IMPROVEMENT OF SILICA FUME BLENDED CEMENTS BY USING SUPERPLASTICIZER

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In silica fume blended cements, the water of consistency increases with the silica fume content due to its high surface area. Therefore, the porosity is increased and the compressive strength decreased. To get full benefits of the partial substitution by silica fume, it was decided to demonstrate the effect of superplasticizer which reduces the water demand and/or improves the workability of cement paste. The effect of different dosages of superplasticizer BVF addicrete obtained from the Chemicals for the Modern Building Company, namely 0., 0.5, 1.0, 2.0 and 4.0 wt. % of cement, on the blended cement pastes was studied. By adding different dosages of BVF to the blended cement with 20 wt.% silica fume, the water of consistency decreases and the time of set is shortened. It was concluded that a high strength concrete is obtained by adding the superplasticizer to the silica fume blended cement. The free lime content increases up to 7 days then decreases up to 360 days. As the dosage increases the content of combined water decreases.

INTRODUCTION

By definition, pozzolanas are "siliceous materials which in the presence of moisture and at normal temperature react with lime to form cementitious calcium silicate hydrates". Since lime is a by-product of the hydration of Portland cement and by itself is not cementitious, the addition of a pozzolana to Portland cement concrete can contribute to improve the ultimate strength and durability of the product by transforming the free lime into calcium silicate hydrate [1].

At room temperature, the lime-pozzolana reaction is very slow, the rate of the reaction being dependent on the reactivity of the silica present which, in turn, depends on its specific surface area and the degree of amorphousness of the reactive components.

Condensed silica fume is a much finer material than Portland cement or the other supplementary materials used in cement and concrete technology, its grain size being approximately 100 times smaller [2].

Condensed silica fume, a by-product of the silicon and ferrosilicon industries, consists of 85 - 96 wt.% amorphous silica with a specific surface area of 20 - 25 $m^2 g^{-1}$ [3]. This material is commercially available in considerable quantities. The high surface area of silica fume in concrete is responsible for its high pozzolanicity and high water consumption (a high *w/c* ratio) necessary to achieve adequate consistency. Use of superplasticizers is recommended to improve the technological and mechanical properties of concrete [4, 5].

Partial replacement of cement by silica fume and the addition of superplasticizer increases the strength of mortar [6]. It was also demonstrated that superplasticizer in combination with silica fume plays a more effective role in cement mortars than in pastes. This can be attributed to more efficient utilization of superplasticizer in the mortar mixes due to the better dispersion of the silica fume particles.

The aim of the present work is to study the effect of a superplasticizer in 20 wt.% silica fume blended cements on the physico- mechanical properties of cement paste specimens up to one year.

EXPERIMENTAL PART

The materials used in this investigation were ordinary Portland cement provided from Helwan Portland Cement Company, condensed silica fume from Ferrosilicon Alloys Company (Edfo-Komombo) Aswan, and addicrete BVF superplasticizer obtained from the Chemicals for Modern Building Company, Egypt. The chemical composition of the Portland cement and the condensed silica fume is given in table 1. The specific surface area of the cement was about 3000 $cm^2 g^{-1}$, and that of the silica fume was 20 - 25 $m^2 g^{-1}$.

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

oxides	silica fume	ordinary Portland cement
SiO_2	94.82	20.60
Al_2O_3	0.55	5.50
Fe_2O_3	2.12	3.75
CaO	not analysed	63.55
MgO	not analysed	0.78
SO_3	0.70	2.13
ign. Loss	1.22	2.19
total	99.41	98.50

The ingredients of each mix of Portland cement and silica fume were blended in a porcelain ball mill for one hour using two balls to ensure perfect homogeneity. The dosages of BVF superplasticizer, namely 0.5, 1.0, 2.0 and 4.0 wt.% of cement, were added to mixing water. The blending operation was completed by continuous vigorous mixing for about four minutes. The water demand for standard consistency and time of set were determined according to ASTM specifications [7, 8]. The pastes were mixed with the water of consistency and moulded into one-inch cubes, cured in a humidity chamber at 23 ± 1 °C for 24 hours, then demoulded and cured under water for up to 360 days. After the predetermined curing time, the hydration of the paste was stopped using the technique described elsewhere [9]. The kinetics of hydration was followed by determining the free lime content [10] as well as that of combined water which is equivalent to the percentage of ignition loss of the dried sample in the ignited weight after introducing the correction for the water of free lime. The apparent density and total porosity were determined as described elsewhere [11]. The compressive strength of the hardened cement pastes was also determined at intervals for up to one year.

RESULTS AND DISCUSSION

BVF addicrete is a concrete superplasticizer containing sulphonate naphthalene condensate. According to the supplers, this admixture reduced considerably the water demand without having any retarding effect on concrete or mortar setting and hardening. The admixture increases in particular the early strength and promotes hardening at lower temperatures.

The effect of different dosages of BVF superplasticizer, namely 0.0, 0.5, 1.0, 2.0 and 4.0 wt.% of cement, on the properties of blended cement pastes was studied.

The water of consistency and time of initial and final set of blended cement pastes are graphically plotted as a function of different dosages of BVF admixture in figure 1. As a result of the BVF superplasticizer addition, the water of consistency decreases with the amount of admixture due to its dispersion action.

The time of initial set of blended cement pastes is accelerated as the dosage of BVF sperplasticizer increases. This may be due to the decrease of water of consistency. The time of initial set of cement paste without BVF admixture is mainly retarded as a result of coating which is formed of condensed silica fume and the hydration products on the surface of cement particles and delays further hydration, but may also be due to the higher amount of mixing water.

The time of final set of blended cement pastes is accelerated by the addition of the BVF superplasticizer due to the dispersing effect of the admixture as well as owing to the reduced amount of mixing water.

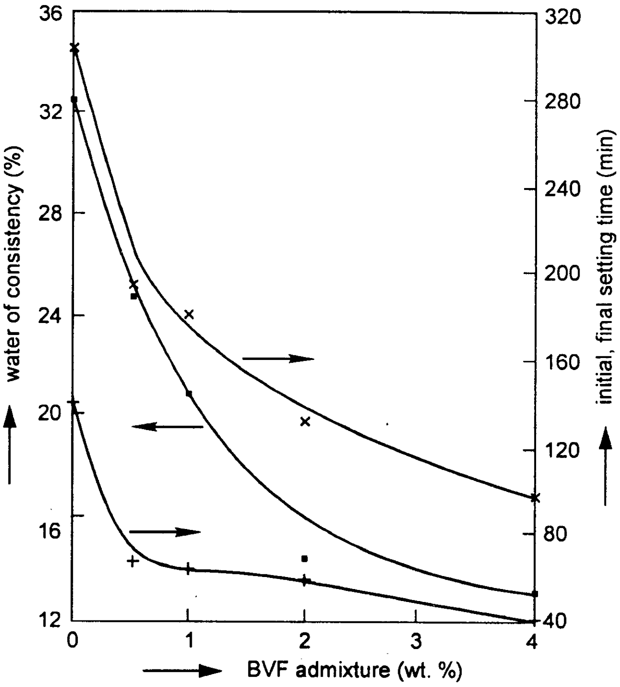

Figure 1. Water of consistency and setting time of blended cement pastes as a function of different dosages of BVF superplasticizer.

■ - W. cons.; + - init. set; × - fin. set.

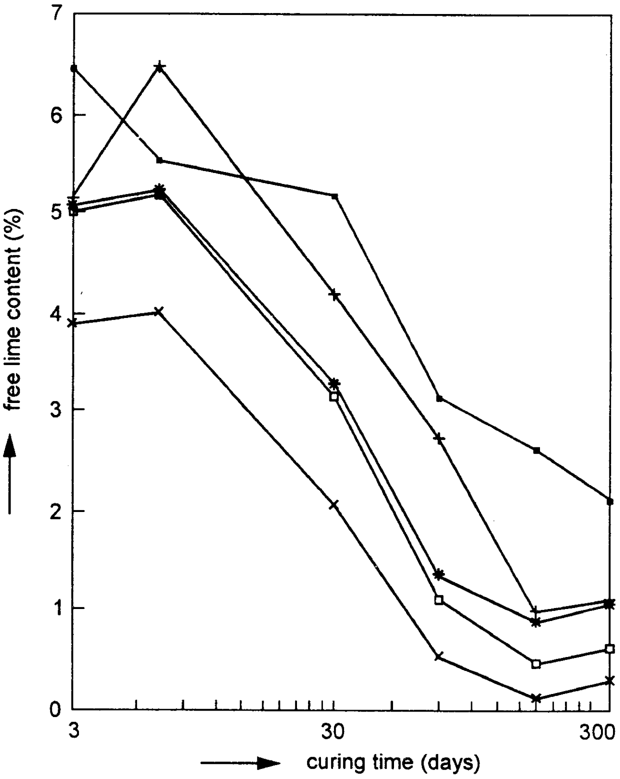

Figure 2. Free lime content of blended cement pastes with different dosage of BVF superplasticizer as a function of curing time.

■ - 0; + - 0.5; * - 1.0; □ - 2.0; × - 4.0 (wt.%)

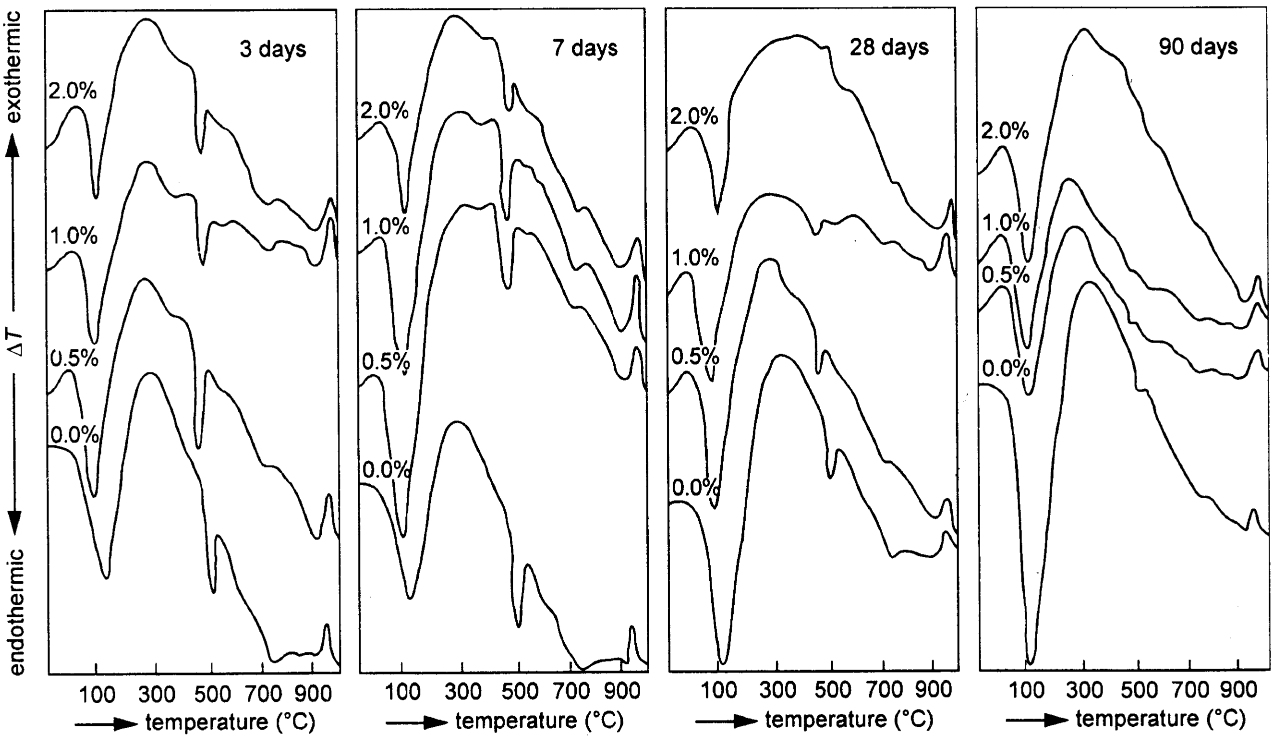

Figure 3. DTA thermograms of hydrated 20 wt.% silica fume-blended cement pastes withdiffrent dosage of BVF superplascticizer, as a function of curing time.

The free lime contents of the blended cement pastes are plotted as a function of curing time in figure 2. Additions of BVF superplasticizer to blended cement pastes cause the free lime content to decrease due to the decrease of mixing water which retards the hydration of cement paste.

The DTA thermograms of hydrated 20 wt.% silica fume-blended cement pastes containing 0.0, 0.5, 1.0 and 2.0 wt.% BVF superplasticizer cured for 3, 7, 28 and 90 days are shown in figure 3. The thermograms exhibit three endotherms at 120, 500 and 720 °C. The first peak is due to dehydration of interlayer water of calcium silicate and calcium sulphoaluminate hydrates. The second peak at 500 °C is due to the decomposition of $Ca(OH)_2$ formed during the hydration of cement pastes. The third peak at 720 °C is attributed to decomposition of $CaCO_3$. The exothermic peak at 950 °C is characteristic of calcium monosilicate hydrate formed from cement in the course of curing and by the reaction of condensed silica fume with $Ca(OH)_2$ [12].

Samples hydrated for 3-7 days contain CSH and sulphoaluminate hydrates with various compositions and crystalline strustures, $Ca(OH)_2$ and $CaCO_3$. The content of hydration products decreases with increasing dosages of BVF sperplasticizer. This is due to the lower content of water of consistency caused by the addition of BVF superplasticizer which slows down the hydration rate of the cement in addition to reducing the $Ca(OH)_2$ content. There are additional factors which reduce the amount of free lime, for example the reaction with condensed silica fume. This reduction increases with increasing dosage of BVF superplasticizer. At 7 days the crystallinity of CSH increases as indicated by the exotherm in the range of 900 - 1000 °C. After (28 - 90) days the endotherm at 120 °C for better crystalline CSH is confirmed with continuous increasing the sharpness of the exotherm over the range of 950 °C [13], while the endotherm representing $Ca(OH)_2$ decreases continuously with curing time, appears in a form indicating trace amounts in samples cured for 90 days and cannot be detected in samples containing 2.0 wt.% BVF superplasticizer. The behaviour of the endotherm of $Ca(OH)_2$ is in good agreement with the results of chemical analyses.

The content of combined water in blended cement pastes is plotted as a function of curing time in figure 4. The content of combined water is shown to increase with curing time in all of the hardened cement pastes. The results indicate that when the dosage of BVF is raised from 0.5 to 4.0 wt.%, the content of combined water is diminished in all of the cement pastes. This is due to the decrease of mixing water which retards the hydration of calcium silicates of the anhydrous cement. Yogendran et al. [14] concluded that at a lower $w/c + SF$ ratio, the content of combined water in hydrates formed by the pozzolanic reaction is lower than the reduction of the content of hydration products due to the reduction of cement content by the substitution with silica fume. Moreover, the amount of combined water would usually indicate the amount of the hydrates and $Ca(OH)_2$ formed in Portland cement paste, but in a blended cement paste the amount of combined water is not a good indicator of the degree of hydration, because of the reduction in the $Ca(OH)_2$ content due to the pozzolanic reaction.

The apparent density and total porosity are graphically represented as a function of curing time in figures 5, 6. It is clear that as the curing time proceeds, the total porosity decreases and the apparent density increases due to continuous filling up of a part of the available pore volume with the hydration products. With increasing dosages of the BVF sperplasticizer the apparent density increases and the total porosity decreases in all cement pastes as a result of the reduction of mixing water.

The superplasticizer added to the mix to improve dispersion of cement particles also appears to aid the dispersion of silica fume particles [15]. The mechanism may be related to interparticular tension generated by the dispersant, which helps keep the silica fume particles separated until the dissolution process begins. The Ca^{2+} ions detected on some reacted particles indicate that silica fume may act as a nucleating agent. A similar nucleation

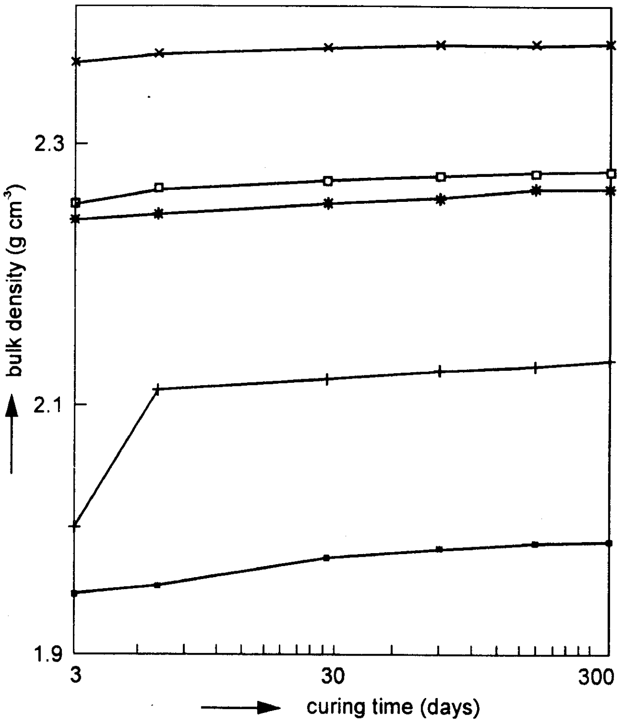

Figure 5. Apparent density of blended cement pastes with different dosages of BVF superplasticizer, as a function of curing time.

■ – 0; + – 0.5; * – 1.0; □ – 2.0; ■ – 4.0 (wt.%)

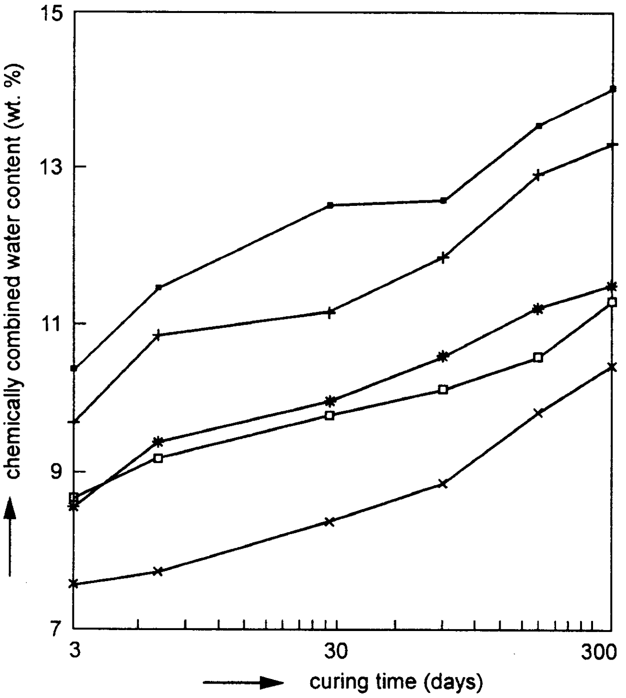

Figure 4. Combined water content in blended cement pastes with different dosages of BVF superplasticizer, as a function of curing time.

■ – 0; + – 0.5; * – 1.0; □ – 2.0; × – 4.0 (wt.%)

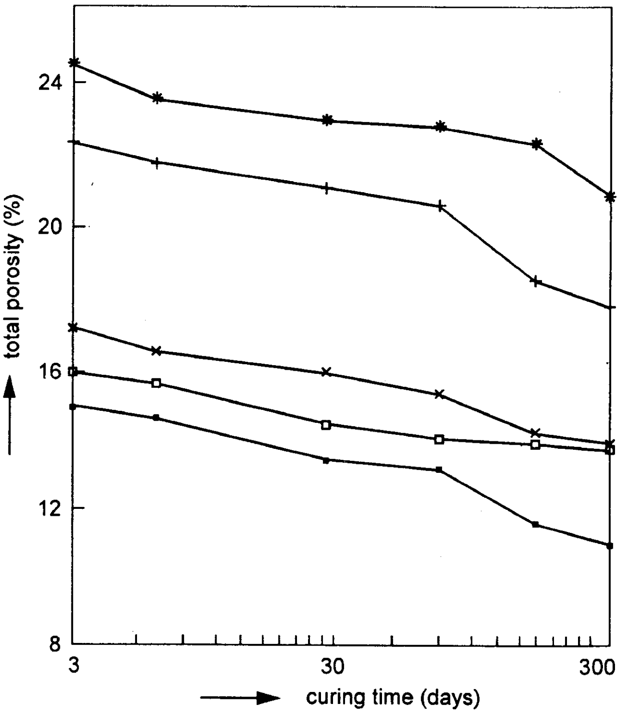

Figure 6. Total porosity of blended cement pastes with different dosages of BVF superplasticizer, as a function of curing time.

■ – 0; + – 0.5; * – 1.0; □ – 2.0; ■ – 4.0 (wt.%)

affects the surface of silica fume [16]. Gradual dissolution of silica fume into a gel in the matrix and its reaction with $Ca(OH)_2$ to form CSH occur. This is strongly reflected in the total porosity of very high strength concrete undergoing progressive hydration.

Beyond 28 days, the total porosity of the blended cement pastes decreases rapidly for up to 360 days as a result of the reaction of silica fume with the lime liberated by the hydration. This results in further decrease of porosity in terms of time, in an additional increase in strength and in conversion of CSH into more stable morphological types which are more dense and thus increase the apparent density of the blended cement pastes with increasing dosage of BVF superplasticizer.

The compressive strengths of hardened cement pastes cured for up to 360 days are plotted in figure 7. The compressive strength increases with curing time as well as with superplasticizer dosage. An increase in BVF superplasticizer dosage from 0.5 to 4.0 wt.% caused the compressive strength to increase at all ages. This is due to the decrease of the water of consistency which tends to decrease the total porosity and increase the apparent density, the two factors that combine to increase the compressive strength. Addition of the superplasticizer improves workability and facilitates compaction [17]. The blended cement pastes show high compressive strength at later ages (28 - 360 days). This is due to the high pozzolanic activity of condensed silica fume which is promoted by increasing dosages of the BVF superplasticizer. The resulting low total porosity is also responsible for closer packing of condensed silica fume particles and better conditions for their reaction with free lime, yielding additional calcium silicate hydrates with a low CaO/SiO_2 ratio or CSH [1], as the main source of compressive strength.

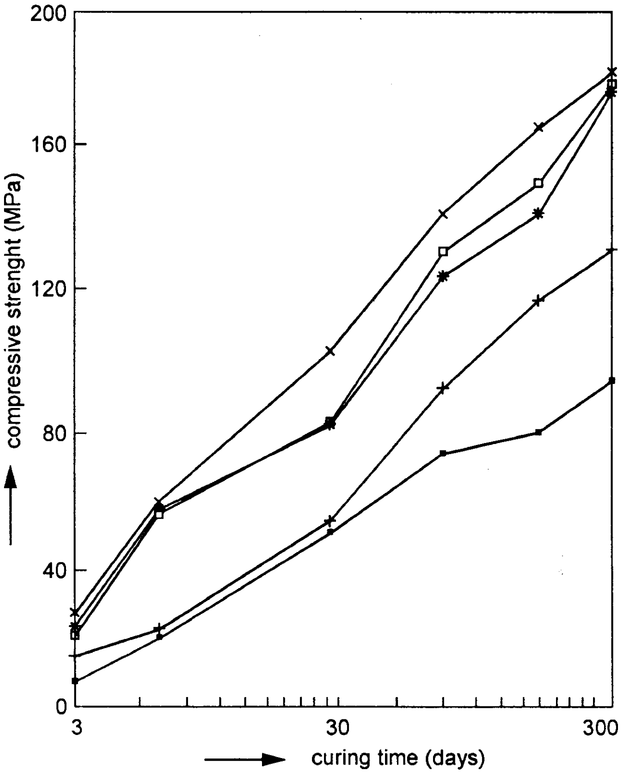

Figure 7. Compressive strength of blended cement pastes with different dosage of BVF superplasticizer, as a function of curing time.

■ – 0; + – 0.5; * – 1.0; □ – 2.0; × – 4.0 (wt.%)

CONCLUSION

The following conclusions can be formulated on the basis of the results obtained:

1. Upon addition of BVF superplasticizer to a 20 wt.% silica fume blended cement the amount of water of consistency decreases with increasing amount of the admixture up to 4.0 wt.% of cement.
2. The times of initial and final set of the cement pastes are retarded in the case of blended cement free of superplasticizer admixture, whereas the additions of superplasticizer accelerate the initial and final setting of cement pastes.
3. The free lime and combined water content decrease with the increase dosages of the superplasticizer.
4. The apparent density increases and the total porosity decrease with increasing additions of BVF with all cement pastes due to the reduction of mixing water. The apparent density increases and the total porosity decreases with increasing dosage of the BVF admixture.
5. The blended cement pastes show high compressive strengths at later ages of 28 - 360 days, due to the pozzolanic activity of silica fume and the reduced amount of mixing water resulting from addition of the superplasticizer. The strength also increases with increasing dosage of the superplasticizer.
6. The dosage of BVF corresponding to 2 wt.% of cement is a suitable amount which gives good reduction of mixing water and also improved the compressive strength.

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ZLEPŠENÍ SMĚSNÝCH CEMENTŮ S KONDENZOVANÝM OXIDEM KŘEMIČITÝM POMOCÍ SUPERPLASTIFIKÁTORU

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Pucolány jsou podle definice "křemičité materiály, které za přítomnosti vlhkosti a za normální teploty reagují s vápnem a vytvářejí kalciumhydrosilikáty s pojivými vlastnostmi." Přídavkem pucolánu k portlandskému cementu lze dosáhnout zvýšení konečné pevnosti betonu a jeho odolnosti tím, že volné vápno v hydratovaném cementu obsažené s ním reaguje a vytváří kalciumhydrosilikáty.

Kondenzovaný oxid křemičitý jako vedlejší produkt z výroby křemíku a ferosilicia obsahuje 85 - 96 hmot.% amorfního oxidu křemičitého, a jeho specifický povrch činí 20 - 25 $m^2 g^{-1}$. Tento velký specifický povrch podporuje výrazné pucolánové vlastnosti betonu, ale také zvyšuje vodní součinitel. Cílem této práce bylo ověřit účinky přídavků superplastifikátoru BVF na fyzikálně mechanické vlastnosti kaší směsného cementu obsahujícího 20 hmot.% kondenzovaného oxidu křemičitého.

Tento směsný cement byl připraven smícháním 80 hmot.% běžného portlandského cementu s 20 hmot.% kondenzovaného oxidu křemičitého. Plastifikátor BVF byl dávkován do záměsové vody v množstvích 0,5, 1, 2 a 4 hmot.% z hmotnosti cementu. Kinetika hydratace byla měřena stanovením obsahu volného vápna a vázané vody v zatvrdlé cementové kaši. Rovněž byla stanovována objemová hmotnost a pevnost v tlaku zatvrdlých cementových kaší do stáří jednoho roku.

Výsledky ukazují, že normální vodní součinitel se snižuje a doby tuhnutí se zkracují s množstvím přidávaného superplastifikátoru. Obsah volného vápna se snižuje s dobou tvrdnutí u všech zkoušených kaší v důsledku pucolánové aktivity kondenzovaného oxidu křemičitého. Optimální dávka superplastifikátoru BVF byla stanovena jako 2 % z hmotnosti cementu.