potassium water glass and KOH solution.

The introduction of a metal compound into the mix of AA fly ashes mostly results in decreased values of the compressive strength. The investigation into the compressive strength of cement samples revealed a rapid decrease in the strength taking place only after the copper addition ($\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$) to the mix when the C_3S particles are coated by copper hydrates. At the same time, also the formation of new copper-containing crystalline phases could be observed. The mechanical properties of Portland cement containing salts of heavy metals are comparable - except for copper - with the strength of the Portland cement itself; however, the strength of almost all samples decreased after 180 days, see figures 1-6.

The compressive strength observed after the addition of salts of heavy metals (specifically zinc as ZnO) was not only higher but - in some cases - it was even superior to that of the AA fly ash itself.

The strength of AA fly ashes is affected in a quite complex way by a variety of factors: the concentration and the composition of the alkaline activating agent, the conditions existing during the synthesis and the resulting porosity of the geopolymer. The porosity of the geopolymer is given not only by the microscopic pores in the geopolymer itself but also by the entrapped air and macroscopic pores in residual particles of the fly ash. The samples without any addition of heavy metals were characterized by a smaller value of the total porosity. It was found that the value of the total porosity increased with the increasing concentration of the metal in the mix. Nevertheless, the differences in the porosity values obtained for the individual samples were not large. It seems that the effect of added heavy metals on the strength of AA fly ashes is most probably related with the changes in the structure, respectively with the composition of the products (ie the geopolymer, respectively the hydrates in case of Portland cement).

It is evident from RTG diffraction spectra that amorphous products form the main part of the products resulting from the alkali activation of fly ashes. Only the diffractions of mullite and quartz corresponding to the residues of fly ashes in the product occur in the diffractographs obtained. No formation of a new crystalline phase was observed in geopolymers or cement samples after the addition of metal compounds.

The addition of heavy metals to the mixes of AA fly ashes did not affect the character of IR spectra (see figure 7). Vibration bands of individual salts (except for Cd, Pb) could always be found in the individual spectra, and

no shift in the position of these bands was recorded. Pronounced shifts mostly began after the chromium addition (chromium oxide) as well as after the introduction of zinc sulfate and copper sulfate. This phenomenon is most probably due to the presence of a precipitated salt occurring in the geopolymer gel. However, it can not be said with certainty whether a new crystalline phase was formed or whether this was due to the compound bonding to the amorphous part of the matrix. The characteristic vibration outlined in the spectra corresponds to the vibration of Si-O and Al-O bonds (the region ranging from 1024 to 1087 cm^{-1}). This central peak is the main feature corroborating the formation of the geopolymer. The largest value was recorded in the spectrum of the fly ash itself. The shifting of this peak towards lower values is characteristic for the remaining spectra. This shift is interpreted in the papers dealing with zeolites as the aluminium penetration into the original structure. It means that the vibration value drops while aluminium is penetrating into the Si-O-Si network. The more pronounced the shift the higher the extent of aluminium penetration into the $(\text{SiO}_4)^+$ network. Four small peaks in a broad band ranging from 900 to 1200 cm^{-1} may be attributed to the expansion of Si-O bonds whereas the bending of Si-O-Si bonds may occur in the range from 550 to 750 cm^{-1} . These bands are characteristic for the silicate bond [23]. Certain absorption bands in the spectrum of the silicate bond network were attributed to the vibrations of weak molecules of water. Water is absorbed at the surface or it is retained in extensive cavities between the individual bond networks (broad bands in the range from 3400 to 1650 cm^{-1}). A change in the geopolymer structure can be observed in the range from 600 to 800 cm^{-1} which is not, however, very different for samples containing various metal salts.

The MAS NMR method in the solid phase was applied with the aim to obtain crucial information about the environment arising around Si and Al atoms during the process of alkali activation of fly ashes. Na^+ ions enclosed in the structure cavities and observing the neutrality principle can be imagined in the structure of sodium-silicate geopolymer [24]. Individual Na^+ ions are also surrounded by water molecules, which may cause the ion motion towards the body surface and the formation of efflorescences. The peak -86.7 ppm in the ^{29}Si spectrum corresponds to the formation of the "tectosilicate" (ie to the silicate building unit, $\text{Si}(3\text{Al})$ units) rich in aluminium. Small peaks in the region of -96.8, -103.3 and -109.2 ppm correspond to the unreacted fly ash ($\text{Si}(0-1)\text{Al}$, $\text{Si}(1\text{Al})$ units). However, the signal at -87 ppm occurs even here after the alkali activation; it corresponds to unsolved mullite. The compounds of tetrahedral silicon are surrounded by 4Al, $\text{Si}(3\text{Al})$, $3\text{Si}(\text{Al})$ and 4Si [25]. However, the ^{27}Al spectra are

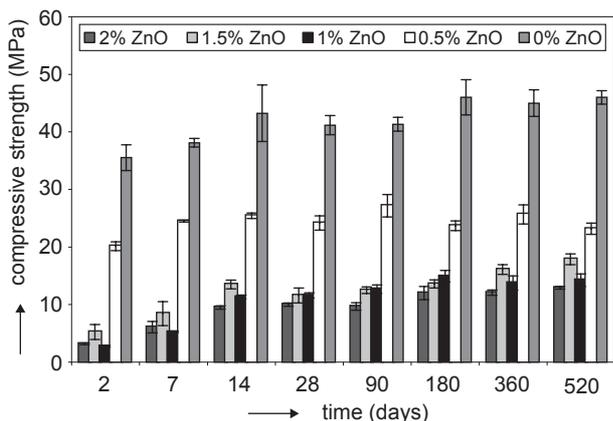


Figure 1. Compressive strength vs. time of alkali activated brown coal fly ash - geopolymer with Zn (ZnO) admixture.

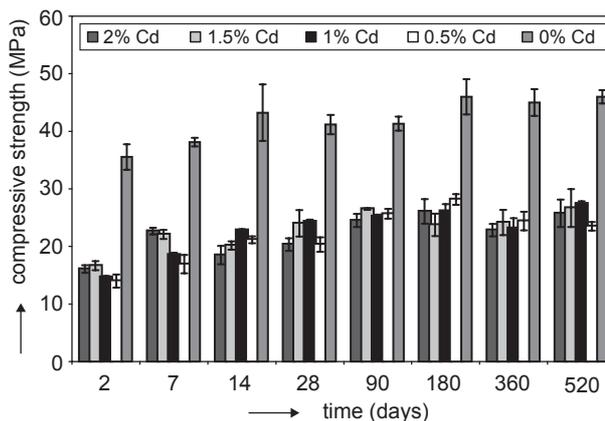


Figure 4. Compressive strength vs. time of alkali activated brown coal fly ash - geopolymer with Cd (CdCO_3) admixture.

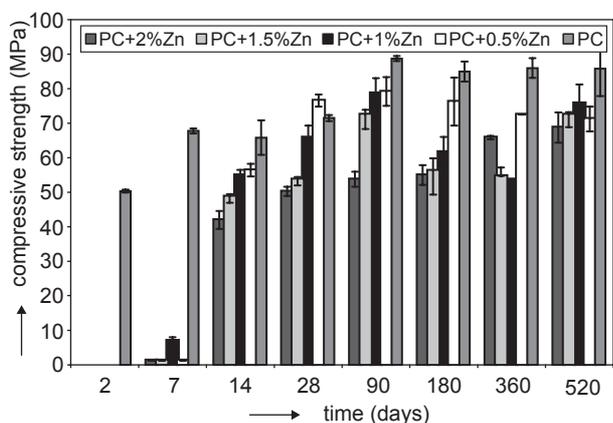


Figure 2. Compressive strength vs. time of Portland cement CEM I with Zn (ZnO) admixture.

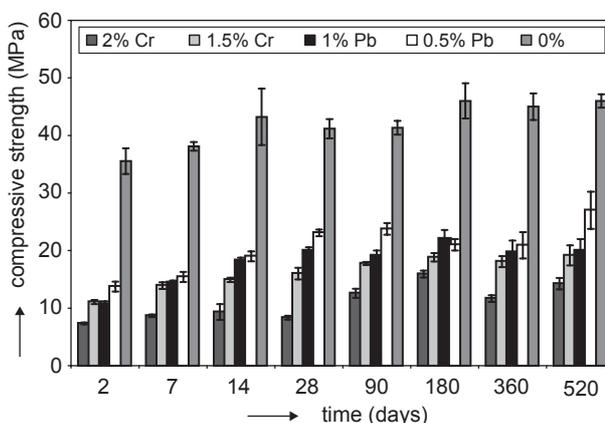


Figure 5. Compressive strength vs. time of alkali activated brown coal fly ash - geopolymer with Pb (PbO) and Cr [$(\text{NH}_4)_2\text{CrO}_4$] admixture.

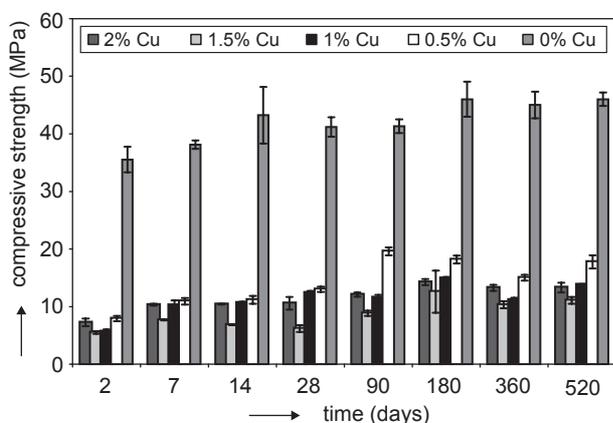


Figure 3. Compressive strength vs. time of alkali activated brown coal fly ash - geopolymer with Cu ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) admixture.

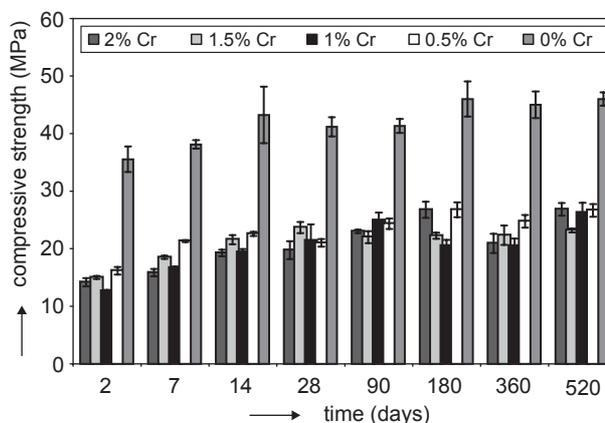


Figure 6. Compressive strength vs. time of alkali activated brown coal fly ash - geopolymer with Cr (Cr_2O_3) admixture.

almost identical. The (tetrahedral) Al redistribution takes place after the alkali activation of fly ash and the structure is re-transformed. This change is not very pronounced because the spectra are very similar, see figures 8 and 9.

It was assumed that the structure would be affected when metals were added during the geopolymer preparation. However, it is obvious from the NMR spectra that there are no significant differences in individual spectra; therefore, the addition of heavy metals did not result in any pronounced change of the structure (within the investigated concentration ranges of heavy metals), figure 10.

The occurrence of an amorphous phase and unreacted particles of fly ashes as well as the presence of minority acicular phase (probably an alkali silicate) are obvious at fracture surfaces of synthesized geopolymers. The investigation of all samples containing

Table 2. Limit values of element concentrations (mg/l) indicated in the announcement No. 383/2001 of the Ministry of Environment of the Czech Republic.

Parameter	Limit value		
	I	II	III
Zn	5.0	5.0	not indicated
Cu	0.5	1.0	not indicated
Cr	0.1	1.0	50.0
Cd	0.005	0.05	0.5
Pb	0.1	0.5	10.0

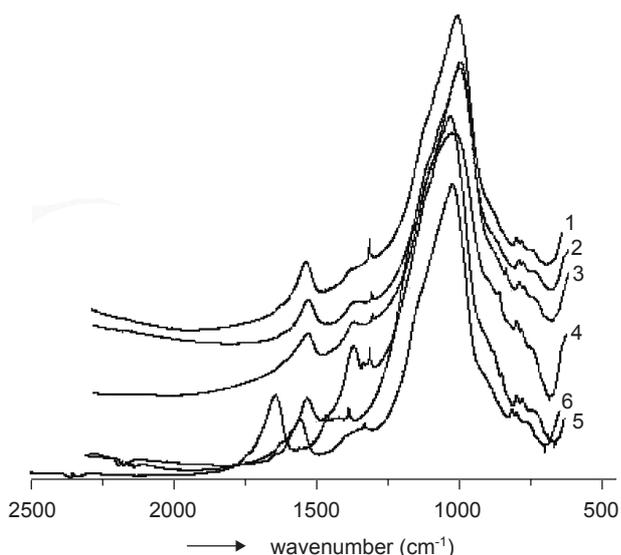


Figure 7. IR spectra of alkali-activated fly ash and those of alkali-activated fly ash-geopolymer containing 0.5% by weight of metals. 1 - alkali activated brown coal fly ash - geopolymer, 2 - with Zn (as ZnO), 3...Zn (ZnSO₄·7H₂O), 4 - Cu (CuSO₄·5H₂O), 5 - Cr (Cr₂O₃), 6 - Cd (CdCO₃).

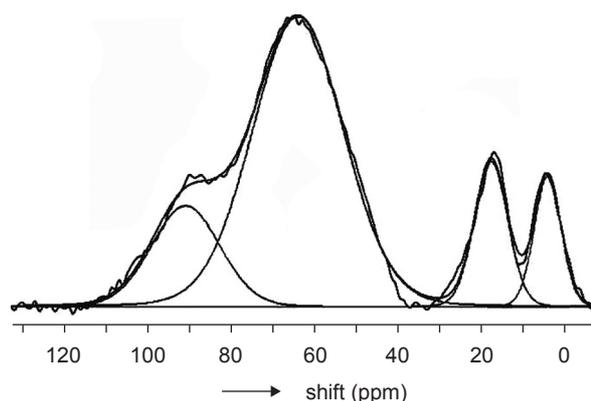


Figure 8. NMR MAS ²⁷Al of brown coal fly ash (Al-O units with low symmetry, AlQ_{2,3} (2-3Si) (original spectrum + deconvolution).

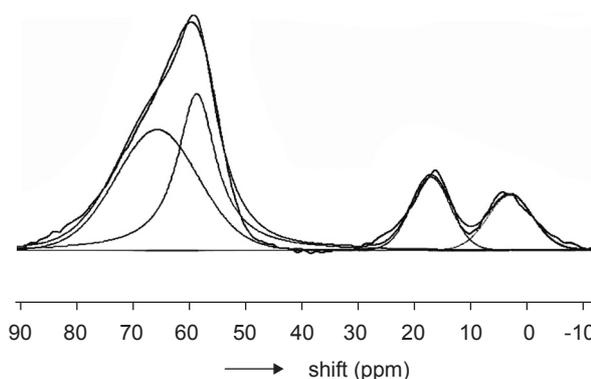


Figure 9. NMR MAS ²⁷Al of alkali activated brown coal fly ash (geopolymer), AlQ₄ (4Si), AlQ_{2,3} (2-3Si) units (original spectrum + deconvolution).

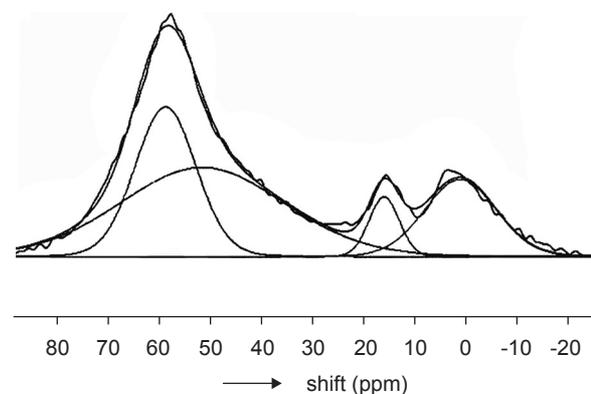


Figure 10. NMR MAS ²⁷Al of alkali activated brown coal fly ash (geopolymer) with 1% Pb (PbO), AlQ₄(4Si), AlQ_{2,3} (2-3Si) units (original spectrum + deconvolution).

cations of heavy metals showed that they were distributed almost uniformly in the whole volume; hence, they are not concentrated in a certain phase. However, in comparison to the samples of the AA fly ash itself, the surface morphology of samples did not suffer any change in result of the addition of heavy metals, figures 11 and 12.

The main attention of the present work was devoted to the leaching of heavy metals from AA fly ashes. The durability classes (table 2) indicated in the announcement No. 383/2001 of the Ministry of Environment of the Czech Republic (inspired by the respective EU directive) and the leaching values obtained for Portland cement mixes were used as a reference basis.

The results characterizing the resistance of zinc to leaching from AA fly ashes both during the Na activation and the K one are given in table 3. The leaching from the mix containing AA fly ash and 0.5 % by weight of Zn (ZnO) at the maximum also meets the requirements of all durability classes. The formation of a $Zn(OH)_2$ precipitate occurring in the amorphous gel can namely be assumed. The decrease in the amount of compounds leached from AA fly ashes in presence of gypsum is indeed remarkable: the presence of calcium in the geopolymer structure makes it namely stronger.

The amounts leached from mixes containing 0.5 % by weight of Cd meet the 3rd class of durability at the most. As regards the copper-containing mixes of AA fly ashes only those containing 0.5 and 1.0 % by weight

approach the values specified for the 2nd class of durability. All chromium-containing mixes (samples to which Cr_2O_3 was added) meet the requirements of the 3rd class of durability. Only the mix containing 0.5 % by weight of Cr meets the requirements of all classes of durability. The lead-containing mixes meet the requirements of the 3rd class of durability (table 4).

The leaching values characterizing Portland cements containing the same metals are smaller than those obtained for alkali-activated fly ashes. As regards Portland cement, heavy metals are bonded to the C-S-H phase or, respectively, to calcium thus giving rise to calcium-metal hydrates. The resistance of fly ashes to leaching is influenced by the solubility of the compounds formed in result of the salt reaction in the basic environment (metal hydroxides, respectively sodium chromites are formed). At the same time, the resistance to leaching is influenced by the way the analysis is being carried out. The method that was applied is rather destructive (the mixing of the mixture with water by

Table 3. Amounts of zinc leached from various matrices (A, B, C, D). The concentrations are given in mg/l.

Zinc concentration	Matrix type			
	A	B	C	D
0.5 % by weight	2.37	0.94	0.91	5.71
1.0 % by weight	8.01	1.10	1.35	8.41
1.5 % by weight	16.4	1.89	1.96	10.02
2.0 % by weight	17.3	1.98	2.35	12.3

A - Alkali-activated fly ash with sodium silicate, NaOH and Zn (ZnO); B - Alkali-activated fly ash with sodium silicate, NaOH, gypsum and Zn (ZnO); C - Alkali-activated fly ash with potassium silicate, KOH, gypsum and Zn (ZnO); D - Alkali-activated fly ash with sodium silicate, NaOH and Zn ($ZnSO_4 \cdot 7H_2O$)

Table 4. Amounts of various metals leached from the matrix of alkali-activated fly ash (soda water glass and NaOH solution). Concentrations indicated in mg/l.

Amount of added metal	Cu	Cd	Cr	Pb
0.5 % by weight	1.24	0.32	0.94	2.73
1.0 % by weight	1.19	0.44	1.09	7.60
1.5 % by weight	1.89	0.66	1.97	---
2.0 % by weight	2.77	0.95	2.29	---

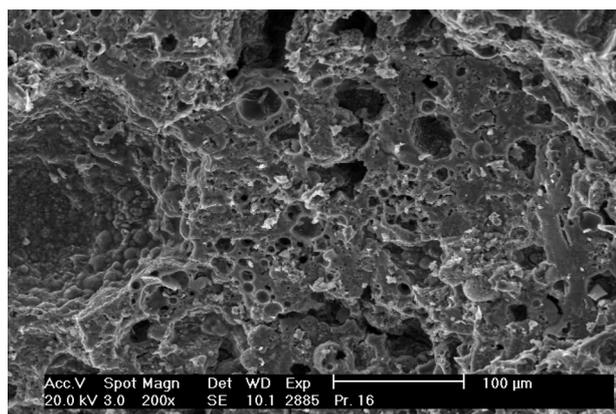


Figure 11. SEM of alkali activated brown coal fly ash - geopolymer with 0.5 hm.% Cu ($CuSO_4 \cdot 7H_2O$).

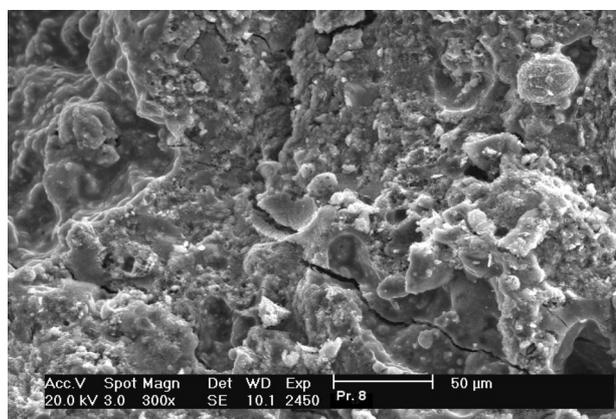


Figure 12. SEM of alkali activated brown coal fly ash - geopolymer with 0.5 hm.% Zn (ZnO).

rotating the bottle upside-down by 360 degrees); therefore, the metal leaching is also affected by the strength of the matrix. To be specific, we found that the strength values of fly ashes were by as much as a half smaller than those characterizing the cements.

We may conclude by stating that heavy metals can be fixed in the matrix of the geopolymer on the basis of brown coal fly ash even if higher concentrations of metals were attained in the solution as compared to the traditional material (Portland cement). However, the leaching values dropped substantially after the addition of calcium-containing compounds (Portland cement, ground blast-furnace slag or gypsum) to the mixes of AA fly ashes.

The comparison of our results with the data published in earlier papers is quite difficult because different methods were used for determinations (environment, pH, sample grain size). In the future our attention will focus on the possibility of decreasing the amounts of compounds leached from AA fly ashes (geopolymers) containing additions of heavy metals by reducing the water coefficient of the mix (decrease in porosity) as well as by optimizing the calcium-containing admixture.

CONCLUSION

1. The alkali-activated brown coal fly ash - geopolymer - can be used as a matrix for the fixation of heavy metals.
2. The addition of heavy metals does not result in any substantial extension of the setting time as this happens in the case of Portland cement. The materials prepared by the alkali activation of fly ashes exhibit measurable properties in contrast to some cement mixes containing heavy metals (the mixture of cement and zinc as ZnO: the setting time lasts 4 days).
3. In contrast to the Portland cement mixes, the strength values of AA fly ashes containing metal admixtures (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} and Pb^{2+}) do not drop in the time horizon of 180 - 520 days.
4. An amorphous phase is predominating in AA fly ashes. The addition of heavy metals does not trigger any formation of new crystalline phases.
5. The IR and NMR spectroscopy corroborate the penetration of aluminium ions into the original Si-O-Si structure.
6. The morphology of fraction surfaces of AA fly ashes is not affected significantly by the addition of heavy metals. The salts of heavy metals are distributed uniformly within the geopolymer body.
7. The leaching values characterizing the mixes containing salts of heavy metals are not the same for the individual investigated metals (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} and

Pb^{2+}) and they vary within the ranges of the 1st - 3rd class of durability (as per regulations valid in the Czech Republic). The best results could be achieved for the zinc fixation when the solidification in Portland cement was practically impossible.

8. The resistance of AA fly ashes to leaching is influenced significantly by the presence of calcium ions in the geopolymer matrix.

Acknowledgement

The authors wish to express their thanks to Dr. Schmidt, Technical University Bergakademie Freiberg, for his assistance during the investigation into the geopolymer microstructure as well as for his valuable contribution to the discussion.

The present work was implemented as a part of the research project MSM 6046137302 "Preparation and investigation of structural materials and material technologies by using micro- and nanoscopic methods" and thanks to the grant GACR No. 103/05/2314 "Mechanical and Engineering Properties of Geopolymer Materials on the Basis of Alkali-Activated Fly Ashes".

References

1. Gluchovskij V. D.: *Gruntosilikaty*, Kijev, Strojizadt (1959)
2. Glukhovskii V. D., Petrenko I. Yu., Skurchins'ka Z. V.: *Dopovidi Akademii Nauk Ukrain'skoi RSR, Seriya B: Geologiya, Geofizika, Khimiya ta Biologiya* 30, 454 (1968).
3. Gluchovskij V. D., Pachomov V. A.: *Šlakošočolnyje cementy i betony*, Budivelnik, Kijev, 1978
4. Davidovits J., Lavau J., Emberger A.: Patent FR 2341522 (1977)
5. Škvára F. et al: US Patent 4,168,985 (1979), 5,125,976 (1991), 5,076,851 (1991)
6. Davidovits J.: Patent FR 2464227 (1981)
7. Davidovits J: Annual Pacific Technical Conference, [Technical Papers] (Society of Plastics Engineers) p. 151-4 (1979).
8. Krivenko P.: *Specialnyje šlakošočolnyje cementy*, Budivelnik, Kijev (1992)
9. Krivenko P.: Proc. 1st Intern. Conf. "Alkaline cements and concretes", Vol.1., p. 11-130, VIPOL Stock Comp., Kiev 1994.
10. Davidovits J.: *Concrete International* 16, 53 (1994).
11. Davidovits J.: Proc. 1st Intern. Conf. "Alkaline cements and concretes", Vol.1., p. 131-150, VIPOL Stock Comp. Kiev (1994).
12. Davidovits J.: Patent FR 2709258 (1995).
13. Davidovits J.: Proc. 2nd Geopolymer Inter. Conf. "Geopolymère '99 (1999).

14. Swanepoel J. C., Strydom C. A.: *Applied Geochemistry* 17, 1143 (2002).
15. Xu, H., VanDeventer J. S. J. : *Cem.Concr.Res.* 32, 1705-1716 (2002).
16. Buchwald A., Kaps CH., Hochmann M.: *Proc. 11th Intern. Congress on the Chemistry of Cement (ICCC)*, 1238-1246 (2003)
17. Tashiro C., Oba J., Akama K.: *Cem.Concr.Res.* 9, 303 (1979).
18. Tashiro C., Oba J.: *Cem.Concr.Res.* 9, 253 (1979).
19. Olmo I. F., Chacon E., Irabien A.: *Cem.Concr.Res.* 31, 1213 (2001).
20. Rovnaníková, P: *Proc. Conf. Corrosion and Anti-Corrosion Protection of Metals*. Praha: AKI, 8 pages, CD.
21. Farmer V. C.: *Infrared spectra of minerals*, Adlard and Son Ltd, London 1974.
22. Mackenzie, J. D. K.: *Ceramic Transactions* 153, 175 (2003).
23. Palomo A., Alonso S., Fernández-Jimenez A.: *J.Am. Ceram.Soc.* 87, 1141 (2004).
24. Minaříková M.: PhD Thesis, ICT Prague 2006.

FIXACE TĚŽKÝCH KOVŮ V GEOPLYMERNÍ MATRICI
NA BÁZI HNĚDOUHELNÉHO POPÍLKU

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Alkalicky aktivovaný hnědouhelný popílek (geopolymer) může být použit jako matrice pro fixaci těžkých kovů. Geopolymerní materiály a kaše portlandského cementu byly připravovány za přídavku solí těžkých kovů (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} a Pb^{2+}). Při přípravě geopolymerního materiálu byla použita směs vodního skla a NaOH jako alkalický aktivátor. Přítomnost těžkých kovů v geopolymerním materiálu nezpůsobuje prodloužení doby tvrdnutí, jak je tomu u portlandského cementu. Přísada těžkých kovů do portlandského cementu způsobuje neakceptovatelné prodloužení doby tuhnutí až na několik dní. IČ a NMR spektra geopolymerních materiálů potvrzují průnik Al atomů do struktury Si–O–Si, kdy se vytvářejí struktury obsahující AlQ_4 (4Si), $AlQ_{2,3}$ (2-3Si) a Si(3Al). Těžké kovy jsou v amorfní matrici geopolymeru rovnoměrně rozptýleny a nezpůsobují vznik nových krystalických látek. Vyluhovatelnost těžkých kovů (Zn^{2+} , Cu^{2+} , Cr^{3+} , Cd^{2+} and Pb^{2+}) z matrice geopolymeru není stejná a je v hodnotách odpovídající 1. až 3. třídě vyluhovatelnosti (podle předpisů platných v ČR). Nejlepších výsledků bylo dosaženo při fixaci Zn, kdy použití portlandského cementu je prakticky nemožné. Hodnoty pevností i vyluhovatelnosti geopolymerních materiálů se výrazně zlepšují při přídavku látek obsahujících Ca.