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Cement & Concrete Composites 28 (2006) 21-25



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Effectiveness of new silica fume alkali activator

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Received 6 April 2004; accepted 19 July 2005 Available online 10 October 2005

Abstract

The effectiveness of a new type of alkali activator is studied. The activator is a product of silica fume. The results obtained showed the silica fume activator as a highly effective substance for the alkali activation of the combinations of Portland cement, silica fume and blast furnace slag, and slag alone. The positive effect of activator is based on the intensification of the production of calcium silicate hydrates and the densifying of the forming pore structure of the activated binder. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Alkali activation; Alkali activator; Silica fume; Slag; Portland cement

1. Introduction

In recent years, alkali activated slags (AAS) have been developed in many countries owing to their energy conservation, low cost and excellent performance such as high strength, low heat evolution, low porosity, low solubility of the hydrates and resistance to chemical attack.

For effective utilization of the possibilities enabled by AAS it is most important to understand the relationships between processing of AAS materials and their properties. Compared to the Ordinary Portland cement, the quantitative or qualitative relations between strength and other properties and processing parameters of AAS materials are much less well understood [1,2].

Among the processing parameters like slag reactivity, composition of the starting AAS materials mixtures and curing conditions the alkali activator used a significant role plays. The hydration and hardening rate of AAS materials and subsequently their properties is influenced significantly by this component.

The significant role of alkali activator is based on the fact that slag alone reacts with water very slowly. But hydroxyl ions (OH⁻) supplied by alkali activator are known

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to increase the hydration rate by promoting dissolution of aluminate and silicate network in the slag. The hydrolytic ions may be introduced from strong alkalies such as NaOH, KOH, and Na₂SiO₃. Alkalies may be also produced trough various chemical reactions, for example by the reaction of sodium sulphate with calcium hydroxide under the production of calcium sulphate and sodium

The commonly used activators are sodium hydroxide, silicate, carbonate and sulphate. Sodium silicate or water glass is considered the most common and effective activator. A concentrated solution of water glass consists mainly of SiO₃²⁻ and HSiO₃⁻ ions with a SiO₃²⁻/HSiO₃⁻ ratio from 50:1 to 10:1. Main contributions of silicate anions to the strength of AAS materials are from both alkaline activation and the formation of silica gel. This can react with the calcium to form silica reach calcium silicate hydrates.

The most important property of water glass is the weight ratio of SiO₂/Na₂O. Commercially produced silicates have the ratio range of 1.5–3.2.

The efficiency of an activator depends on several factors. Among them the kind of type, dosage, ambient temperature and water-to-slag ratio are significant.

The significant factor also is the physico-chemical nature of the material to be activated. The presence of amorphous phases plays a significant role due to its considerable

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reactivity towards alkalies. The final structure of hardened AAS system is determined by the raw materials curing process [3–8]. One new type of activator represents silica fume activator (SFA) [9–12].

The subject of the paper is the presentation of the results of the study on the effectiveness of SFA compared with the current activator sodium hydroxide.

2. Experimental

2.1. Test specimens preparation

For the study mortar test specimens -20 mm edge cubes were used. The used mortars were prepared from the mixtures of silica sand (SS), Portland cement (PC), its combinations with silica fume (SF), slag (SL), and the studied SFA activator. For the comparison were prepared these mortars:

- the same mortars prepared instead of SFA activator with water,
- the mortar prepared from, slag, water, and sodium hydroxide expressed as 7% Na₂O.

The fresh mortar mixtures represented the material of identical consistency. More detailed information on the composition of the mortars in Table 1 is given.

The moulds with fresh mortar test specimens were cured 24 h at relative humidity of \approx 95% and 20 °C, and after demoulding in water at ambient temperature of 20 °C.

The properties of the test specimens studied were: compressive strength, chemically bound water, hydration products produced, and pore structure.

2.2. Test and methods used

These tests and methods were used:

• Standard method for the estimation of the compressive strength.

Table 1 Composition of the used mortars

Composition of binder	Mixtures prepared with SFA activator (g SFA/g cement)	Mixtures prepared with water (w/c)
Portland cement 100%	_	0.49
70% Portland cement	0.76	0.72
+ 30% silica fume		
50% Portland cement	1.06	1.00
+ 50% silica fume		
30% Portland cement	0.74	0.52
+ 70% slag		
10% Portland cement	0.74	0.52
+ 90% slag		
Blast furnace slag 100%	0.80	$0.41 + 7\% \text{ Na}_2\text{O}$

Weight ratio binder:sand is 1:3.

Table 2 Chemical composition and properties of the materials used

Composition (%)	Portland cement CEM I 42.5	Silica fume	Blastfurnace slag
Loss on ignition	1.38	2.35	2.25
Insoluble residue	1.18	2.34	_
SiO ₂	20.91	94.14	37.14
CaO	62.18	0.13	37.40
Al_2O_3	5.82	0.13	9.15
Fe_2O_3	3.40	0.18	1.05
MgO	2.36	0.18	11.70
SO_3	2.78	0.28	0.37
Specific weight (g cm ⁻³)	3.116	2.269	2.842
Specific surface (m ² kg ⁻¹)	334.3	15898	231.5
Normal consistency	29		Maximal size
			of grain 90 μm
Setting beginning end	2 h 45 min 4 h		- '

Mineralogical composition (Bogue)—% of Portland cement: C_3S —42.46; C_3A —9.73; C_3SO_4 —6.03; C_2S —27.90; C_4AF —10.21.

- Differential (DTA) and gravimetric (TG) thermal analysis using SDT 2960 device and standard thermal analysis programme T.A. Instruments.
- Mercury intrusion porosimeter using the combination of microporosimeter mod. 2000 and macropore unit 120, ERBA Science. Wetting angle 141.3° and surface tension of mercury 0.48 N m⁻¹ for the calculation of the results have been used. The estimation of pore with radius between 3.75 nm and \approx 0.3 mm was possible.
- Specific surface area calculated by means of the results of pore structure analysis.
- Content of chemically bound water in the hydration products calculated from the values of weight loss in the interval 100–500 °C estimated by means of TG.

2.3. Materials used

The composition and properties of the used Portland cement, blast furnace slag and silica fume are given in Table 2. The used sand was silica sand according to STN 720208.

The studied SFA activator represents a suspension of silica fume and water solution of alkali compound of the defined composition, and cured under the defined ambient temperature and time.

3. Results and discussion

It can be seen in the Figs. 1 and 2 the increased compressive strength of the mortars prepared with SFA activator opposite to those prepared with water. In Fig. 3 it can be seen again the increased compressive strength of the mortar prepared from slag and SFA activator opposite to that prepared with water, and Na_2O .

In Figs. 4 and 5 the DTA curves of the mortars are illustrated.

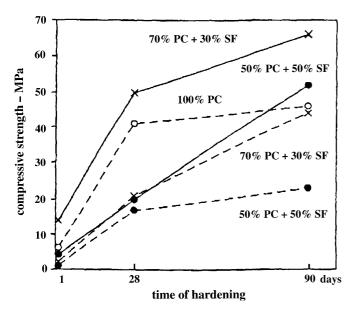


Fig. 1. Compressive strength of the mortars prepared from combinations of silica fume (SF) and Portland cement (PC) with SFA activator (full lines) and with water (interrupted lines).

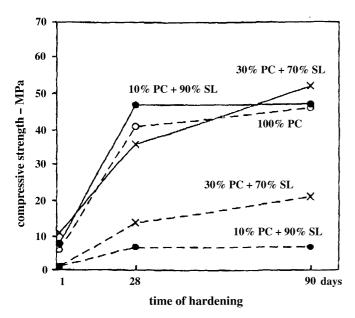


Fig. 2. Compressive strength of the mortars prepared from combinations of slag (SL) and Portland cement (PC) with SFA activator (full lines) and with water (interrupted lines).

DTA-grams showed endothermic peak at 120–180 °C. It is known that it usually conducts the presence of the hydration products. Then DTA-grams showed the endothermic peak at 540–560 °C corresponding to the present silica sand, and an exothermic peak at 770–850 °C. This usually conducts the presence of C–S–H phases in the material. Its position on the DTA curve on the CaO:SiO₂ ratio of the phases is dependent [13]. The increased exothermic peaks occurring on the DTA curves of the mortars 10% PC + 90% SL, 100% SL prepared with SFA activator

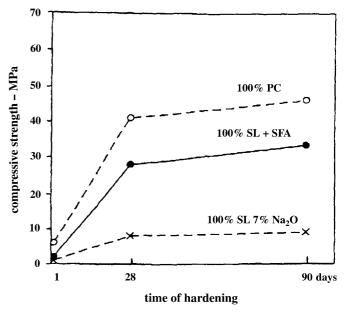


Fig. 3. Compressive strength of the mortars prepared from slag (SL) with SFA activator (full line) and with water and Na₂O (interrupted lines).

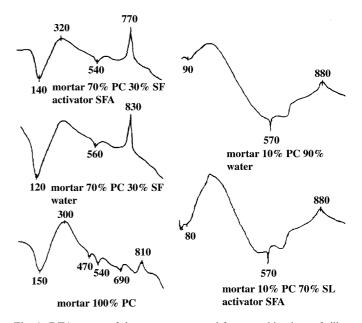


Fig. 4. DTA curves of the mortars prepared from combinations of silica fume and slag and Portland cement with SFA activator and water.

opposite to the Portland cement and slag mortars prepared with water, and Na₂O activator suggests that SFA activator may promote the formation of C–S–H phases in the material.

The observed significant increase of the content of chemically bound water (Table 3) at the mortar prepared from 10% PC + 90%, 100% SL, and SFA activator, representing the values 120%, and 303% seems to confirm the mentioned promoting effect of SFA activator. A good picture about the effect of SFA activators were

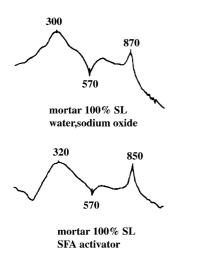


Fig. 5. DTA curves of the mortars prepared from slag with SFA activator and Na_2O .

provided by the results of pore structure analysis given in Table 3.

In comparison with the identical mortars prepared with water these effects of SFA activator could be observed:

- 1. Decrease of total porosity about 29–54%.
- 2. Significantly increased pore median about 260-3660%.
- 3. Decreased specific surface area.
- 4. Increase of macropore content.

These effects indicates these consequences:

- (i) densifying of pore structure showed by decrease of total porosity (effect 1),
- (ii) increase of heterogeneity of pore structure showed by the increased of macropore content, pore median, and by the decrease of specific surface area (effects 2–4).

It is well known that densifying of pore structures contributes to the strengthening of the cement based materials.

On the contrary consequences (ii) contribute to the decrease of the quality of the pore structure and compressive strength reduction.

It is evident that both consequences are clearly of a contradictory character. If the negative consequences (ii) of SFA activator would be minimalized the positive strengthening consequence (i) of SFA activator would be probably increased. This represents a potential way for the increasing of the effectiveness of SFA activator.

4. Conclusion

The results obtained showed silica fume activator as a very effective alkali activator for the binding systems based on the combination of Portland cement, silica fume and slag, and slag alone. According to the results obtained the positive effect of SFA activator seems to be based on the intensification of the production of calcium silicate hydrates and the densifying of the forming pore structure. The observed result was the increase of compressive strength of the activated binding system especially at the slag binder. This positive effect conducted the negative one causing a partial increase of heterogeneity of the pore structure reducing the strengthening effect of SFA activator. The possibilities of the minimalization of the reduction effect of SFA activator are worthy of more detailed study.

Acknowledgement

The author would like to thank the Slovak Grant Agency VEGA for its support towards this work (Grant 2/2039/23).

Content of chemically bound water and pore structure parameters of mortars after 28 days of their hardening

Composition of binder and water or SFA activator added	Chemically bound water (%)	Pore structure parameters			
		Total porosity (%)	Pore median (nm)	Macropore content (%)	Specific surface (m ² g ⁻¹)
100% PC water	2.67	10.9	82	13.7	2.78
70% PC water	5.22	18.9	36	8.68	8.85
30% SF SFA	4.03	8.7	1353	27.68	4.03
50% PC water	3.64	26.2	20	6.05	18.78
50% SF SFA	3.82	18.1	692	21.18	7.72
30% PC water	1.37	18.9	257	21.06	5.02
70% SL SFA	1.01	10.9	1485	24.00	4.23
10% PC water	1.76	20.1	438	17.08	1.76
90% SL SFA	3.87	12.5	2192	27.55	3.87
100% SL water $+$ Na ₂ O	1.15	23.8	3081	38.34	1.15
100% SL SFA	4.64	16.8	3894	33.70	1.43

PC—Portland cement; SF—silica fume; SL—slag, dosages of water and SFA—see Table 1.

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