CHEMICAL ACTIVATION OF SUBSTANCES WITH LATENT HYDRAULIC PROPERTIES

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Alkaline activation (brought about by the effect of NaOH and Na_2SiO_3 solutions) is capable of increasing significantly the reactivity of substances with latent hydraulic properties, such as fly-ash or mixtures of fly-ash with blast-furnace slag. The optimum properties (compressive strength of 120 - 170 MPa) were achieved with ash-slag mixtures over the composition range 70 - 50 wt.% fly-ash and 30 - 50 wt.% slag, activated with alkaline activator having a M_S modulus of 0.6 and containing 7 wt.% Na_2O. The microstructure of hardened activated fly-ash and ash-slag mixtures is composed of amorphous hydrates of sodium aluminosilicates and the C-S-H phase.

INTRODUCTION

Slag-alkaline cements [1, 2], alkali-activated gypsum-free cements [3], Pyrament-type cements [4] or geopolymeric binders [5] have in common the alkaline activation of clinker or of substances with latent hydraulic properties, such as blast-furnace 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 is based on disintegration of Si-O-Si bonds, yielding hydrates of alkali-calcium aluminosilicates similar to zeolites, apart from C-S-H phase hydrates, gehlenite hydrate and hydrogarnates. Alkali-activated binders provide the possibility of utilizing inorganic waste materials because the properties of mortars and concretes based on activated binders are sometimes superior to those of standard Portland cements. The presence of zeolite-type substances is responsible for advantageous changes in the alkali-activated binders, for example a higher resistance to acids.

Most studies concerned with alkali-activated binders were devoted to slag-alkaline cements. The literature presents comparatively little data on binders based on alkali-activated fly-ash. The papers by Silverstrim et al. [6], Blaakmer and van Loo [7] indicate that alkaline activation can also be used in the case of fly-ash type materials, in a way similar to that of blast-furnace slags.

The present article is devoted to the study of the effects of alkaline activators (NaOH and Na_2SiO_3) on aqueous suspensions of fly-ash and ground granulated blast-furnace slag [8].

EXPERIMENTAL PART

The materials used in the study were power-station fly-ash Chvaletice and ground granulated blast-furnace slag Vítkovice. The chemical compositions of the substances are given in table 1.

In the experiments, use was made of non-ground fly-ash with a specific surface area of 210 $m^2\ kg^{-1}$ (Blaine) as well as of fly-ash samples ground in ball mill to a surface area of 450 - 600 $m^2\ kg^{-1}$. The blast-furnace slag was ground in a vibration mill to a surface area of 350 and 520 $m^2\ kg^{-1}$ respectively. The binder was prepared by blending the ash and the slag over a proportion range of 100 - 5 wt.% ash + 0 - 95 wt.% slag. The SiO_2/Na_2O ratio (the M_S modulus) in the alkaline activator was adjusted in the individual experiments over the modulus range from M_S = 0.6 to 1.6 by additions of NaOH to the water glass, which itself had a modulus of M_S = 1.68. The total concentration of the alkaline activator was kept so that the Na_2O content amounted to between 4 and 10 % of the binder weight. The alkaline activator was added in the form of solution to the dry

Table 1. Composition of slag Vítkovice and fly-ash Chvaletice (wt.%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	Ign. loss
Slag	43.25	7.51	0.5	41.47	4.36	0.82	0.63				
Ash	52.4	26.7	8.6	3.1	1.16	0.87	1.64	0.37	2.1	0.15	1.26

mixture of ash and slag. The pastes were mostly prepared with a water ratio of 0.30 which provided acceptable workability.

The pastes prepared were characterized by the time of early set (Vicat) and by determining their relative visual workability. The latter was based on ratings ranging from 4 (for a freely flowing paste) to 0 (an unworkable paste). The binder pastes were formed into specimens 20 × 20 × 20 mm in size which were subject to two ways of curing: "moist curing" consisted of keeping in moulds in 95 % relative humidity (R.H.) for 24 hours, then unmoulding (if strong enough) and keeping in the same environment until testing. The "hydrothermal curing" comprised 24 hours in moulds at 95 % R.H., then heating up to 60 °C during 1 hour and to 40 - 90 °C during two hours. The specimens were kept at the final temperature (in most cases 80 °C) for 4 hours. After that the specimens were stored "dry" at 20 °C at 40 to 50 % R.H. until the testing. Compressive strengths were determined after 2, 7 and 28 days. The broken specimens were subjected to X-ray diffraction and DTA analyses. The microstructure of fracture surfaces was studied by scanning electron microscopy, and selected areas analyzed by the ED spectrometer (ZAF correction, oxygen counted up to 100 %).

Apart from pastes, also mortars were prepared with water ratios ranging from 0.30 to 0.35 and binder-to-sand ratios of 1:3 to 1:2, and with alkali activator concentrations based on the optimized values found for the binder pastes.

The rheological properties of activated slag-ash mixtures pastes depend on the M_S modulus and on Na_2O content (cf. figure 1). An improvement of workability and thus the possibility of reducing the water ratio results from increasing the proportion of ground slag in the ash-slag mixtures, from reducing the M_S modulus of the alkaline activator, and from increasing the overall Na_2O concentration. The paste workability is impaired by grinding the ash and slag to a greater fineness.

The time of early set of the mixture is reduced when the content of ground slag is increased (figure 2). This rule holds for all the Na_2O concentrations studied and for all of the M_S moduli. With respect to the time of early set, mixtures with a high ash content should use activators with a M_S modulus ranging from 0.6 to 1.0, whereas activators with M_S moduli higher than 1.0 are more suitable for mixtures richer in ground slag. The effect of particle size on the time of set is slight, the latter becoming somewhat shorter as a result of grinding to higher fineness.

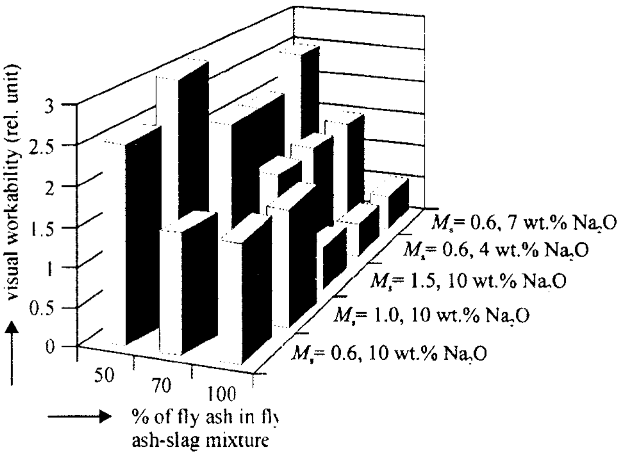

Figure 1. Visual workability vs. composition of alkali-activated ash-slag mixtures.

The strengths of alkali-activated ash-slag mixtures depend on the ash/slag ratio, on M_S modulus, on Na_2O concentration and on curing conditions (figures. 2 - 7). For systems with a high ash content the initial strengths (at 20 °C) are very low and virtually independent of Na_2O concentration and the M_S modulus. The 28-day strengths of the systems cured at 20 °C are likewise relatively low. An increase in the slag content brings about distinct improvements in both short- and long-term strength development at 20 °C.

Hydrothermal curing has a considerably strong effect on strength development of the systems in question (figures 6, 7) when both short- and long-term strengths increase with increasing temperature and time of the hydrothermal treatment. However, prolonging of the hydrothermal curing beyond 6 to 8 hours has no significant effect.

At a high M_S modulus of 1.5 the initial reactivity of the mixture is very poor and the strengths are virtually immeasurable. Somewhat higher strengths are only achieved at higher contents of slag and with hydrothermal curing. A considerable increase in strength can be attained with M_S modulus values of less than 1.0. A very rapid rise in strength was established for mixtures containing 50 - 70 wt.% fly-ash and 50 - 30 wt.% slag. Still higher slag contents cause the strength to fall a little. The results obtained indicate that a high content of alkaline activator (10% Na_2O) and a low M_S modulus would be required to achieve measurable strengths with systems containing 100-95 wt.% fly-ash. Alkali-activated systems comprising fly-ash alone (free of ground slag additions) exhibit poor strengths even under conditions of hydrothermal curing.

With mixtures containing 50 wt.% fly-ash and 50 wt.% slag, high strengths can be achieved at low M_S moduli even at a lower Na_2O concentration (7 wt.%). Lower Na_2O concentrations can only be used with systems containing prevailing proportions of slag. A comparison of 2-day and 28-day strengths shows that the strength rise in the case of hydrothermal conditions is small compared to humidity curing. The speeding up

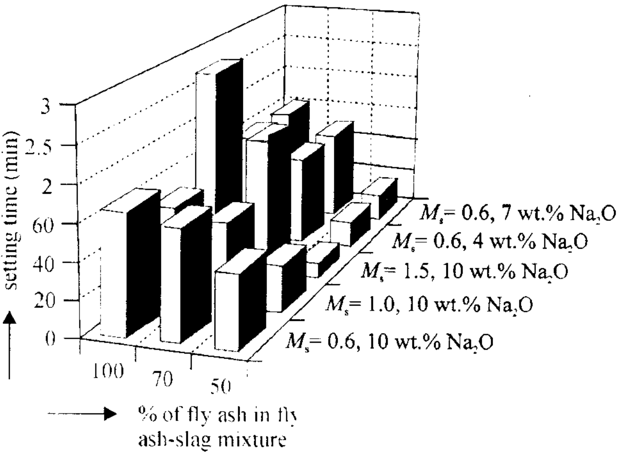

Figure 2. Setting point vs. composition of alkali-activated ash-slag mixtures.

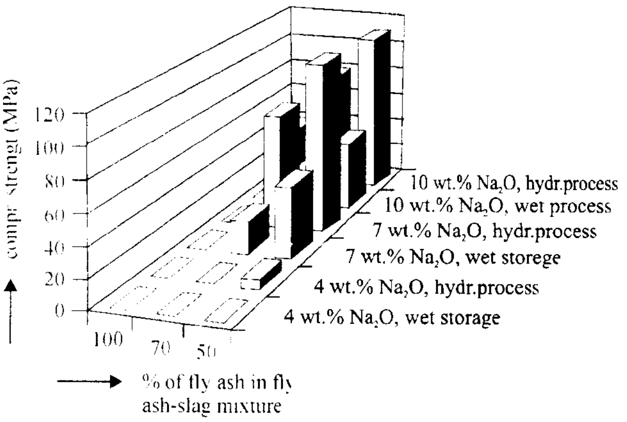

Figure 3. Two-day compressive strength at M_S = 0.6 in terms of composition of alkali-activated ash-slag mixtures cured at 20 °C as well as under hydrothermal conditions.

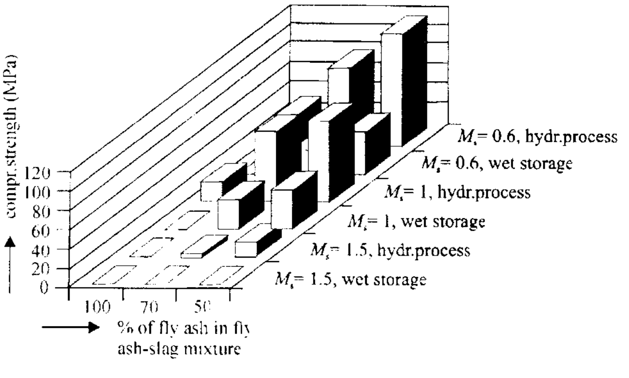

Figure 4. Two-day compressive strength at a content of 10 wt.% Na_2O (alkaline activator) in terms of composition of alkali-activated ash-slag mixtures cured at 20 °C as well as under hydrothermal conditions.

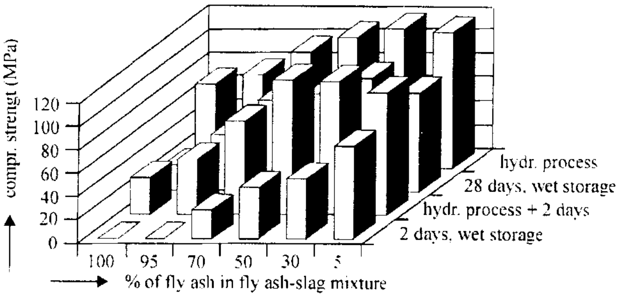

Figure 5. Effect of composition of alkali-activated ash-slag mixture on 2-day and 28-day strengths after curing at 20 °C and under hydrothermal conditions.

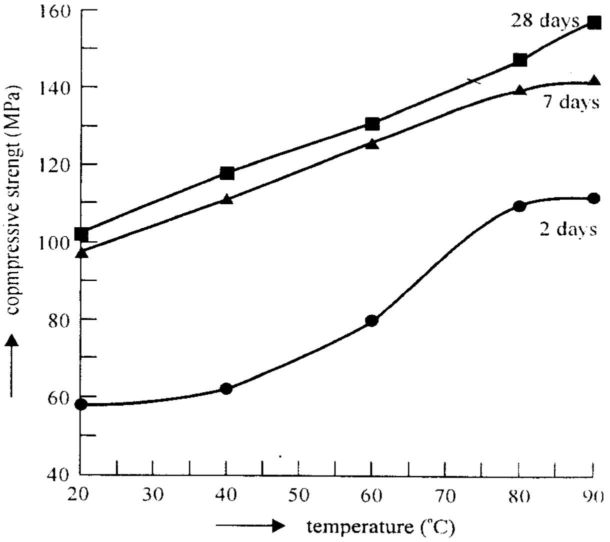

Figure 6. Compressive strength vs. temperature of isothermal heating at 80 °C under hydrothermal conditions of alkali-activated mixture of 50 wt.% slag and 50 wt.% fly-ash.

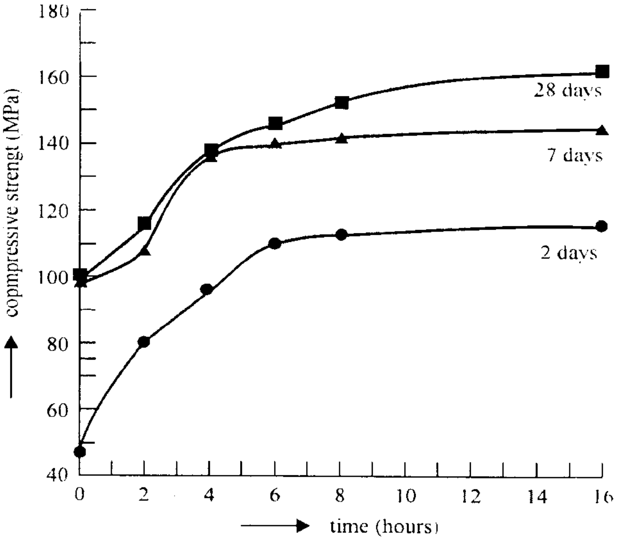

Figure 7. Compressive strength vs. time of isothermal heating at 80 °C under hydrothermal conditions of alkali-activated mixture of 50 wt.% slag and 50 wt.% fly-ash.

of hydration by hydrothermal conditions is considerable. Long-term strengths (over 180-270 days) of alkali-activated mixtures show further increase in strength under the "dry curing" conditions.

The fly-ash particle size has an only limited effect on the strength achieved but this does not apply to slag where the fineness of grinding is of great importance (figure 8). With the system containing 50 wt.% fly-ash and 50 wt.% slag, use of additionally ground slag, a M_S modulus of 0.6, a content of 10 wt.% Na_2O and hydrothermal curing resulted in 28-day strengths of up to 170 MPa.

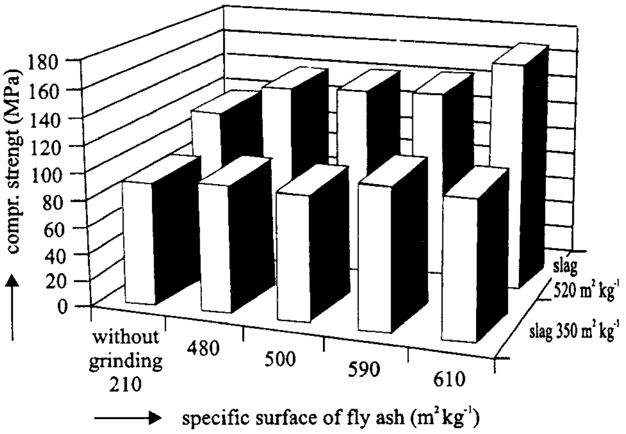

Figure 8. Effect of grinding fineness of fly-ash and slag on compressive strength of alkali-activated ash-slag mixtures. Fly-ash: slag = 0.5, M_s = 0.6, 10 wt.% Na_2O.

Analogous results were obtained with mortars where strengths ranging from 100 to 140 MPa were obtained both after curing at 20 °C and after hydrothermal treatment.

The experimental data on the properties of the systems in question show that the principle of alkaline activation is also applicable to power-station fly-ash. However, the formation of hydrates in mixtures comprising 100 wt.% fly-ash is much slower, even under hydrothermal conditions, than in the case of slag. The higher content of Al_2O_3 and CaO in slag as compared to fly-ash obviously contributes to formation of bonding hydrates, in particular those similar to zeolites. The data obtained indicate that high strengths can be obtained by optimizing the composition of the solid phase of the binder, namely the ash-to-slag ratio and the composition of the alkaline activator. In contrast to slag-alkaline cements, the optimum composition of the alkaline activator lies at lower values of M_S.

After curing at normal temperatures as well as after hydrothermal curing, materials based on alkali-activated substances with latent hydraulic properties (ash-slag mixtures) attain high strengths which markedly exceed those achieved with standard Portland cements. The strengths attained are even comparable to strengths of new materials, as shown by table 2.

Table 2. Comparison of compressive strength (MPa) of alkali-activated fly-ash with other hydrated materials.

Portland cement	DSP materials	MDF materials	Slag-alkaline materials	Alkali-activated fly-ash
22.5 - 62.5	120 - 130	100 - 300	50 - 120	up to 170

The basic products of hydration in alkali-activated mixtures were identified in specimens hydrated at 20 °C and cured hydrothermally at 80 °C, following further 28 days of "dry curing". The basic material of the hydrates (regardless of the curing conditions) is of prevailingly amorphous character only seldom containing needle-shaped minority formations. X-ray diffraction patterns (figure 9) show that the hydration products are prevailingly of X-ray amorphous character where the only diffraction (apart from those of the original materials) is that at d = 0.304 nm, solely occurring in systems with a high content of slag. The line obviously corresponds to the C-S-H phase formed. The results of DTA (figure 10) are likewise indicative of amorphous (gel-like) products characterized by the width of the endothermic peaks. The results of ED spectrometer analyses of fracture surfaces are listed in table 3. It appears that most of the hydrates consist of amorphous matter composed of sodium aluminosilicate hydrates. The Na_2O content in the solid phase of the dominant products virtually corresponds to Na_2O concentration in the alkali activator, which means that the sodium from the activator has been built into the crystalline lattice of the hydrates. The minority part of the hydrates is probably composed of polymerized water glass where Si was partially substituted by Al.

The materials based on chemically activated substances with latent hydraulic properies obviously belong among materials which, due to their high strength and a prevailingly amorphous microstructure, represent a transition between classical inorganic binders and ceramics, and can be ranked in the group called "chemically bonded ceramics" together with materials like MDF or DSP which are often prepared by special methods such as isostatic pressing, evacuating, and the like. However, the materials based on chemically activated hydraulic substances are prepared by standard methods, show acceptable rheological properties and a suitable setting point. In this respect one can see further application possibilities for these binders.

Table 3. ED spectrometer analysis of hydration products (wt.%), (ZAF correction, O calculated up to 100 %) on fracture surfaces, hydrothermal curing at 80 °C, 10 wt.% Na_2O, $M_S = 0.6$, $w = 0.30$.

	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Main amorphous part of hydrates, 100 wt.% ash	7.74	23.47	61.44	1.39	1.22	0.81	3.93
Minority part of hydrates (needles), 100 wt.% ash	26.87	10.88	55.43	1.33	2.05	0.83	2.61
Main amorphous part of hydrates, 50 wt.% ash + 50 wt.% slag	7.64	27.34	57.51	1.16	2.54	0.84	2.07

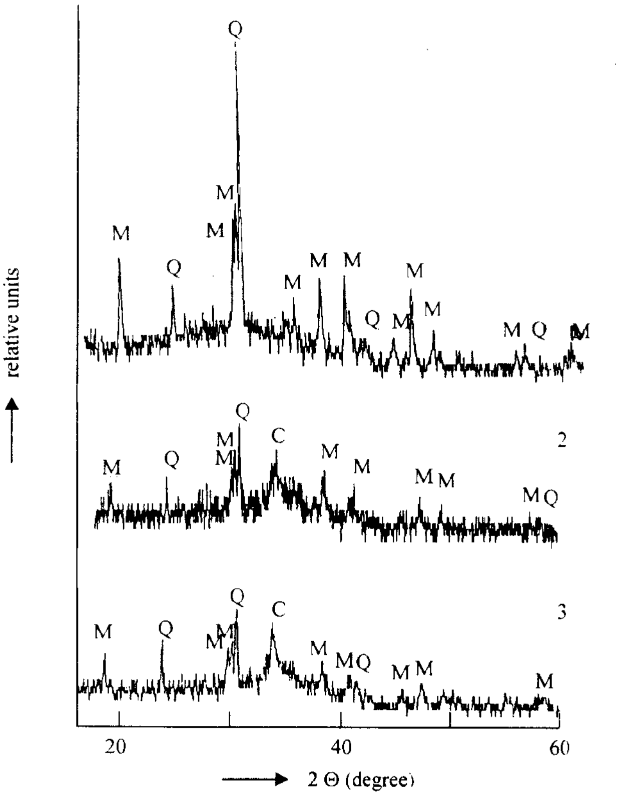

Figure 9. X-ray diffraction patterns.
A - original fly-ash, B - alkali-activated mixture of fly-ash and slag, 28 days of curing at 20 °C, C - alkali-activated ash-slag mixture, hydrothermal curing (80 °C) + 28-day "dry cure".

Further studies in the field of alkali-activated substances with latent hydraulic properties will be aimed at preparing materials of maximum strength by reducing the water ratio, at optimizing the hydrothermal curing and at studying the properties of materials prepared from these binders (in particular their resistance to aggressive environments and elevated temperatures).

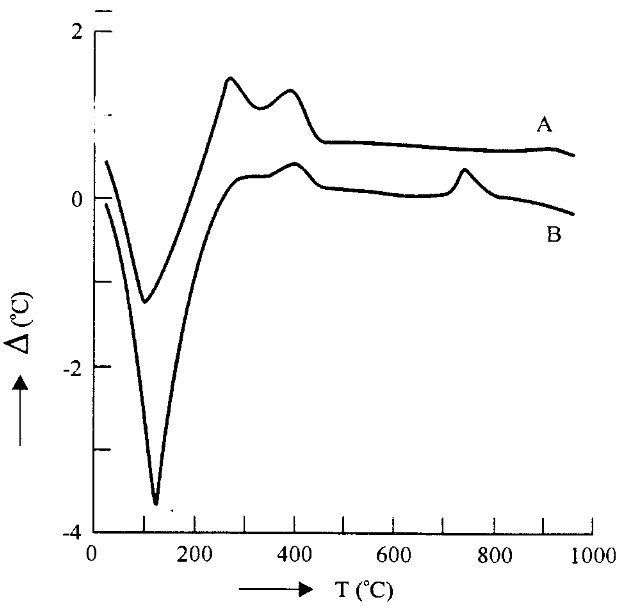

Figure 10. DTA curves: 1 - alkali-activated ash-slag mixture, 28 days of curing at 20 °C, 2 - alkali-activated ash-slag mix, hydrothermal conditions (80 °C) + 28-day "dry cure" 3 - hydrothermal process + 28 days

CONCLUSION

Alkaline activation (by the effect of NaOH and Na_2SiO_3 solutions) is capable of significantly promoting the reactivity of substances wqith latent chemical properties such as fly-ash or mixtures of fly-ash with ground slag.

Chemically activated mixtures of fly-ash alone (without additions of ground slag) exhibit poor strength even under conditions of hydrothermal curing.

Mixtures with a high fly-ash content activated by a low activator concentration (< 4 wt.% Na_2O) attain low 28-day strengths even when cured hydrothermally. A higher proportion of alkaline activator (more than 7% Na_2O) with a low M_S modulus ($M_S < 1$) is necessary for activating systems with a higher fly-ash content (of more than 70 wt.%).

Attainment of high strengths requires a certain minimum content of slag in the ash-slag mixture (approx. 10 – 30 wt.%). The presence of slag brings about a marked increase in reactivity of alkali-activated fly-ash mixtures at all of the activator concentrations studied, obviously due to the CaO brought into the mixture by the slag. In this way, also calcium hydrosilicates and hydroaluminates can take part in producing the strengths. The optimum properties (compressive strength 120 to 170 MPa) were achieved with systems composed of 70 – 50 wt.% fly-ash and 30 – 50 wt.% slag, activated by alkaline activator of 7 wt.% Na_2O concentration and with modulus $M_S = 0.6$.

The hardened alkali-activated fly-ash or fly-ash/slag materials consist of amorphous hydrates composed of sodium aluminosilicates and the C-S-H phases.

The materials based on alkali-activated substances with latent hydraulic properties obviously belong among materials which as a result of their high strengths and prevailingly amorphous microstructure constitute a transition between classical inorganic binders and ceramics, and can be ranked to the group called "chemically bonded ceramics".

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CHEMICKÁ AKTIVACE LATENTNĚ HYDRAULICKÝCH LÁTEK

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Alkalickou aktivací (působením roztoků NaOH a Na_2SiO_3) lze výrazně zvýšit reaktivitu latentně hydraulických látek jako je popílek resp. směsi popílku a strusky. Alkalicky aktivované směsi samotného popílku (bez přídavku mleté strusky) vykazují jen malé hodnoty pevností a to i v podmínkách hydrotermálního tvrdnutí. Směsi s vysokým obsahem popílku aktivované při nízké koncentraci aktivátoru (< 4 % Na_2O) mají velmi nízké pevnosti po 28 dnech i v případě tvrdnutí za hydrotermálních podmínek. Pro aktivaci systému s vyšším podílem popílku (více než 70 %) je nutný vyšší podíl alkalického aktivátoru (více než 7 % Na_2O) s nízkým modulem M_S ($M_S < 1$). Pro dosažení vysokých pevností je nutný určitý minimální podíl strusky ve směsi s popílkem (cca 10 - 30 %). Za přítomnosti strusky dochází k výraznému zvýšení reaktivity alkalicky aktivovaných popílků a to při všech studovaných koncentrací alkalického aktivátoru zřejmě proto, že struska přináší do směsi CaO. To také ukazuje, že se na pevnostech podílejí i vápenaté hydrosilikáty a hydroalumináty. Optimálních vlastností (pevností v tlaku 120 - 170 MPa) bylo dosaženo v systému s obsahem popílku a strusky v rozmezí 70 - 50 % popílku a 30 - 50 % strusky, který byl aktivován alkalickým aktivátorem v koncentraci 7 % Na_2O s modulem $M_S = 0.6$. Zatvrdlé alkalicky aktivované popílky resp. směsi popílku a strusky tvoří amorfní hydráty tvořené sodnými alumosilikáty a C-S-H fází. Materiály na bázi alkalicky aktivovaných latentně hydraulicky aktivních látek patří zřejmě mezi materiály, které v důsledku svých vysokých pevností a převážně amorfní mikrostruktury tvoří přechod mezi klasickými anorganickými pojivy a keramikou a řadí se mezi skupinu nazývanou "chemibally bonded ceramics".