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Alkali activated fly-ash

Introduction

Slag-alkaline cements [1,2,3], alkali-activated gypsum-free cements [4], Pyrament-type cements [5] or geopolymeric binders [6,7] 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, Na₂CO₃ or Na₂SiO₃ on hydraulically active substances is based on disintegration of Si-O-Si bonds, yielding hydrates of alkali-calcium aluminosilicates similar to zeolites $M_n[-(Si-O)_z - Al-O]_n \cdot wH_2O$, apart from C-S-H phase hydrates, gehlenite hydrate and hydrogarnets. Alkali-activated binders provide the possibility of utilising 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 [9,11].

Most studies concerned with alkali-activated binders were devoted to slag-alkaline cements [1,2,3]. The literature presents comparatively little data on binders based on alkali-activated fly-ash. The papers by Silverstrim et al. [8], Blaakmer and van Loo [9] and Palomo et al. [12] 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 Na₂SiO₃) on aqueous suspensions of fly ash, fly ash + ground granulated blast-furnace slag [10], fly ash + blended Portland cement [11].

Experimental

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.

Table 1. Composition of slag Vítkovice, fly ash Chvaletice and blended Portland cement

wt.%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅
Slag	43.2	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
Blend. PC	32.2	5.8	1.3	45.0	9.1	3.6	0.3	0.4		

In the experiments, use was made of non-ground fly-ash with a specific surface area of $210 \text{ m}^2/\text{kg}$ (Blaine) as well as of fly-ash samples ground in ball mill to a surface area of $450 - 600 \text{ m}^2/\text{kg}$. The blast-furnace slag was ground in a vibration mill to a surface area of 350 and $520 \text{ m}^2/\text{kg}$ respectively. The blended cement (20% clinker+80% slag + gypsum) was ground in ball mill to specific surface $290 \text{ m}^2/\text{kg}$. The binder was prepared by blending the ash and the slag (or blended PC) over a proportion range of $100 - 5 \text{ wt.}\%$ ash + $0 - 95 \text{ wt.}\%$ slag. The $\text{SiO}_2/\text{Na}_2\text{O}$ 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 mixture of ash and slag or blended PC. The pastes were mostly prepared with a water ratio of 0.30 , which provided acceptable workability.

The pastes prepared were characterised by the time of early set (Vicat) and by determining their relative visual workability. The binder pastes were formed into specimens $20 \times 20 \times 20 \text{ mm}$ in size which were subject to two ways of curing: "moist curing" consisted of keeping in moulds in $95\% \text{ r.h.}$ 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 $95\% \text{ R.H.}$, then heating up to 60°C during 1 hour and to $40 - 90^\circ\text{C}$ 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 $50\% \text{ r.h.}$ until the testing. Compressive strengths were determined after 2 , 7 and 28 days. The broken specimens were subjected to X-ray diffraction, TA analyses, Fourier transform infrared spectroscopy (FTIR) and high pressure Hg-porosimetry. The microstructure of fracture surfaces was studied by scanning electron microscopy, and selected areas analysed by the ED spectrometer (ZAF correction, oxygen counted up to 100%).

The rheological properties of activated slag-ash mixture pastes depend on the M_S modulus and on Na_2O content. 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. This rule holds for all the Na_2O concentrations studied and for all of the M_S module. 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 module 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.

The strengths of alkali-activated ash-slag mixtures depend on the ash/slag ratio and ash/blended PC, on M_S modulus, on Na_2O concentration and on curing conditions (Fig.1-4). 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 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% fly-ash and 50-30% 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% 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% fly-ash and 50% slag, high strengths can be achieved at low M_S moduli even at a lower Na_2O concentration (7%). 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 of hydration by hydrothermal conditions is considerable. Long-term strengths (over 360 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 (Fig.4). With the system containing 50% fly-ash and 50% slag, use of additionally ground slag, a M_S modulus of 0.6, a content of 10% Na_2O and hydrothermal curing resulted in 28-day strengths of up to 170 MPa.

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% 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 optimising the composi-

tion 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 DSP materials and MDF materials

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 prevalingly amorphous character only seldom containing needle-shaped minority formations. The results of TA (Fig.5) are likewise indicative of amorphous (gel-like) products characterised by the width of the endothermic peaks. XRD patterns (Fig.6) show that the hydration products are prevalingly 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 FTIR spectra (Fig.7) of alkali activated fly ash show differences when compared with the spectrum of the starting fly ash:

- The presence of added water increases intensity of bands at 3500 and 1650 cm^{-1}
- The main band due to Si-O and Al-O vibrations which is at 1080-1090 cm^{-1} in the fly ash, moves towards lower frequencies (1039 and 980 cm^{-1})

The results of porosity measurement are on Fig.8. The change in the concentration of Na_2O changed the pore size distribution. At same w/c is the porosity and pore size distribution of alkali activated fly ash lower than on Portland cement. The results of ED spectrometer analyses of fracture surfaces (Fig.9) appear 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 polymerised water glass where Si was partially substituted by Al.

The materials based on chemically activated substances with latent hydraulic properties obviously belong among materials, which, due to their high strength and a prevalingly amorphous microstructure, represent a transition between classical inorganic binders and ceramics. These alkali-activated materials can be ranked in the group called "chemically bonded ceramics" together with materials like MDF or DSP. 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.

Conclusion

Alkaline activation (by the effect of NaOH and Na₂SiO₃ solutions) is capable of significantly promoting the reactivity of substances with 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% Na₂O) attain low 28-day strengths even when cured hydrothermally. A higher proportion of alkali activator (more than 7% Na₂O) with a low M_S modulus (M_S < 1) is necessary for activating systems with a higher fly-ash content (of more than 70%).

Attainment of high strengths requires a certain minimum content of slag in the ash-slag mixture (approx. 10 - 30%). 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% fly-ash and 30 - 50% slag, activated by alkaline activator of 7% Na₂O 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 new materials based on alkali-activated substances with latent hydraulic properties obviously belong among materials which as a result of their high strengths and prevalingly amorphous microstructure constitute a transition between classical inorganic binders and ceramics, and can be ranked to the group called "chemically bonded ceramics".

References:

1. Talling B., Brandštetr J. in: An 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. Proceedings of the 1st Intern. Conf. „Alkaline cements and concretes” VIPOL Stock Comp. Kiev 1994
3. Proceedings of the 2nd Intern. Conf. „Alkaline cements and concretes” VIPOL Stock Comp. Kiev 1999
4. Škvára F. : 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
5. Heitzmann R.F., Gravit B.B., K.J.L. Sawyer : US patent 4,842,649
6. Davidovits J.: Proc. 1st Intern. Conf. „Alkaline cements and concretes“, vol.1., p.131-150, VIPOL Stock Comp. Kiev 1994

7. Proceedings of G'99 "Geopolymer International Conference" July 1999, Saint-Quentin
8. Rostami H., Silvestrim T.: Proc. 13th Ann. Int. Pittsburgh Coal Conf., vol.2, p. 1074-1079, University of Pittsburgh, Pittsburgh 1996
9. Blaakmer J., van Loo W.: Proc. 1st Intern. Conf. „Alkaline cements and concretes“, vol.1., p. 347-360, VIPOL Stock Comp. Kiev 1994
10. Bohuněk J.: Thesis, Institute of Chemical Technology (Technical University), Dept. Glass and Ceramics, Praha (1998)
11. Marková A.: Thesis, Institute of Chemical Technology (Technical University), Dept. Glass and Ceramics, Praha (1999)
12. Palomo A., Grutzeck M.W., Blanco M.T.: Cem. Conr. Res. **29**, 1323-1329 (1999)

This study was part of the research project CEZ:MSM 223100002 "**Chemistry and technology of materials for technical applications, health and environment protection**" and research project of Czech Grant Agency No.104/99/0440 "**Revaluation of dangerous waste on the basis of ferric oxides with portion of heavy metals as a new additive to building materials**".

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