

EGYPTIAN SILICA FUME IN PORTLAND CEMENT

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The influence of silica fume which emerges as a by-product of the production of ferro-silicon (Edfo - Kom Ombo, Co., Egypt) on the properties of blended cement pastes has been studied. Percentages of 5, 10, 15 and 20% by weight of cement of silica fume were mixed with ordinary portland cement. It is concluded that the addition of silica fume to portland cement enhances the hydration kinetics, i.e. increases the chemically combined water and decreases the liberated $\text{Ca}(\text{OH})_2$ contents. It was also found that 5% silica fume improved the mechanical properties of cement paste in tap water as well as in MgSO_4 and Na_2SO_4 solution.

Key words: Silica fume, Portland cement, Ferro-silicon.

Introduction

The pozzolana are mainly siliceous and aluminous materials which in presence of moisture can react with lime at room temperature to produce cementitious products similar to those found in the hydration of portland cement. They are natural and artificial materials such as silica fume, opal, diatomite, zeolite, fly ash, rice husk ash and metakaolin. In portland pozzolanic cements the lime for the pozzolanic reactions is furnished by the hydration of the calcium silicates ($\beta\text{-C}_2\text{S}$ and C_3S) present in the portland cement components.

The use of pozzolanic and blended cement is increasing worldwide because the blended cements need less energy for production. They usually have lower heat of hydration, higher ultimate strength and better durability to chemical and aggressive attack.

In previous studies [1-3], it has been shown that the silica fume addition to portland cement leads to considerable improvements of the mechanical properties and resistance of cement mortars to sulphate attack. It has been also claimed that silica fume is highly pozzolanic [4]. However, Traetteberg [5] and Chatterje *et al.* [6] reported that in 90:10 portland cement: silica fume paste only 2% of the liberated lime was consumed by silica; i.e. its pozzolanic activity is comparatively low.

Silica fume was added to cement in concentrations of 2, 5, 8 and 11% by weight [7]. It has been established that the cement mortar containing 8wt% of silica dust shows the highest compressive strength.

In the manufacture of ferro silicon (Edfo - Kom Ombo, Co., Egypt), silica fume being collected in filters as extremely fine silica dust (silica fume) and its accumulation represents a huge ecological problem. The present work aims to study the influence of the silica fume on the hydration kinetics, compressive strength as well as sulphate resistance of the hardened portland cement pastes.

Experimental

The materials used were ordinary portland cement and silica fume, a by-product of a manufacture of ferro-silicon. Table 1 shows the chemical analysis of these materials. The surface area of the portland cement is $3150 \text{ m}^2 \cdot \text{g}^{-1}$ whereas the silica fume consists fine spherical ($< 2 \mu\text{m}$) and amorphous particles with specific surface of $18 \text{ m}^2 \cdot \text{g}^{-1}$ [7].

Dry mixes were prepared from 5, 10, 15 and 20 silica fume wt% and portland cement, respectively (Table 2). The ingredients were mixed for 1 hr. in a porcelain ball mill containing two balls to assure complete homogeneity. The mixing of the pastes was done as described in a previous work [8]. The pastes were moulded in a cubic moulds, cured in humidity chamber at $23 \pm 1^\circ$ for 24 hrs then demoulded and curing was completed under water till the time for testing.

TABLE 1. CHEMICAL COMPOSITION OF THE ORDINARY PORTLAND CEMENT AND SILICA FUME, %.

Constituents	Silica fume	Portland cement
SiO_2	94.69	21.06
Al_2O_3	0.5	5.43
Fe_2O_3	2.29	3.41
CaO	Nil	64.00
MgO	Nil	0.75
SO_3	0.67	2.42
I.L.	1.26	2.42

TABLE 2. MIX COMPOSITION OF BLENDED CEMENTS, %.

Cement	Portland cement	Silica fume
M_0	100	00
M_1	95	5
M_2	90	10
M_3	85	15
M_4	80	20

The kinetic of hydration was followed by determining the free CaO as well as the chemically combined water contents after 3, 7, 28 and 90 days. The compressive strength was also measured at these intervals. After the measuring of the compressive strength, the hydration was stopped [9]. The free lime content was estimated using ammonium acetate method [10]. The chemically combined water content was measured by the ignition loss on the ignited weight basis minus the amount of water held by the free $\text{Ca}(\text{OH})_2$ in the sample. X-ray powder diffraction was used to identify the hydration product of the cement paste. XRD analysis was carried out with COK radiation. The relative resistance of different pozzolanic cements to sulphate attack was determined by measuring the strength and weight changes of the hardened pastes accompanying the sulphate immersion, that followed a normal curing cycle. The sulphate resistance of cement pastes was determined by an accelerated method [11]. The pastes were removed from water after 14 days and dried at 105° for 24 hrs. Dried samples were cooled to room temperature and immersed in 5% solutions of either sodium or magnesium sulphate, separately. At the age of 21 days, the cubes were removed from the sulphate solutions, also redried at 105° for 24 hrs cooled and reimmersed in the same solution. The compressive strength and also the weight changes were measured at the age of 28 days.

Results and Discussion

The pozzolanic cement was prepared by blending a mixture having the composition of 95:5, 90:10, 85:15 and 80:20 weight percent portland cement and silica fume, respectively. The water demand for normal consistency tends to increase with the substitution of portland cement with silica fume. The mixing water required for the normal consistency of portland cement pastes was 26%. On the other hand, the pozzolanic cement pastes made from silica fume in concentrations of 5, 10, 15 and 20 wt % needed 27, 29, 30 and 31%, respectively.

The combined water contents of the hardened pozzolanic cement as well as portland cement pastes cured for 3, 7, 28 and 90 days are plotted in Fig. 1. The combined water contents increase with curing time for all hardened cement pastes. It is also seen that all pozzolanic cement pastes give higher combined water contents than portland cement paste. Only mixes with 15 and 20 weight percent silica fume have lower combined water contents at 3 days than that of portland cement and then show higher values at later ages from 7-90 days. The lower values at 3 days may be attributed to the high amount of silica fume. The content of clinker decreases, therefore, the hydrated calcium sulphoaluminate such as ettringite and monosulphate is diminished. These hydrates have higher values of combined water and hydrated at early ages. Hence the combined water decreases at early ages of hydration

(3 days). On prolong hydration silica fume hydrates forming calcium silicate hydrate which shows an increase in the chemically combined water contents. This indicates that the samples containing 15 wt % of silica may be considered as the optimum concentration at which the maximum amount of reaction can occur. It is noticed that 20% silica fume decreases the combined water contents of the hardened cement paste than the other that contains 15%. Therefore, with the increase of silica fume the hydration kinetic decreases linearly.

The free lime contents of the hardened pozzolanic cement pastes as well as portland cement were plotted as a function of curing time in Fig. 2. The free lime contents were corrected to 100% of portland cement in each mix. This means the amount of CaO liberated from pure portland cement. The free lime

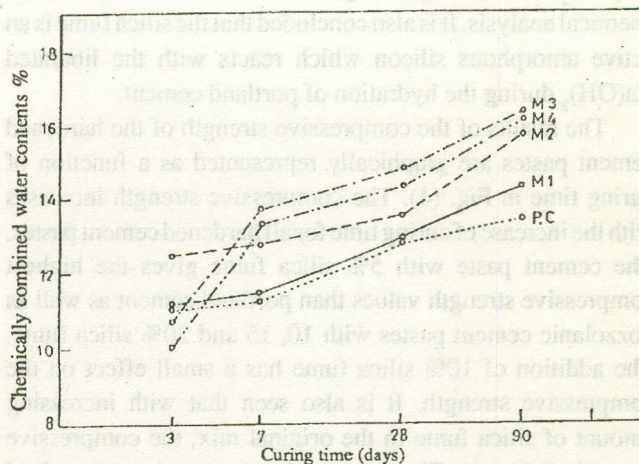


Fig. 1. Chemically-combined water contents of hardened blended cement and portland cement pastes as a function of curing time.

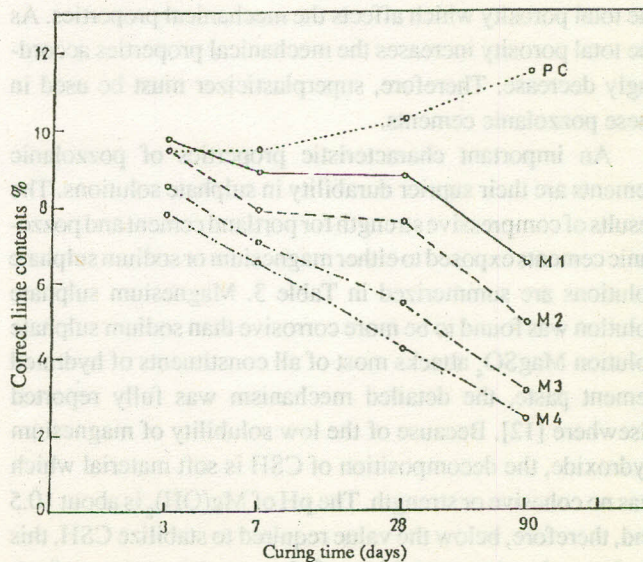


Fig. 2. Free lime contents of hardened cement pastes in relation with silica fume content as a function of curing time.

contents decrease with curing time for all pozzolanic cement pastes whereas increase for portland cement pastes. This increase is due to the continuous liberation of $\text{Ca}(\text{OH})_2$ during the hydration of portland cement. The decrease of free $\text{Ca}(\text{OH})_2$ in pozzolanic cement is mainly attributed to the consumption of the liberated lime by the added silica fume. Silica fume is an amorphous active form of silica [7]. This leads to the formation of hydrated calcium silicate. Therefore, the remaining $\text{Ca}(\text{OH})_2$ decreases linearly with the increase of silica fume. As the hydration progresses, the free lime reacts with silica fume and then the hydration products are enhanced.

Figure 3 shows the X-ray diffraction pattern of hydrated cement pastes cured for 28 days in tap water. It is clear that the addition of silica fume decreases the intensity of the peaks of $\text{Ca}(\text{OH})_2$. This is in good agreement with the results of the chemical analysis. It is also concluded that the silica fume is an active amorphous silicon which reacts with the liberated $\text{Ca}(\text{OH})_2$ during the hydration of portland cement.

The results of the compressive strength of the hardened cement pastes are graphically represented as a function of curing time in Fig. (4). The compressive strength increases with the increase of curing time for all hardened cement pastes. The cement paste with 5% silica fume gives the highest compressive strength values than portland cement as well as pozzolanic cement pastes with 10, 15 and 20% silica fume. The addition of 10% silica fume has a small effect on the compressive strength. It is also seen that with increasing amount of silica fume in the original mix, the compressive strength decreases. The decrease in compressive strength of the blended cement pastes may be attributed to the high demand of mixing water. The increase of W/C ratio increases the total porosity which affects the mechanical properties. As the total porosity increases the mechanical properties accordingly decrease. Therefore, superplasticizer must be used in these pozzolanic cements.

An important characteristic properties of pozzolanic cements are their superior durability in sulphate solutions. The results of compressive strength for portland cement and pozzolanic cements exposed to either magnesium or sodium sulphate solutions are summarized in Table 3. Magnesium sulphate solution was found to be more corrosive than sodium sulphate solution MgSO_4 attacks most of all constituents of hydrated cement paste, the detailed mechanism was fully reported elsewhere [12]. Because of the low solubility of magnesium hydroxide, the decomposition of CSH is soft material which was no cohesive or strength. The pH of $\text{Mg}(\text{OH})_2$ is about 10.5 and, therefore, below the value required to stabilize CSH, this leads to the decomposition of the cement paste to form gypsum. In fact, portland cements are chemically stable when the pH value of the ambient is more than 11.5.

Na_2SO_4 solution has pH value more than 11.5 and MgSO_4 has value lower than 9 [13], therefore, the samples

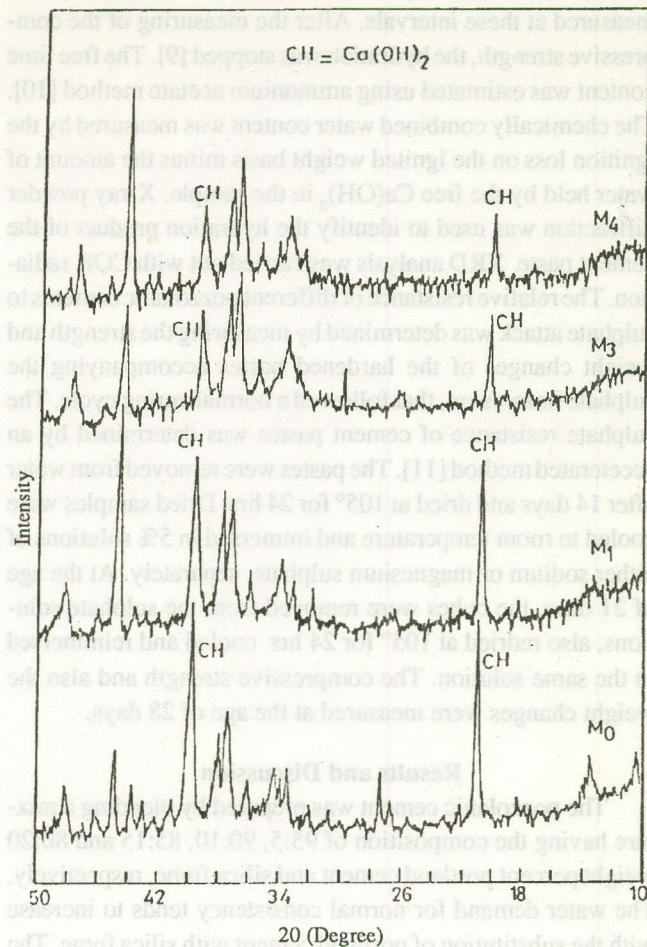


Fig. 3. XRD patterns of hardened portland as well as blended cement pastes hydrated for 28 days in tap water.

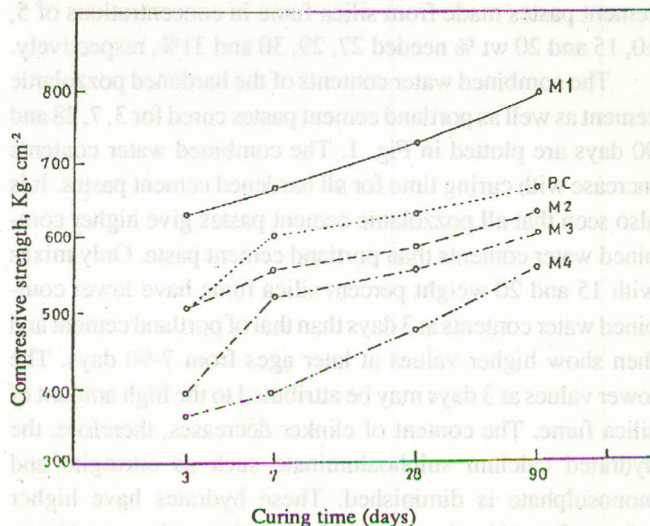


Fig. 4. Compressive strength of portland as well as blended cement pastes as a function of curing time.

TABLE 3. STRENGTH AND WEIGHT CHANGES OF HARDENED CEMENT PASTES AFTER IMMERSION IN SULPHATE SOLUTIONS.

Cement	Strength in water kg. cm ⁻²	Strength in MgSO ₄	Change in strength %	Change in weight %	Strength in Na ₂ SO ₄ kg. cm ⁻²	Change in strength %	Change in weight %
M ₀	632	400	-36.71	-4.45	474	-25.00	+2.43
M ₁	727	632	-13.07	-4.02	680	-6.64	+4.65
M ₂	585	363	-37.95	-6.81	474	-18.97	+2.77
M ₃	553	347	-37.25	-6.37	474	-14.29	+2.16
M ₄	474	316	-33.33	-7.29	442	-6.75	-0.27

immersed in sodium sulphate solution has an increase in weight but in MgSO₄ solution has a decrease in weight. Only mix 80:20 portland cement: silica fume shows a decrease in weight in Na₂SO₄ solution. The sulphate attack can be due to conversion of Ca(OH)₂ to gypsum or alumina bearing hydrates to ettringite. The most likely reaction is that of the formation of gypsum. Due to the high temperature used, the loss of strength and/or weight can be due to the recrystallization of sulphate in the drying cycle. It is clear that the mix 95:5 portland cement: silica fume has the highest resistivity to sulphate solutions. This mix has higher resistance than ordinary portland cement paste. This is in good agreement with the results of compressive strength in tap water. This mix gives the optimum suitable mix composition to be sulphate resisting cement.

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