Original papers

EFFECT OF CALCIUM ACETATE AS ACCELERATOR AND WATER REDUCER ON THE PROPERTIES OF SILICA FUME BLENDED CEMENT

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In the present work calcium acetate is used as accelerator and water reducer for the silica fume blended cement. The blended cement was prepared from 80 wt.% of ordinary Portland cement and 20 wt.% of silica fume. The dosages of calcium acetate were 0.0, 1.0, 2.0 and 2.5 wt.%. The water of consistency, and the times of initial and final set were determined. The rate of hydration was established by determining the content of free lime, that of chemically combined water, apparent density, total porosity and compressive strength of the hardened cement pastes. Calcium acetate acted as plasticizer, reducing the water of consistency of the blended cement pastes. It also shortened the times of initial and final set, reduced the content of free lime and increased the content of chemically bound water. The compressive strength increased with additions of calcium acetate up to 2.0 wt.% (the optimum), while higher additions caused the strength to decrease.

INTRODUCTION

Many substances are known to act as hardening accelerators for concrete. They include alkali hydroxides, silicates, fluorosilicates, various organic compounds, calcium formate, calcium nitrate, calcium thiosulphate, aluminum chloride or soluble calcium salts, potassium carbonate, sodium chloride, and calcium chloride. Of these, calcium chloride is the most widely used one because of its ready availability, low cost, predictable performance characteristics and successful application over several decades [1].

This is the case although some authors [2] prefer nitrite, nitrate and formate. The highest strength increases are achieved between the first and the third days of curing. The effect on strength decreases with time and the final strength can be reduced. A number of other compounds, such as calcium formate, have been found to have properties similar to those of calcium chloride, moreover not reducing the 28-day strength and presenting no risk of reinforcement corrosion [3].

Condensed silica fume is a by-product of the manufacture of silicon or its alloys, e.g. ferrosilicon, which is produced in so-called submerged-arc electric furnaces. Condensed silica fume particles appear to be formed by oxidation and condensation of gaseous silicon suboxide, SiO, which is formed in the reaction zone [4]. The pozzolanic activity of condensed silica fume in cement pastes has been demonstrated by determining the content of calcium hydroxide in terms of curing time. The results generally show a high pozzolanic activity [5, 6], although some studies have established a medium reactivity [7] or even a low one [8].

The high surface area of condensed silica fume $(20-25 \text{ m}^2 \text{ g}^{-1})$ in concrete is responsible for high pozzolanicity and a high water demand [9]. It was concluded that when using silica fume with Portland cement or with slag cement in the preparation of blended cements, a suitable admixture such as superplasticizer or water reducer must be used [10]. This is due to high water demand of the silica fume blended cement, and this increase in water demand is mainly due to the high specific surface area of silica fume, amounting to about 20 m² g⁻¹.

In a previous work it was shown that condensed silica fume is a highly pozzolanic material [10]. Also, the results revealed that the addition of 5-10 wt.% of silica fume improves the physico-mechanical properties of ordinary Portland as well as slag cement pastes.

The aim of the present work was to evaluate the influence of calcium acetate as an accelerator and water reducer on the properties of blended cement pastes containing 20 wt.% of condensed silica fume.

EXPERIMENTAL PART

The materials used in this investigation were ordinary Portland cement provided by Helwan Portland Cement Company, and condensed silica fume from Ferrosilicon Alloys Company (Edfo-Komombo), Aswan, Egypt. Calcium acetate as a chemical material was used as accelerator as well as water reducer. The chemical composition of the Portland cement and of condensed silica fume is given in table 1. The specific surface area of the cement was about 3000 cm² g⁻¹, whereas that of the condensed silica fume was about 20 m² g⁻¹ [4].

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	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO3	LOI
ordinary Portland							
cement	20.60	5.50	3.75	66.55	0.78	2.13	2.19
condensed							
silica fume	94.82	0.55	2.12	n.a.	n.a.	0.70	3.22

Table 1. Chemical composition of the starting materials (wt.%)

LOI - Loss of ignition, n.a. - Not analysed.

The blended cement was prepared from 80 wt.% of ordinary Portland cement and 20 wt.% of condensed silica fume. The dry constituents were mechanically mixed for one hour in a porcelain ball mill using two balls to attain complete homogeneity. The respective amounts of calcium acetate were added to the mixing water. The mixing operation was completed by continuous vigorous mixing for about four minutes. The water demand for standard consistency and setting were determined according to ASTM specifications [11,12]. The pastes were mixed with the water of consistency and moulded into one-inch cubes, cured in a humidity chamber at $23 \pm 1^{\circ}$ C for 24 hours, then demoulded and cured under water till the time of testing up to 360 days. After the predetermined curing time the hydration of the paste was stopped using the technique described elsewhere [13]. The kinetics of hydration was followed by determining the content of free lime [14], as well as that of chemically combined water which is equivalent to the percentage of ignition loss of the dried samples after introducing a correction for the water contained in free lime. The apparent density and total porosity were determined as described elsewhere [15]. The compressive strength of the hardened cement pastes was determined after 3, 7, 28, 90, 180 and 360 days.

RESULTS AND DISCUSSION

The effect of different dosages of calcium acetate as an accelerator and water reducer on the properties of the blended cement pastes was studied. The dosages of calcium acetate were 0.0, 1.0, 2.0 and 2.5 wt.%.

The water of consistency of the blended cement pastes is graphically represented as a function of dosages of calcium acetate in figure 1. The results show that the water of consistency of the blended cement pastes decreased with the amount of calcium acetate added. Calcium acetate acts as plasticizer when added to blended cement pastes. The water of consistency of cement pastes decreased by 7.69, 13.85 and 16.92 wt.% for calcium acetate dosages of 1.0, 2.0 and 2.5 wt.% respectively.

The time of initial set of the blended cement pastes is also reduced with the amount of calcium acetate addition. The time of initial set of the blended cements

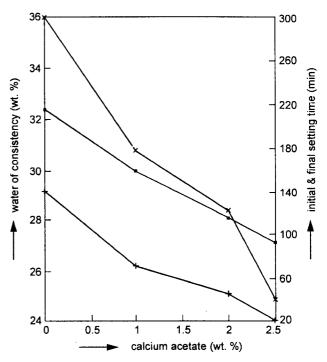


Figure 1. Water of consistency, initial and final setting time of silica fume blended cement pastes in presence of calcium acetate. ■- water of consistency, + - initial setting time, × - final setting time

was anyway shorter than that of plain Portland cement pastes. This is due to the decrease of the water of consistency of blended cement in the presence of different dosages of calcium acetate as well as to its accelerating effect. The time of final set of blended cement pastes is also shortened in terms of dosage of calcium acetate.

The content of free lime is represented as a function of the amount of calcium acetate and curing time in figure 2. The free lime content decreases with curing time for hardened cement pastes with different dosages of calcium acetate due to the pozzolanic effect of silica fume. As the hydration proceeds, the liberated lime reacts with condensed silica fume and subsequently the free lime content of blended cement is diminished. Additions of calcium acetate accelerate the formation of CSH. This is due to adsorption of calcium acetate on the surface of CSH particles or penetration of the ions into the CSH lattice [16]. The amount of free lime decreases with calcium acetate content as a result of the high accelerating effect of calcium acetate.

The content of chemically combined water in hardened blended cement pastes is plotted as a function of curing time in figure 3. The chemically combined water content obviously increases with curing time with all of the hardened cement pastes. The content of combined water likewise increases with the amount of calcium acetate added. Collepardi et al. [17] showed that the CH₃COO⁻ anion is one of the best accelerators for the hydration of C₃S.

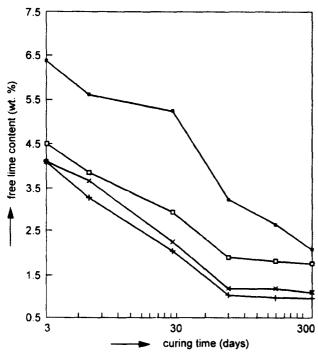


Figure 2. Free lime content of silica fume blended cement pastes cured up to 360 days in presence of different dosages of calcium acetate.

a - 0 wt.%, **+** - 1.0 wt.%, × - 2.0 wt.%, **b** - 2.5 wt.%

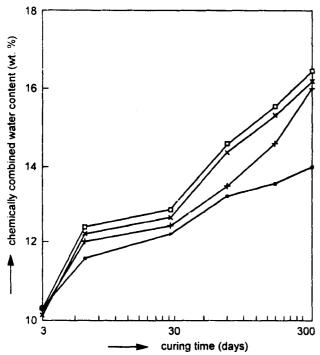


Figure 3. Combined water contents of silica fume blended cement pastes cured up to 360 days in presence of different dosages of calcium acetate. $\blacksquare - 0$ wt.%, + - 1.0 wt.%, $\times - 2.0$ wt.%, $\square - 2.5$ wt.%

The apparent density and total porosity of hardened blended cement pastes are plotted as a function of curing time in figure 4. The results show that apparent density

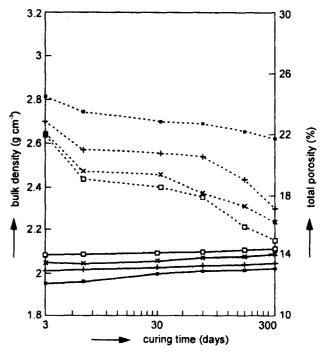


Figure 4. Bulk density and total porosity of silica fume blended cement pastes cured up to 360 days in presence of different dosages of calcium acetate.

🗰 - 0 wt.%, + - 1.0 wt.%, × - 2.0 wt.%, 🗖 - 2.5 wt.%

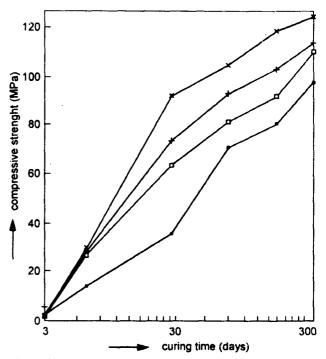


Figure 5. Compressive strength of silica fume blended cement pastes cured up to 360 days in presence of different dosages of calcium acetate.

■ - 0 wt.%, + - 1.0 wt.%, × - 2.0 wt.%, □ - 2.5 wt.%

increases with curing time and total porosity decreases. As the hydration progresses, the hydration products fill a part of pore volume and consequently the apparent density increases and total porosity decreases. The apparent density of blended cement pastes increases with increasing dosages of calcium acetate due to the accelerating effect of calcium acetate which forms more hydration products which preciptate in the open pores, thus increasing the apparent density.

The total porosity decreases with increasing dosage of calcium acetate, due to the decrease of the water of consistency which influences significantly the value of total porosity. As the content of free water increases, the volume left behind after its evaporation, that is the total porosity, is correspondingly increased.

The values of compressive strength of hardened blended cement pastes made with 20% condensed silica fume cured up to 360 days are plotted as a function of curing time in figure 5. The compressive strength increases with curing time, due to the accumulated amounts of hydrated calcium silicate. The compressive strength of blended cement pastes increases with increasing dosage of calcium acetate up to 2.0 wt.%, but higher dosages (2.5 wt.%) result in reduced strength. This is mainly due to the decrease of the amount of mixing water. Generally, the addition of any amount of calcium acetate brings about higher compressive strength of hardened cement pastes as compared to cement paste without admixture.

CONCLUSION

The following conclusions may be formulated on the basis of the above findings:

- 1. The water of consistency of silica fume blended cement paste decreases with the dosage of calcium acetate admixture up to 2.5 wt.%. The times of initial and final set are shortened.
- 2. Dosage of 1.0 wt.% calcium acetate results in a decrease in the content of free lime, but higher additions (2.0 and 2.5 wt.%) bring about an increase in its content. On the other hand, the content of combined water increases with the amount of calcium acetate added.
- 3. The apparent density of hardened silica fume cement paste increases with the dosage of calcium acetate and the total porosity decreases in the opposite direction.
- 4. The additions of calcium acetate up to 2.0 wt.% improve the compressive strength of the hardened cement paste, but higher dosages (2.5 wt.%) cause the compressive strength to decrease.
- 5. It can be concluded that calcium acetate can be used as an accelerator and water reducer for 20 wt.% silica fume blended cement pastes.

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VLIV OCTANU VÁPENATÉHO JAKO URYCHLOVAČE TVRDNUTÍ A PLASTIFIKÁTORU NA VLASTNOSTI CEMENTU S PŘÍSADOU AMORFNÍHO OXIDU KŘEMIČITÉHO

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Mezi urychlovače tvrdnutí portlandského cementu patří hydroxidy alkalických kovů, jejich silikáty, fluorosilikáty, organické sloučeniny, thiosíran vápenatý, chlorid hlinitý a rozpustné soli vápníku, chlorid sodný a chlorid vápenatý. Nejznámějším anorganickým urychlovačem je $CaCl_2$. Cílem této práce bylo vyhodnotit vliv octanu vápenatého jako urychlovače tvrdnutí a plastifikátoru na vlastnosti kaší směsného cementu s přísadou 20 % kondenzovaného oxidu křemičitého, který je vedlejším produktem výroby křemíku pro metalurgické účely.

Příslušný cement byl připraven smísením 80 % běžného portlandského cementu s 20 % kondenzovaného oxidu křemičitého. Octan vápenatý byl přidáván do záměsové vody v množstvích 1,0, 2,0 a 2,5 % hmotnosti cementu. Kinetika hydratace byla měřena stanovením volného vápna a obsahu vázané vody v zatvrdlé cementové kaši. Dále byla zjišťována objemová hmotnost a pevnost v tlaku zatvrdlých cementových kaší. Výsledky ukazují, že vodní součinitel se snižuje a doba tuhnutí se zkracuje se vzrůstajícím množstvím přidávaného octanu vápenatého. Obsah volného vápna se snižoval u všech zkoušených kaší v důsledku pucolánového působení oxidu křemičitého. Nejnižší obsah volného vápna vykazovaly vzorky s 1,0 % octanu vápenatého. Toto množství se proto ukazuje jako optimální přísada. Obsah vázané vody se zvyšuje s množstvím přidaného octanu vápenatého v důsledku jeho urychlovacího účinku. Všechny vzorky zatvrdlých kaší s obsahem octanu vápenatého vykazovaly vyšší objemové hmotnosti a vyšší pevnosti v tlaku než směsný cement s kondenzovaným oxidem křemičitým bez přísady octanu. Bylo zjištěno, že přísada octanu vápenatého v množství mezi 1,0 a 2,0 % hmotnosti cementu vykazovala optimální výsledky.