

# INFLUENCE OF SUBSTITUTION OF ORDINARY PORTLAND CEMENT BY SILICA FUME ON THE HYDRATION OF SLAG-PORTLAND CEMENT PASTES

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*Effect of gradual substitution of ordinary Portland cement by a few percent of silica fume (0.0, 2.5, 5.0 and 7.5 wt.%) on the hydration properties of slag-Portland cement pastes up to 12 months was investigated. The results show that the composite cement pastes containing silica fume give the higher physico-mechanical properties than that of the slag-Portland cement. Also, the XRD results reveal that the peak of  $\text{Ca}(\text{OH})_2$  shows higher intensity in the sample without silica fume and completely disappears in the sample containing 7.5 wt.% silica fume content. Also, the intensity peaks of  $\text{C}_4\text{AH}_{13}$  sharply increase with silica fume content.*

## INTRODUCTION

Granulated Blast-furnace slag (GBS) is defined as the glassy granular materials formed when molten blast-furnace slag is rapidly chilled as by immersion in water [1-3]. Fast cooling results with minimum crystallization and converts the molten slag into fine aggregate sized particles (smaller than 4 mm), composed of predominantly non-crystalline materials [1].

Due to its high content of silica and alumina in an amorphous state, ground granulated blast-furnace slag (GGBS) shows pozzolanic behavior similar to that of natural pozzolanas, fly ash and silica fume [1]. Blast-furnace slag has been widely utilized as ingredients in cement or concrete with potential hydraulicity from the point of view of effective use industrial by-products [4].

The use of GGBS in concrete increases the workability, reduces bleeding of fresh concrete or mortar. It improves strength, reduces heat of hydration. Reduces permeability and porosity, reduces the alkali-silica expansion [1, 4-7].

In order to reduce the cost of production and improve the quality of cements, blended cements known as composite cements are made. Recent trend in European countries, US and Russia is towards manufacture of composite cements with more than two components. In this connection composites blends of OPC-GBFS-Fly ash called pozzolana metallurgical cements have already been commercialized in some countries [8].

The addition of silica fume increases the rate of cement hydration at early hours due to release of  $\text{OH}^-$  ions and alkalis into pore fluids. This is attributable to the ability of silica fume to provide nucleating sites to hydration products like lime, CSH and ettringite [9]. When siliceous products like silica fume, fly ash, and GBFS are mixed with Portland cement and hydrated, they produce pore structure more discontinuous and impermeable than that of hydrated cement paste [10]. It has been reported that silica fume accelerates both  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  hydration during the first few hours [11]. Silica fume tends to affect the pattern of crystallization and degree of orientation of CH crystals at the aggregate surface during the first few days of cement hydration [12].

The role of silica fume in the reaction kinetics and mechanisms of the early stage hydration of Portland-slag cement-silica fume pastes has been studied [13]. The investigations have shown that the addition of silica fume of more than 8 % reduces the duration of the phase boundary interaction as a rate-determined process resulting in the fast diffusion rate-determining process. Also, the results of this study have revealed evidence of the accelerator effect of silica fume during the first 8 h of hydration when it still exists as chemically inert filler. The pozzolanic reaction between silica fume and CH formed during hydration is occurring after three days of hydration.

The aim of the present work is to study the influence of substitution of ordinary Portland cement by silica fume on the hydration properties of slag-Portland cement. The physico-mechanical properties of the cement pastes such as water of consistency, setting time, total porosity and compressive strength were determined. The kinetics of hydration such as free lime and combined water was estimated up to 360 days. Also, a choice of hydrated samples were investigated by XRD technique.

## EXPERIMENTAL WORK

### Materials

#### *Ordinary Portland cement*

The Portland cement was obtained from National Cement Company, Helwan. The chemical analysis of ordinary Portland cement (was carried out using the XRF technique) aided with normal wet chemical analysis technique (ASTM C114-1988) [14]. The results are given in Table 1.

#### *Granulated blast-furnace slag*

It was obtained from the Egyptian Iron and Steel Company, Helwan. It is usually obtained by water quenching of the molten slag. It was ground in a steel ball mill to obtain a Blaine surface area (4.56 m<sup>2</sup>/kg). The results of chemical analyses of granulated slag were given in Table 1.

#### *Silica fume*

It is a by-product of the manufacture of ferro-silicon metals. It was obtained from ferrosilicon company, Edfo, Upper Egypt. The chemical analysis of the silica fumes (SF) after drying at 105°C for two hours is given in Table 1. Its surface area measured by the BET method is 20 m<sup>2</sup>/g.

#### Preparation of slag-OPC-silica fume composite cement

The dry constituents of OPC, silica fume and slag were mechanically mixed for 30 minutes in a porcelain ball mill to attain complete homogeneity. The samples were kept in airtight containers until the time of paste preparation. The mix composition of different cements is shown in Table 2.

Table 2. Mix composition of different prepared cements (wt %).

Mix no	Granulated slag	Silica fume	OPC
M0	45	0.0	55.0
M1	45	2.5	52.5
M2	45	5.0	50.0
M3	45	7.5	47.5

The water of consistency (ASTM C187) [15] and setting time (ASTM C191) [16] were determined. The pastes were mixed with water of consistency, molded in one inch cubic molds for 24 hours, de-molded then immersed in tap-water up to one year. The kinetic of hydration were followed by the determination of free lime (ASTM 114) [14] and combined water contents after firing at 950°C for 30 minutes minus the weight of water in Ca(OH)<sub>2</sub>. The total porosity (ASTM C373) [17] and compressive strength were also measured up to one year. The mixing, molding and stopping of hydration were described elsewhere [18].

The compressive strength test was carried using a machine of the Seidener model having a maximum load of 600 kN. For each group, at least three specimens were tested and the average of the results was considered.

X-ray diffraction (XRD) analyses were performed using BRUKER D<sub>8</sub> ADVANCE, Target: Cu K<sub>α</sub>. The phases were identified with the help of the Appendix 1, on Tabulated crystallographic Data of Taylor [1997] [19].

## RESULTS AND DISCUSSION

Initial and final setting times as well as water of consistency for the cement pastes are shown in Figure 1. The results show that the water of consistency slightly increases with silica fume content. Also, the initial setting time of the cement pastes sharply decreases with increasing silica fume content, while the final setting time slightly decreases as the silica fume increases. It can be seen that the presence of silica fume increases the percentage of hydration during the first hours of hydration compared with cement paste free of silica fume. This may be due to the enhanced precipitation of hydration products on the surface of silica fume particles, which possibly serves as nucleation sites. Previous studies

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

Materials	Oxides							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O
Portland Cement	21.3	5.41	3.77	63.14	1.21	2.35	0.09	0.4
Silica fume	96.89	1.03	0.56	0.21	0.15	0.16	0.62	0.17
Granulated slag	39.89	13.72	2.56	26.38	3.47	1.22	1.06	1.0

[20-23] have shown that the addition of silica fume or nature pozzolona accelerates the early stage of hydration of Portland cement and its individuals compounds. The authors propose that the increased rate of hydration may be due to enhanced precipitation of hydration products on the surface of the pozzolana, which possibly serves as a nucleation site during the early hours when it exists as a chemically inert filler. Thereafter, lowering of the concentration of calcium ions accelerates the rates of dissolution of cement clinker phases especially  $C_3S$  and  $\beta-C_2S$  [3]. On the other side, the setting process is associated with the formation of calcium sulfoaluminate hydrate. The formation of these hydrates depends on the reaction velocity of the aluminate compounds, amount of the phases, calcium sulfate and calcium hydroxide. The major phases ( $C_3S$  and  $\beta-C_2S$ ) of the Portland cement clinker act as a source of calcium hydroxide that gives correct alkalinity to form sulfoaluminates compounds.

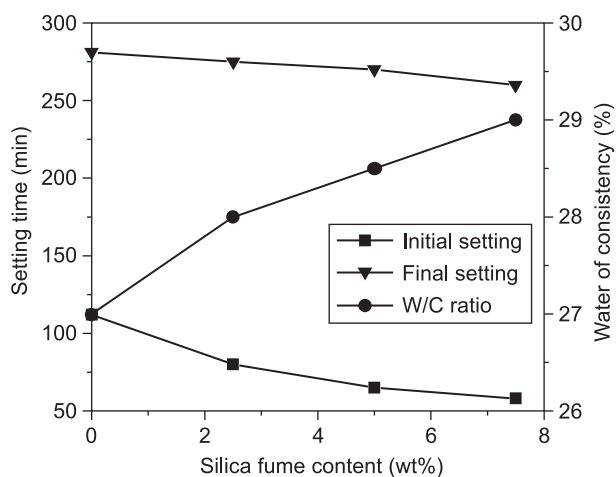


Figure 1. Water consistency, initial and final setting time of different composite cement pastes.

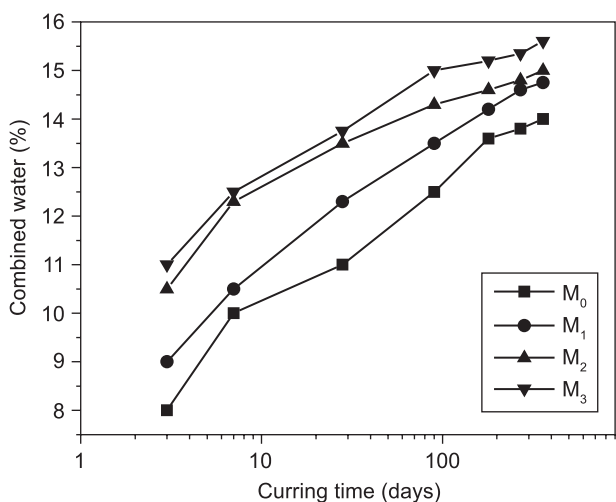


Figure 2. Chemically combined water contents of composite pastes as a function of curing time.

The combined water contents of the cement pastes as a function of curing time is plotted in Figure 2. It is clear that the combined water content increases with curing time for all hardened cement pastes. This is due to the fact that silica fume accelerates hydration of the cement pastes by providing nucleation sites for free  $Ca(OH)_2$  within minutes after reaction commences and by reacting with it to give rise of CSH products formed [24]. In addition, as the amount of silica fume increases, the combined water gradually enhances for all cement pastes. This indicates that the presence of silica fume plays an important role in the hydration of slag-Portland cement pastes. On the other hands, the sample without silica fume has lower values of combined water than the other pastes at all ages of hydration and the amount of combined water content increases with the substituted silica fume. It can be concluded that the addition of silica fume to cement pastes accelerates the early stage of hydration of the slag-Portland cement and its individual compounds. This may be due to enhanced precipitation of hydration products on the surface of pozzolana, which possibly serves as a nucleation site during the early hours when exists as a chemically inert filler and as a pozzolan, reacting chemically with CH formed during hydration of cement. The starting time of pozzolanic reaction varied with the properties of pozzolana from 1 day to 28 days [3].

The free lime content of hardened cement pastes are shown in Figure 3. The data show that the cement paste without silica fume gives a higher amount of  $Ca(OH)_2$  than the other samples at all ages, while, as the silica fume proportion increases the free lime decreases. In the early stage of Portland cement hydration, mainly the clinker minerals  $C_3S$  and  $C_2S$  react with water. Though slag hydration takes place simultaneously with the hydration of Portland cement, major acceleration of the slag component hydration occur later [25]. Moreover,

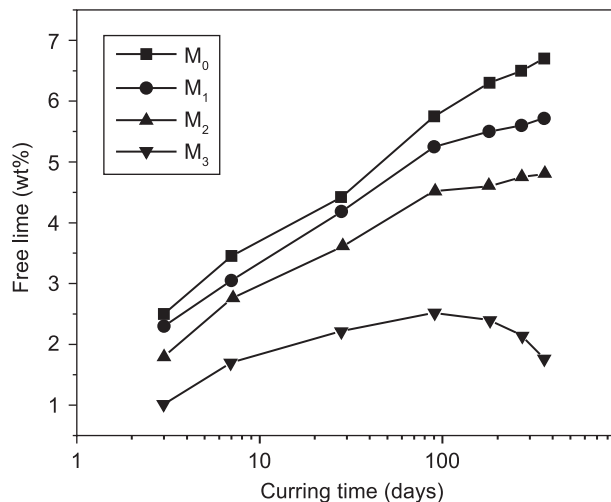


Figure 3. Free lime contents of composite cement pastes as a function of curing time.

alkalis and lime released by Portland cement are retained in hydration products of the slag fraction and do not seem to contribute to the hydration of slag [26]. Also, as the amount of silica fume increases the free lime sharply decreases especially at early ages (3-28 days). This indicates the higher reactivity of silica fume towards reaction with  $\text{Ca}(\text{OH})_2$  liberated during the hydration time. On the other hand, the cement paste containing 7.5 wt. % silica fume gives a lower amounts of  $\text{Ca}(\text{OH})_2$  than those other pastes at all ages. The cement pastes with 7.5 wt. % silica fume shows slightly increases of the free lime up to 90 days and then decreases up to 360 days. This is due to the pozzolanic reaction, silica fume reacts with lime during the hydration of the paste. Also, the rate of liberation of free lime is lower than its consumption with silica fume at later ages. Therefore, the residual free lime of cement paste containing 7.5 wt.% silica fume decreases after 90 days.

The total porosity of the hardened composite cement pastes cured up to 360 days is illustrated in Figure 4. The total porosity of the cement pastes decreases with curing time due to filling up a part of the available pores by the hydration products. The cement sample without silica fume exhibits higher values of porosity than those samples containing silica fume at 3-360 days. On the other, as the silica fume content increases, the total porosity decreases, especially at early ages. Cement pastes containing 5.0 and 7.5 wt.% silica fume give the lowest values of total porosity with curing time. This is attributed to that the addition of silica fume acts as an active component in the hydration reaction of Portland cement, i.e. the rate of hydration increases and the amount of hydration products enhances. Moreover, silica fume reacted with free  $\text{Ca}(\text{OH})_2$  which liberates during hydration of silicates phases to produce CSH which deposits in the open pores of the hardened cement paste and leads to decrease the total porosity. The addition

of silica fume increases the rate of cement hydration at early hours due to releases of OH ions and alkalis into pore fluid [27]. This is attributed to the ability of silica fume to provide nucleating sites to the hydration products like lime, calcium silicate hydrate and ettringite [23]. When siliceous products like silica fume and or are mixed with Portland cement and hydrated, they produce pore structure more discontinuous than that of Portland cement paste [28]. It is evident that the addition of silica fume to slag-Portland cement plays an important role in the activation of hydrated paste formation and crystallization of CSH as well as formation of a dense structure. On the other side, silica fume acts as filler which accelerates the hydration of the cement phases in addition to filling some pores. Therefore, the total porosity is decreased.

The compressive strength of the hardened cement pastes cured up to 360 days is shown in Figure 5. The results reveal that the compressive strength increases with curing time for all hardened cement pastes. This is attributed to the increasing amount of hydrated products that leads to an increase in the compressive strength of the cement paste. The cement paste without silica fume has lower values of compressive strength than those of other pastes at 3-360 days. Sample with 7.5 wt.% silica fume gives the highest values of compressive strength at all curing time. Also, as the silica fume content increases the compressive strength enhances with time. This is attributed to two effects; (i) the presence of silica fume in the pastes activates the cement phases especially  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  to form hydrates as well as acts as filler, improving the physical structure, (ii) the pozzolanic reaction of the silica fume with liberated lime leads to produce CSH, so that, the amount of binder is increased. Both the two effects increase the compressive strength and give the dense structure. Moreover, as the silica fume reacts with the free lime to produce calcium silicate hydrate, voids

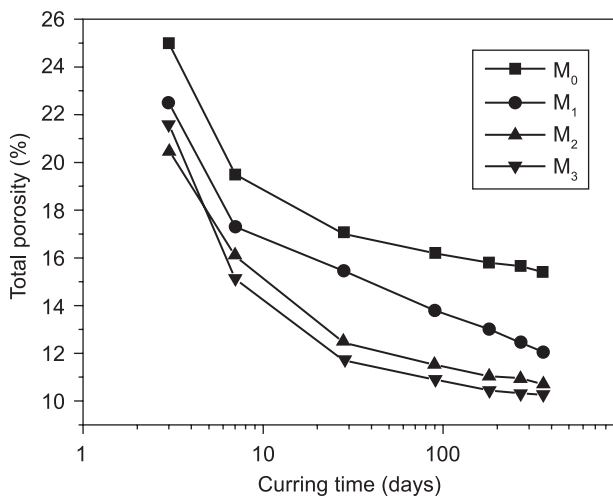


Figure 4. Total porosity of composite cement pastes as a function of curing time.

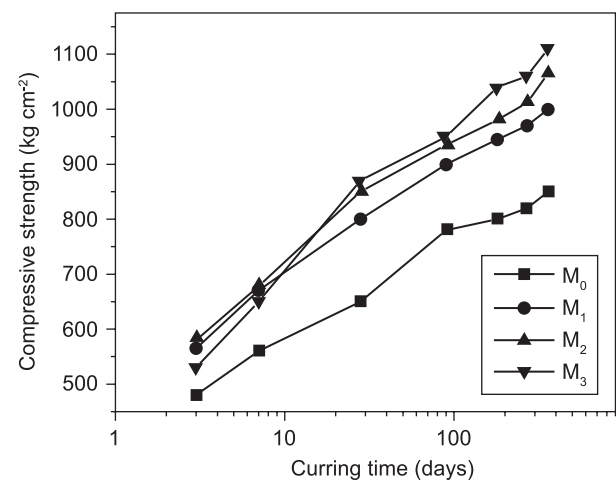


Figure 5. Compressive strength of composite cement pastes as a function of curing time.

and pores within the cement paste are filled by the new hydration products and become more homogenous and dense. It has been reported that silica fume pastes exhibit higher strength at 7 and 28 days than ordinary pastes [29]. Three mechanisms (i). strength enhancement by pore size refinement and matrix densification (ii). strength enhancement by reduction in content of  $\text{Ca}(\text{OH})_2$  and (iii)., strength enhancement by cement paste-aggregate interfacial refinement seem to be responsible for the strength development capability of silica fume. [30-32]. Thus, the addition of silica fume gives greatly improved compressive strength to the slag-Portland cement pastes.

XRD patterns of the hardened cement pastes containing 0.0, 2.5 and 7.5 wt.% silica fume hydrated for 360 days in tap water are shown in Figure 6. The main detected in the patterns are CSH ( $d = 3.07$ ),  $\text{Ca}(\text{OH})_2$  ( $d = 4.90$ ) and  $\text{CaCO}_3$  ( $d = 3.03$ ),  $\beta\text{-C}_2\text{S}$  ( $d = 2.77, 2.74$ ) as well as  $\text{C}_4\text{AH}_{13}$  ( $d = 2.85$ ). The results reveal that the peak of  $\text{Ca}(\text{OH})_2$  shows higher intensity in the sample without silica fume and completely disappear with the sample containing 7.5 wt.% silica fume. Also,  $\text{C}_4\text{AH}_{13}$  was detected in all the samples and the intensity of its peak sharply increases with the increasing of silica fume content. On the other side, the CSH peaks are intensified with available increase indicating more dense structure and large amounts of additional CSH in the presence of 2.5 and 7.5 wt.% silica fume.  $\text{CaCO}_3$  peaks were detected in all the samples. In addition, quartz peaks were also detected as a main constituent of slag. Also, residual unhydrated peaks of  $\beta\text{-C}_2\text{S}$  phase were detected even after 360 days of hydration.

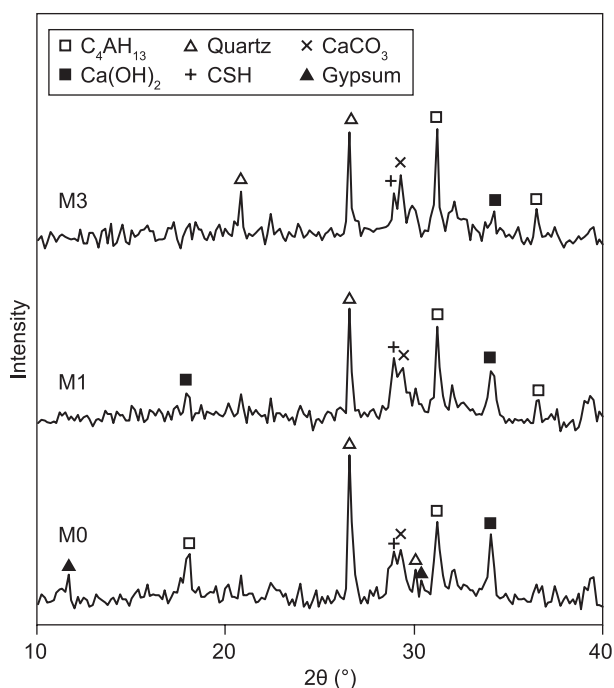


Figure 6. XRD patterns of the hardened cement pastes cured for 360 days.

## CONCLUSION

The main results obtained from this investigation are summarized as follows:-

- The addition of silica fume to slag-Portland cement accelerates the rate of hydration from 3 up to 360 days curing time.
- The addition of 7.5 wt.% silica fume to cement pastes reduces the liberated lime to a minimum value.
- As the silica fume increases till 7.5 wt.%, the rate of hardening enhances to a higher value at all ages
- The CSH and  $\text{C}_4\text{AH}_{13}$  more abundant with available increase of silica fume indicating formation of dense structure and large amounts of additional hydration products in the presence of silica fume.

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