ALKALI-ACTIVATED FLY ASH GEOPOLYMERIC MATERIALS

František Škvára, Jan Šlosar, Jan Bohunek and Alena Marková

Department of Glass and Ceramics, ICT Prague
CZ-166 28 Prague 6, Technická 5, Czech Republic.
E-mail: skvaraf@vscht.cz

ABSTRACT

Alkaline activation of fly ash yields materials whose strength exceeds that of standard Portland cements. Alkaline activation (AA) of fly ash in aqueous medium at pH>12, when the material sets and hardens, is a process differing from hydration of inorganic binders such as Portland cement. In the former process (mostly taking place by the "through solution" mechanism) the atoms of Al (and probably also those of Ca) penetrate the originally silicate lattice of fly ash, producing a 2D-3D inorganic hydrated polymer (geopolymer) having the general formula $M_n\left[-(Si-O)_z - Al-O\right]_n . wH_2O$.

The hydration products of alkali-activated fly ash are amorphous in character, with prevailing $Q^4(2Al)$ arrangement and minority crystalline phases. The properties of alkali-activated fly ash depend on the way of preparing the mix, in particular on the concentration of the alkaline activator and on ambient moisture conditions. The optimum conditions were attained by curing at $60 - 90^oC$ in open atmosphere. Additions of blast-furnace slag to alkali-activated mixes bring about significant increases in strength (more than 150 MPa in compression) under hydrothermal conditions at $60 - 90^oC$ when also the C-S-H phase is formed apart from the geopolymeric one. Materials based on AA fly ash can be characterized as "chemically bonded ceramics", or as geopolymers, or as low-temperature hydrated aluminosilicate glasses.

Key words: Fly ash, geopolymer, high strength, new materials

1. INTRODUCTION

Slag-alkali cements[1,2], alkali-activated gypsum-free cement [3], cements of the Pyrament [4] type or geopolymeric binders [5,6,7] are new types of inorganic binding agents whose common feature is alkaline activation of clinker or substances with latent hydraulic properties, such as slag or fly ash. The effect of solutions of alkaline compounds (such as NaOH, Na_2CO_3 or Na_2SiO_3) on hydraulically active substances consists of disrupting the Si-O-Si bonds and producing hydrates of alkali-lime aluminosilicates similar to zeolites, and hydrates of the type C-S-H phase, gehlenite hydrate and hydrogarnates. Alkali-activated binders provide the possibility of utilizing waste materials, because the properties of materials based on alkali-activated binders are often superior to those of concrete and mortar prepared from standard Portland cement. The presence of zeolite-type substances is responsible for modifying the properties of the alkali-activated binders, for instance by increasing their resistance to acids [8] or improving their ability to immobilise heavy metals [9,10].

The literature presents relatively little information on binders based on alkali-activated fly ash. However, the results published recently [11,12,13] show that alkaline activation is also applicable to materials such as fly ash, similarly to the case of blast-furnace slag.

The Czech Republic produces annually more than 10 million tons of fly ash. Some of it is utilized as an additive to cements and concrete, but the majority is disposed of on dumps (for instance in a mixture with waste gypsum). For this reason we have been dealing with other possibilities of using waste power station fly ash, and with the development of new materials based on alkali-activated fly ash.

The present study is concerned with the effect of alkaline activators of the type NaOH and Na_2SiO_3 on aqueous suspensions of fly ash, also in the presence of ground granulated blast-furnace slag.

2. EXPERIMENTAL

The raw materials employed in the study were power station fly ash and granulated blast-furnace slag. Their chemical compositions are given in Table 1.

Table 1.

wt.%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	Combustible substances
Slag	40.46	7.31	0.25	41.93	6.82	0.95	0.63	0.41	0.19		
Fly ash	53.79	32.97	5.51	1.84	0.92	0.46	1.76	0.37	2.1	0.15	0.74

In the experiments, use was made of non-ground fly ash with a specific surface area of 210 m^2/kg (Blaine), and of fly ash samples ground to a specific surface area of 450 - 600 m^2/kg. The slag was ground to a surface area of 350 m^2/kg and 520 m^2/kg respectively. The binder was prepared by mixing the fly ash and the slag in proportions over the range from 100 to 5 wt.% fly ash and from 0 to 95 wt% slag. The alkaline activator was added in the form of solution to the dry mixture of fly ash and slag. The SiO_2/Na_2O ratio (module M_S) of the alkaline activator was adjusted by adding NaOH to water glass having the module $M_S = 1.68$ so as to obtain values over the range of $M_S = 0.6$ - 1.6. The water glass employed had the composition 25.98% SiO_2, 15.49% Na_2O a 58.53% H_2O. The total concentration of the alkaline activator was varied over the range of 4 to 10% Na_2O of the binder weight. The pastes prepared in the experiments had mostly a w of 0.30 (w = weight of H_2O /weight of fly ash+ slag).

The binder pastes were moulded into specimens 20x20x20 mm in size, which were kept for 24 hours in an environment of 95% relative humidity and then unmoulded. The subsequent curing was carried out under various conditions of temperature and relative humidity. The "moisture cured" specimens were kept in an environment of 95% R.H. up to the time of compressive strength testing. Some specimens was subjected to "hydrothermal curing", namely after the 24 hours of curing at 95% R.H. they were heated up to 60°C during 1 hour, up to 40 – 90°C during 2 hours and kept at the respective temperatures for an additional 4 hours. In the course of the hydrothermal curing process the specimens were kept in an enclosed space where the water vapour pressure corresponded to the respective temperature. Following this hydrothermal treatment the specimens were kept at 20°C and 40-50% R.H. up to the term of strength testing. The remaining part of the specimens were exposed to "dry curing", when following their preparation they were placed in a drying oven at a temperature of 60 – 90°C (in open atmosphere) for 4 to 24 hours and then kept in air at 40 – 50% R.H. up to the time of testing. The compressive strength was tested after 2, 7 and 28 days. The fragments from the compressive strength tests were studied by X-ray diffraction, FTIR and thermal analysis and by high-pressure mercury porosimetry. The NMR MAS spectra ([29]Si, [27]Al) were also measured. The microstructure was studied on fracture surfaces by the scanning electron microscope, and ED spectrometric analysis was carried out at selected points.

2.1 Results and Discussion

It may be generally said that the strength of alkali-activated (hereinafter AA) fly ash is influenced by the M_S modulus and the concentration of Na_2O in the alkaline activator, where the optimum performance was achieved at Na_2O concentration of 7 to 10% and at M_S of 0.6 to 1. The curing conditions are the dominant factor controlling the strength of AA fly ash. The initial strength of the AA fly ash system (for "moist curing" at 25°C) is very low and essentially independent of Na_2O concentration and the M_S module. The 28-day strength of the systems after curing at 20°C is also relatively low. A considerable increase in strength of the AA fly ash system was due to hydrothermal curing. The "dry curing" brought about a significant increase in strength (Figure 1) when the 24-hour strength exceeded the 28-day strength of standard Portland cement.
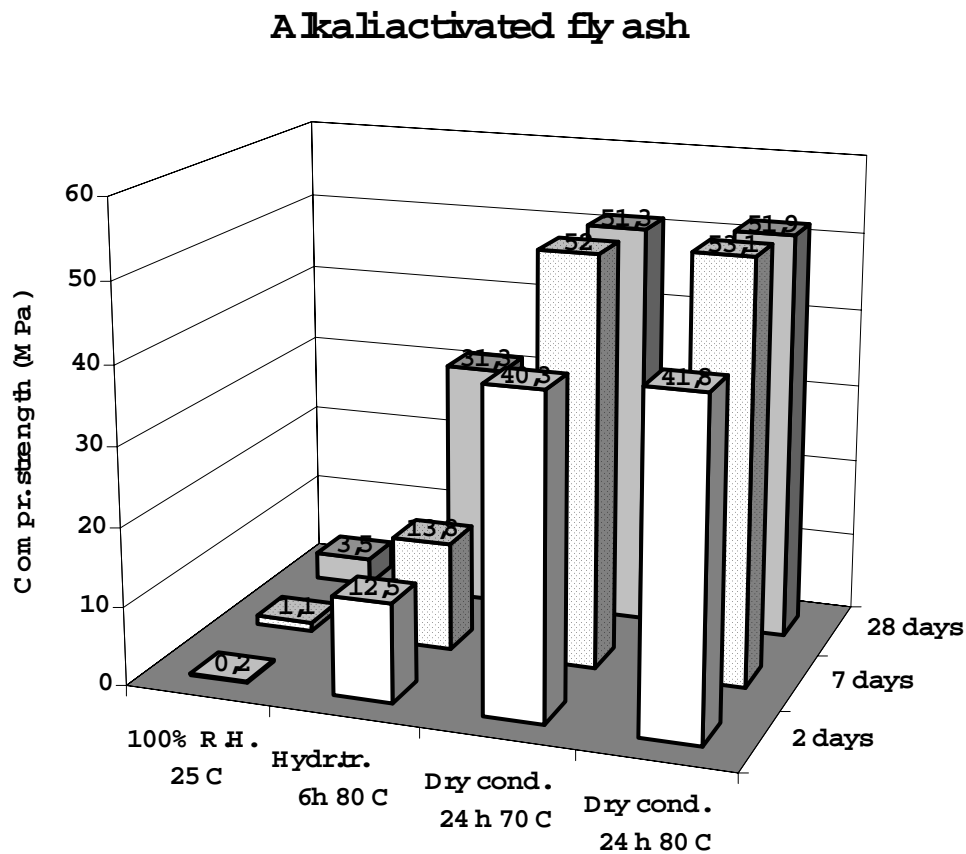

Figure 1. Compressive strength of alkali activated fly ash.

A very rapid increase in strength was found with mixes containing 50 – 70% fly ash and 50 – 30% slag, cured under hydrothermal conditions (Figure 2). However, relatively low strengths were achieved with systems of AA fly ash and slag under "dry curing conditions". Under "hydrothermal conditions of curing" the effect of grinding fineness of slag and fly ash was significant. With the system composed of 50% fly ash and 50% slag, 28-day strengths of up to 170 MPa were achieved by hydrothermal curing. These strengths are comparable to those of the new bonding materials (DSP materials 120 to 130 MPa, MDF materials 100 – 300 MPa).
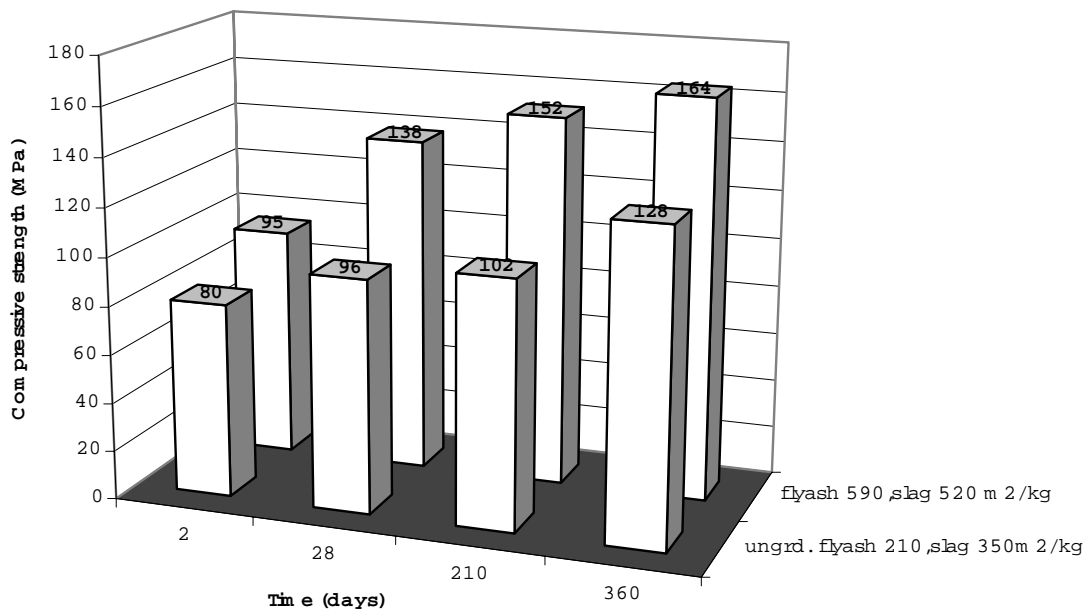
Figure 2. Compressive strength of alkali activated fly ash with slag.

The information obtained on the properties of the systems being studied indicates that the principle of alkaline activation is likewise applicable to power station fly ash. However, the formation of hydrates by alkaline activation of mixes comprising 100% fly ash is distinctly slower under both moisture and hydrothermal curing conditions than in the case of slag. Under the conditions of alkaline activation, the higher content of CaO in slag compared to fly ash obviously contributes to faster formation of bonding hydrates, particularly zeolite-like substances.

The basic hydration products in alkali-activated materials were identified in specimens hydrated at $20^{o}C$, in those cured under hydrothermal conditions, and in specimens first treated by "dry curing" and subsequently moisture-cured for additional 28 days.

The X-ray diffraction patterns (Figure 3) show that the hydration products are mostly of X-ray amorphous character, where the sole diffraction (apart from that of mullite and quartz from the original material) is that of d = 0.304 nm, and that only in the systems with a high content of slag. This line obviously corresponds to the C-S-H phase formed. The results of thermal analysis (Figure 4) likewise indicate the presence of hydrated amorphous (gel-like) products, showing a continuous loss of H_2O in terms of temperature. The loss in weight of the products is listed in Table 2.

Table 2.

Curing conditions	Δm (%)	
	20-200 ^{o}C	200-600 ^{o}C
Dry conditions	8.21	2.53
Hydrothermal curing	8.56	2.68

The TA data show that the H_2O content in the products is virtually identical regardless of the conditions of curing.

Regardless of the curing conditions, the basic matter of the hydrates is positively of amorphous glassy character, only rarely containing acicular minority formations (Figures 5, 6). The results of ED spectrometer analyses of the fracture surfaces show that most of the hydrates are sodium

aluminosilicate ones. The minority of hydrates are probably composed of polymerized water glass in which Al was partially substituted for Ca.

The hydrates contain residues of the original fly ash particles on which the effects of gradual dissolution are apparent. The AA fly ash was found to exhibit a relatively high porosity (of up to 50%) regardless of the curing conditions. The material contains closed spherical pores formed by dissolution of the original ash particles and possibly by air entrapped during the preparation. A distinctly lower porosity is shown by the AA fly ash–slag mixes, where the total porosity amounted to 2-10% and there was a shift towards smaller pore sizes (Figure 7 vs. Figure 8).

On FTIR spectra (Figure 9) one can find the differences due to different conditions of alkaline activation. The band corresponding to Si-O and Al-O vibrations [14,15] of the original fly ash at 1080-1090 cm^{-1} is shifted towards lower values by alkaline activation. This shift is explained as a result of incorporation of aluminium into the original structure of the Si-O-Si lattice, similarly as has been found in the case of zeolites [18] . The more distinct the shift, the higher degree of aluminium penetration from the original mullite into the $[SiO_4]^{4-}$ lattice.

Analogous results have been obtained by NMR measurements of AA fly ash in solid phase. Table 3 presents evaluation ^{29}Si MAS NMR spectra (deconvulence of the spectra obtained).
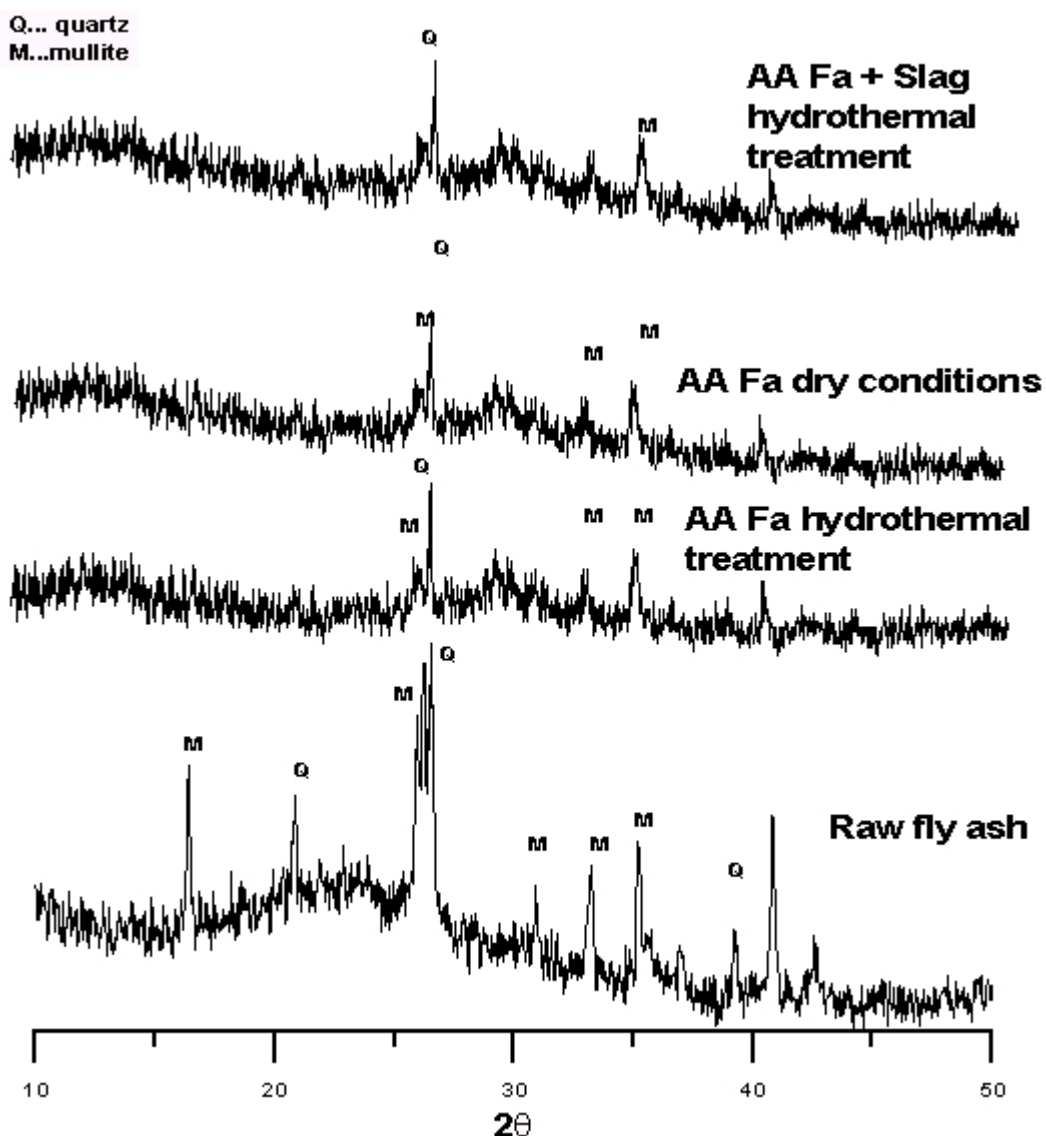

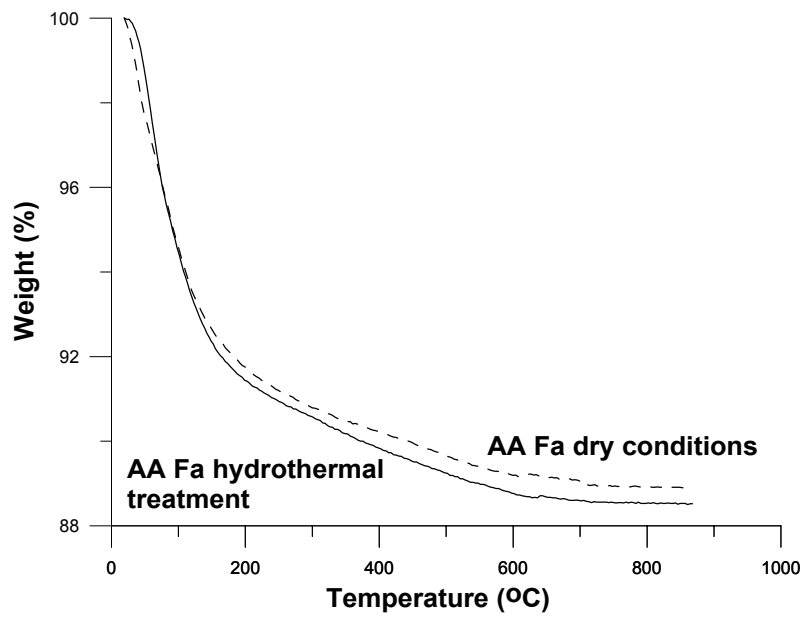Figure 3. X-ray spectrum of alkali activated materials.

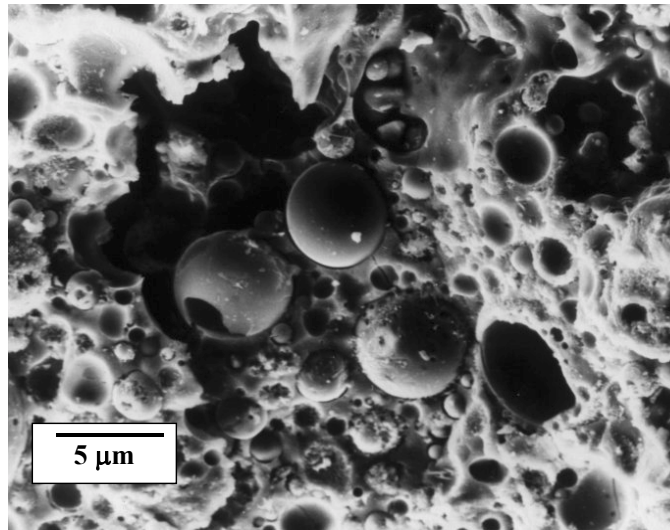Figure 4. TG analysis of alkali activated fly ash.

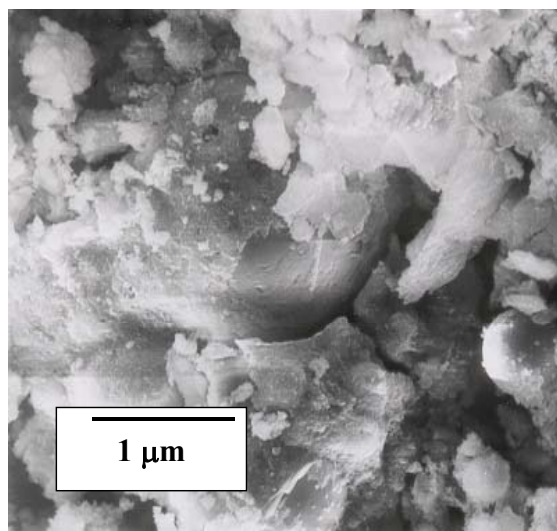Figure 5. Microstructure of alkali activated fly ash.

Figure 6. Microstructure of alkali activated fly ash (detail).
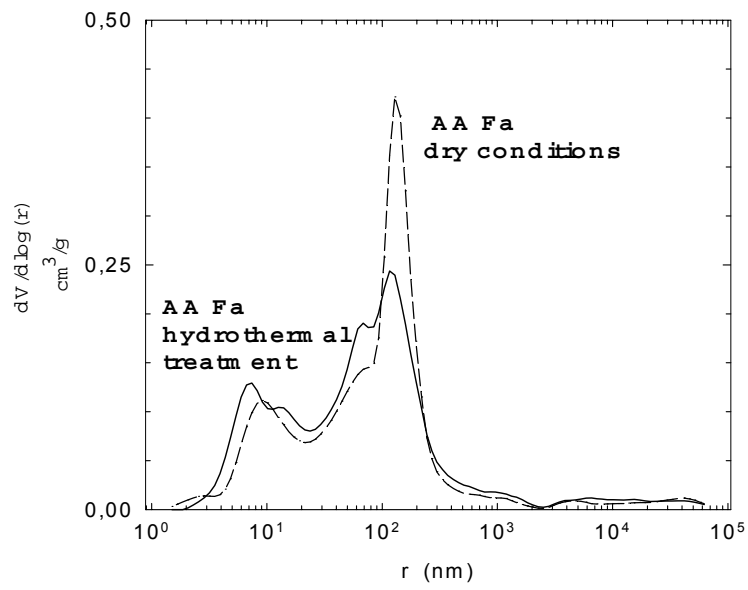
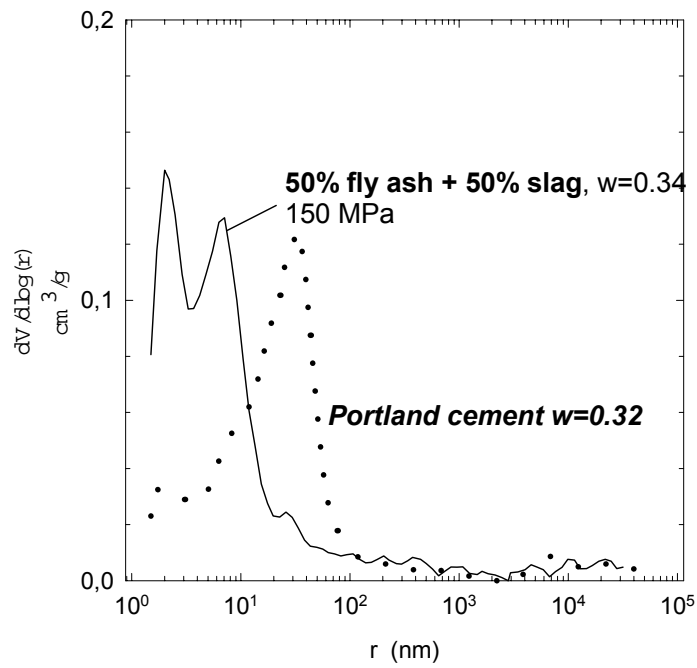Figure 7. Pore size distribution of alkali activated fly ash.

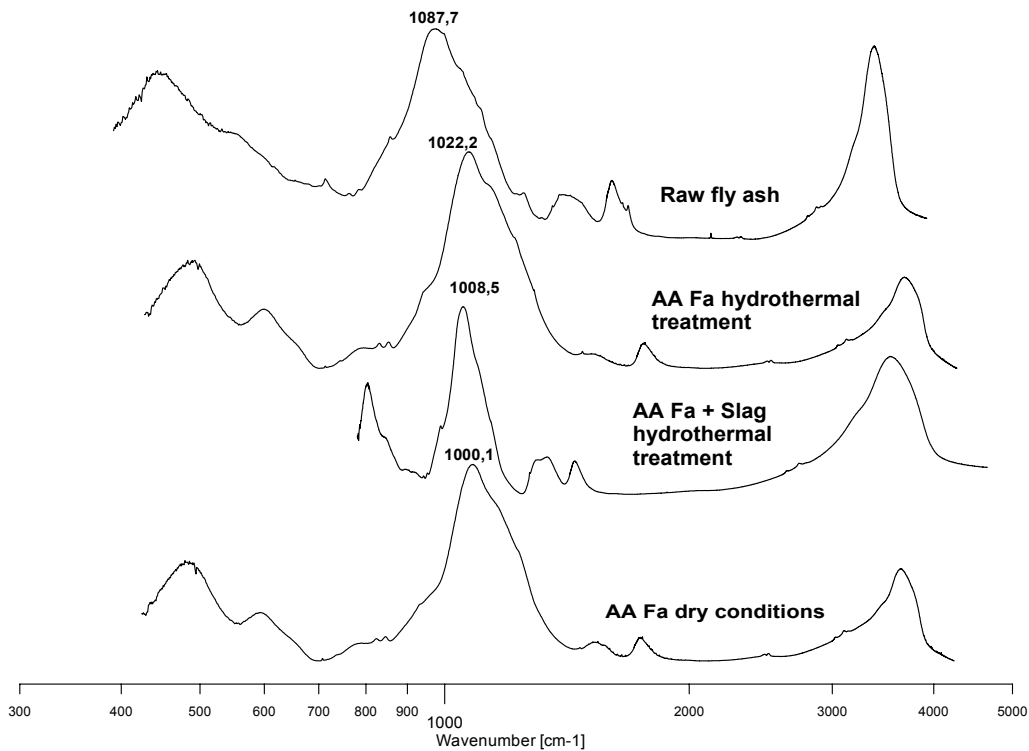Figure 8. Pore size distribution of alkali activated fly ash with slag.

Figure 9. Infrared spectrum of alkali activated materials.

Table 3. Evaluation of ^{29}Si MAS NMR spectra

Co-ordination Si,Al [16,17]	Si(4Al)	Si(3Al,1Si)	Si(2Al,2Si)	Si(0Al)	
Raw fly ash	-79.1 8%	-87.6 23%	-95.8 8%	-107.4 61%	shift (ppm) % in spectrum
AA fly ash hydrothermal curing		-88.5 40%	-96.2 23%	-107.3 32%	
AA fly ash dry curing		-90.1 52%	-98.7 17%	-106.0 28%	
AA fly ash + slag	-81.2 6%	-90.4 51%	-98.9 16%	-104.9 25%	

The deconvolution yielded signals with a very close value of the shift and with various representations in percent. The majority signal of the original fly ash was attributed to tetrahedral $[SiO_4]^{4-}$ (Si(0Al)); the co-ordination Si(2-3Al), also established for this spectrum, probably corresponds to the mullitic phase. A sample of AA fly ash that underwent hydrothermal curing exhibited a quite different structure. The Si(OAl) was eliminated down to 5% (in contrast to 61% in the fly ash), new formations appear in the structure, co-ordination Si(4Al) has a representation of 40% and the content of Si(4Al) was more than 50%. This shift is still more distinct with the sample of AA fly ash cured under "dry conditions". In this case more than 50% of the bonds show Si(4Al) co-ordination and the rest the Si(2-3Al) co-ordination. The ^{27}Al spectra are almost identical, which confirms the similarity of the two materials, where the only difference arises in the signal intensity of about 10 ppm (beyond the framework of the experimental error).

Alkaline activation of fly ash in an aqueous medium at pH >12, which causes the material to set and harden, differs from the processes of hydration of inorganic binders, for example of Portland cement. The former process obviously proceeds by the "through solution" mechanism where the fly

ash particles (SiO_2 and mullite) first dissolve in the strongly alkaline medium and a new geopolymeric structure is formed from the solution. A 2D-3D inorganic hydrated polymer (geopolymer) having the general formula $M_n[-(Si-O)_z - Al - O]_n . wH_2O$ is produced. An elevated temperature of 40 to 95°C is necessary for establishing an adequately interconnected lattice of bonds in the geopolymer. A significant part is played by the moisture conditions, where "hydrothermal curing" yields lower strengths than the "dry curing" conditions. According to the FTIR and NMR results, the "dry curing" causes more Al atoms to become incorporated in the originally silicate lattice of fly ash and to create a more interconnected lattice structure of the geopolymer. According to the results of TA the water content is virtually the same after heating up in open atmosphere and after hydrothermal curing. However, it is possible that the small loss of H_2O due to heating in open atmosphere ("dry curing" conditions) affects positively the process of incorporation of Al atoms and the degree of higher interconnection of the structure.

On the other hand, the hydrothermal curing conditions are optimal in the presence of another hydraulically active substance, namely the slag. In that case the strengths achieved by "dry curing" conditions are distinctly lower (by 30-50%). Under hydrothermal curing and alkaline activation conditions, blast-furnace slag is even capable of forming additional hydrates of type CSH and CAH phases that can contribute to higher strength.

The materials based on alkali-activated substances exhibiting latent hydraulic properties (fly ash, slag) obviously belong among the materials which, due to their high strengths and prevailingly amorphous structure, constitute a transition between the classical inorganic binders and ceramics, and can be affiliated to the group called "chemically bonded ceramics". The materials based on AA fly ash can be characterized as an inorganic polymer similar to zeolitic precursors. The materials can also be described as low-temperature hydrated aluminosilicate glasses.

It should be emphasized that the materials of the type of "chemically bonded ceramics", such as the MDF or DSP modifications, are frequently prepared by special methods such as isostatic pressing, vacuum compaction, etc. In contrast to this, in our experiments the materials based on chemically activated substances with latent hydraulic properties were prepared by standard methods, have acceptable rheological properties and acceptable times of early set.

3. CONCLUSIONS

The products of hydration of alkali-activated fly ash are of amorphous character and contain minority crystalline phases. The FTIR demonstrates the difference between the non-hydrated and the alkali-activated fly ash, where the main band corresponding to SiO and AlO vibrations is shifted towards the lower values. In the Si^{29} MAS NHR spectrum, the hydration products of alkali-activated fly ash exhibit a three-dimensional glassy structure with prevailing $Q^4(2Al)$ arrangement. Alkaline activation brings about penetration of Al atoms into the original silicate network of fly ash.

The properties of alkali-activated fly ash depend on the way the mix has been prepared and treated, particularly on the concentration of the alkaline activator and on moisture conditions. The optimum results were obtained under the "dry curing conditions".

Considerable increases in strength were obtained when blast-furnace slag was added to mixes of alkali-activated slag. "Hydrothermal curing" has proved as being the optimum one for these mixes, as apart from the geopolymeric phase, also C-S-H phases are formed under these conditions, with the resulting compressive strength of more than 150 MPa.

The alkali-activated binders provide the possibility of utilizing waste inorganic materials, and the properties of the resulting binders often surpass those of standard Portland cement. The materials

based on AA fly ash can be characterized as "chemically bonded ceramics", or as geopolymers, or as low-temperature hydrated aluminosilicate glasses.

ACKNOWLEDGMENTS

REFERENCES

[1] Talling B., Brandštetr J. in: Progress in Cement and Concrete, Volume 4: Mineral admixtures in cement and concrete, p. 297-339, editors S.L.Sarkar and S.N.Ghosh, ABI Books Private Ltd., New Delhi 1993.

[2] Krivenko P.: "Alkaline cements", Proc. 1st Intern.Conf. "Alkaline cements and concretes", Vol.1. p. 11-130, VIPOL Stock Comp. Kiev 1994

[3] Škvára F.: "Gypsum-free portland cement pastes with low water-to-cement ratio", MRS Symp.Proc. Vol. 370 "Microstructure of Cement-based systems/Bonding and Interfaces in Cementitious Materials", p. 153-158, editors S.Diamond, S.Mindess, Materials Research Society, Pittsburgh 1994

[4] Heitzmann R.F., Gravit B.B., K.J.L. Sawyer : US patent 4,842,649

[5] Davidovits J.: „Properties of geopolymer cements", Proc. 1st Intern.Conf. „Alkaline cements and concretes", Vol.1., p.131-150, VIPOL Stock Comp. Kiev 1994

[6] Davidovits J.: "Geopolymers - inorganic polymeric new materials", J. Therm. Anal. 37, p. 1633-1656, 1991

[7] Davidovits J.: "Chemistry of geopolymeric systems, terminology", Proc. Geopolymer Inter.Conf. (1999)

[8] Allahverdi A., Škvára F.:"Acid corrosion of geopolymeric cements", Proc. 7th CANMET Intern. Conf on Fly Ash, Silica Fume, Slag and Pozzolans in Concrete 2001, Vol. 2. p. 561-579

[9] Van Jaarsveld J.G.S, Van Deventer J.S.J., Lorenzen L.: The potential use of geoplymeric materials to immobilise toxic materials, Part I., Miner. Eng. 10, 659-669 (1997), Part II ,12, 75-91(1999)

[10] Rostami H., Silvestrim T.: "Chemically activated fly ash, CAFA", Proc. 13th Ann. Int. Pittsburgh Coal Conf., Vol.2, p. 1074-1079, University of Pittsburgh, Pittsburgh 1996

[11] Blaakmer J., van Loo W.: "Diabind, an alkali-activated slag fly ash binder", Proc. 1st Intern.Conf. "Alkaline cements and concretes", Vol.1., p. 347-360, VIPOL Stock Comp. Kiev 1994

[12] Škvára F., Bohunek J.:" Chemical activation of substances with latent hydraulic properties", Ceramics 43, 111-116 (1999)

[13] Palomo A., Grutzeck M., Blanco M.: "Alkali-activated fly ashes - A cement for the future", Cem. Con. Res. 29, 1323-1329 (1999)

[14] Derouane E.: "Infra-red structural study of aluminium deficient zeolites', J. Chem. Soc., Far. Trans. I, 70, 1402-1407 (1974)

[15] Querol X., Plana F., Alastuey A.: "Synthesis of Na-zeolites from fly ash", Inst. of Earth. Sci., 46, 793-799 (1996)

[16] Lippmaa E., Mägi M., Samoson A., Tarmak M.: Investigation of structure of zeolites by solid-state high-resolution ^{29}Si NMR spectroscopy, J. Am. Chem. Soc. 103, 4992-4996 (1981)

[17] Pfeifer H., Ernst H: "NMR studies of Zeolites", Universität Leipzig, Germany, p. 91-187, 1994

[18] Pichat P., Beaumont R., Barthomeuf D.: "Infra-red structural study of aluminium-deficient Y zeolites", J.Chem.Soc. Far.Trans.I 70, 1402-1407 (1974)