

# INFLUENCE OF SILICA FUME ON THE PROPERTIES OF SULPHATE RESISTING CEMENT AND ALUMINA CEMENT MIXTURE

IVON HELMY, HAMDY EL-DIDAMONY, ALI HASSAN ALI\*, TAREK EL-SOKKARY\*

*Faculty of Science, Zagazig University, Zagazig, Egypt*

*\*Housing and Building Research, Centre, Dokki, Cairo, Egypt*

Submitted November 6, 2000, accepted May 24, 2001

**Keywords:** Silica fume, Sulphate resisting cement, Alumina cement

*This work aims to study the effect of silica fume on the properties of alumina cement and sulphate resisting cement composite up to 90 days. The substitution of alumina cement by silica fume tends to increase the water of consistency and elongate the setting time. The apparent porosity increases and the compressive strength decreases with silica fume content. Melamine formaldehyde sulphonate (MFS) was used as super-plasticizer to decrease the mixing water, which affects the properties of the cement paste.*

## INTRODUCTION

Pozzolana is either natural or artificial and contains silica in a reactive form. Pozzolana in its finally divided state can combine with lime liberated during the hydration of cement to form stable calcium silicate hydrates with cementing properties [1]. The influence of amorphous silica (silica dust) on the physico-mechanical properties of concrete has been studied [2].

By addition of amorphous silica to blended cement considerable improvements of the mechanical properties and resistance to sulphate attack were observed [3]. The use of pozzolanic cement is increasing worldwide because it needs less energy for production. It usually has higher ultimate strength and better durability to chemical and aggressive attack.

The possibility of using silica fume was studied [4]. The silica fume contains (85-98 wt.%)  $\text{SiO}_2$  in an amorphous state and have surface area  $\cong 20 \text{ m}^2/\text{g}$  [5]. When it is added to portland cement, the material showed a high degree of pozzolanic activity, and better resistance to chemical attack. The high surface area of silica fume in concrete is responsible for high pozzolanicity and high water demand. To maintain adequate consistency, in silica fume blended cement superplasticizer must be added to improve the mechanical properties [6,7].

Bentsen et al. [8] studied blends of HAC with 30 and 50 wt.% silica fume, up to 7 days. Strätlingite was found to be the dominant hydrate after one week, at 40°C or below.

Similar findings were reported by Marchargent et al. [9] Fu et al. [10] have investigated the effect of a wide range of siliceous additives including silica fume, fly ash, granulated slag, zeolites and sodium silicate on

the hydration of HAC at temperatures up to 38°C. In all cases Strätlingite was formed. Initial strengths were lower than HAC alone, but addition of sodium salts, which increased the *pH*, increased the rate of Strätlingite formation and strength development [11].

The aim of the present work is to study the hydration characteristics of SRC with various proportions of HAC and SF. Alumina cement was substituted by equal amounts of silica fume in the composite 85 wt.% SRC and 15 wt.% HAC. The water of consistency and setting time of cement pastes were measured. The hydration kinetics were also determined from the free  $\text{Ca(OH)}_2$ , combined water contents and the hydration products by the aid of DTA and XRD techniques. The total porosity and the compressive strength of the cement pastes were also measured. Melamine formaldehyde sulphonate MFS superplasticizer was used to show its effect on the physico-mechanical properties of hardened cement pastes up to 90 days.

## EXPERIMENTAL

The materials used in this work were sulphate resisting cement SRC, supplied from Helwan Portland Cement Co. Egypt, high alumina cement HAC, secar 40 wt.%  $\text{Al}_2\text{O}_3$ , imported from Lafarge Company, France and silica fume SF from Egyptian Co., for ferrosilicon alloys Edfo, Egypt. The chemical analysis and surface area of the materials are given in table 1.

Different mixes were made by substituting 5, 10 and 15 wt.% of HAC by SF in the composite 85 wt.% SRC and 15 wt.% HAC. The mixes were denoted as  $M_0$ ,  $M_1$ ,  $M_2$  and  $M_3$ . Each dry mix was homogenized for one

Table 1. Chemical oxide composition and surface area of starting materials (wt.%).

oxides % materials	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>	LOI	Na <sub>2</sub> O	K <sub>2</sub> O	surface area (cm <sup>2</sup> /g)
SRC	20.88	3.697	4.937	64.57	1.987	1.621	2.27	0.0184	0.0351	3561
HAC	7.92	39.81	1.81	44.88	2.61	0.00	2.50	0.25	0.20	2300
SF	94.64	0.97	0.93	0.55	0.35	0.10	2.01	0.20	0.25	200000

hour in a porcelain ball mill using two balls to assure complete homogeneity. The mixing of cement pastes was carried out with the water of consistency. The amount of mixing water was poured on to the cement and mixed for four minutes by the aid of a trowel. The paste was directly poured in cubic moulds 2×2×2 cm and pressed until homogenous specimen was obtained. The moulds were manually vibrated to remove any air bubbles. The surface of the paste was smoothed by spatula. The moulds were cured in a 100% R.H. at 23 ± 2°C for 24 hours, then demoulded and cured under tap water up to 90 days.

The water of consistency, initial and final setting times of cement pastes were determined using a vicat apparatus [12,13]. The kinetics of hydration was followed by the determination of free lime [14] and combined water contents. The total porosity and compressive strength were also measured. After the predetermined curing time the hydration was stopped using the technique described elsewhere [15]. The combined

water content was estimated on the basis of ignition loss of dried sample heated at 1000°C for 30 minutes minus the weight of water in Ca(OH)<sub>2</sub>. The development of hydration products were followed using DTA and X-ray diffraction techniques.

### RESULTS AND DISCUSSION

The water of consistency as well as initial and final setting times of cement pastes are graphically plotted in figure 1. The results show that the water of consistency as well as the initial and final setting times of all cement pastes containing silica fume are higher than those without silica fume. This may be due to the higher surface area of silica fume and the high content of mixing water, which elongates the setting behaviour.

The combined water content of blended cement pastes are represented as a function of curing time in figure 2. The combined water content increases gradu-

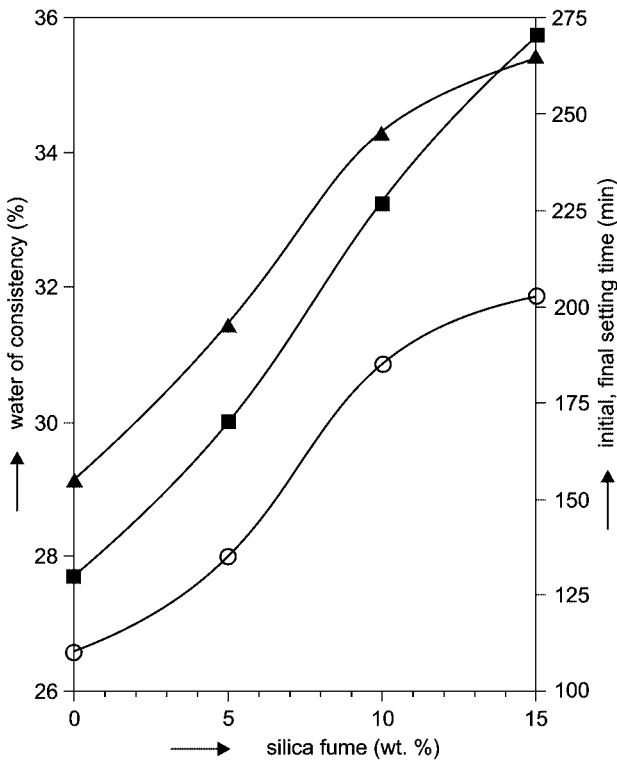


Figure 1. Water of consistency, initial and final setting time of SRC pastes with various proportions of HAC and silica fume. ■ water of consistency; ○ initial setting times; ▲ final setting times

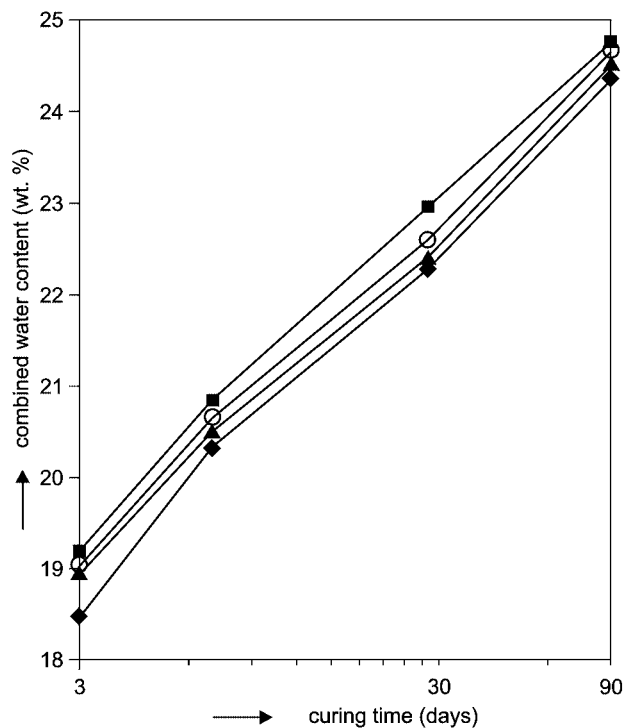


Figure 2. Combined water content of SRC pastes with various proportions of silica fume and HAC up to 90 days. ■ M0; ○ M1; ▲ M2; ◆ M3

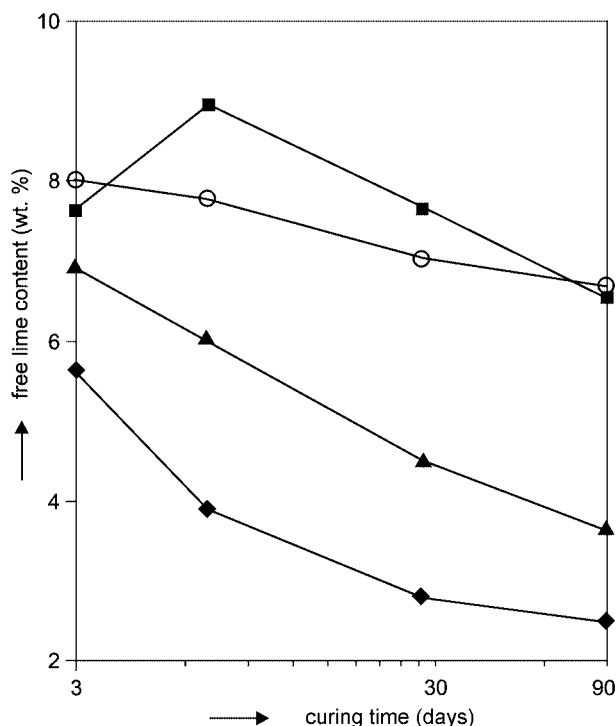


Figure 3. Free lime content of SRC pastes with various proportions of silica fume and HAC up to 90 days. ■ M0; ○ M1; ▲ M2; ◆ M3

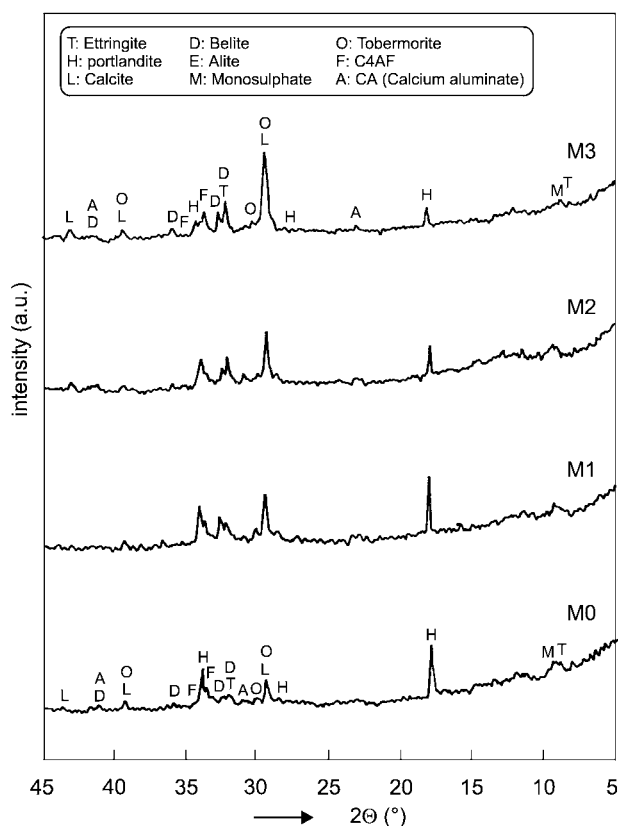


Figure 4. X-ray diffraction patterns of SRC pastes with various proportions of silica fume and HAC up to 90 days.

ally with curing time for all cement pastes. This is due to the progress of hydration and the accumulation of hydration products. On the other side, as the silica fume increases the combined water content decreases. This is due to that the calcium aluminate hydrates need more water of hydration than calcium silicate hydrate.

The free lime content of blended cement pastes are plotted as a function of curing time in figure 3. The free lime content decreases with curing time and SF content for all cement pastes. This is mainly due to that the silica fume consumes some of liberated  $\text{Ca}(\text{OH})_2$  during the hydration of SRC forming CSH. On the other side, the free lime content of cement paste with 15 wt.% HAC increases up to 7 days followed by a decrease up to 90 days. The initial increase of the free lime content up to 7 days indicates that the rate of free lime liberation is higher than its consumption. The decrease of free lime content after 7 days is mainly due to the reaction of liberated  $\text{Ca}(\text{OH})_2$  with HAC as well as silica fume forming hydrated  $\text{C}_4\text{AH}_{13}$  and  $\text{C}_2\text{ASH}_8$  as well CSH.

The XRD of the hydrated cement pastes of 85 wt.% SRC, 15 wt.% HAC substituted with 5, 10 and 15 wt.% SF for 90 days are shown in figure 4. The Figure shows that the tobermorite-gel of CSH is the major phase and increases with SF. On the other side, the portlandite decreases with SF content due to its consumption forming calcium silicate hydrate CSH. The decrease of portlandite in the SRC is also due to the reaction of  $\text{Ca}(\text{OH})_2$  with calcium aluminate and calcium aluminoferrite hydrates. The peaks of  $\text{C}_3\text{S}$  and  $\beta\text{-C}_2\text{S}$  are detected in the presence of silica fume. The peak of ettringite decreases at 15 wt.% silica fume due to the decrease of HAC content. The calcium sulphoaluminate and calcium aluminate hydrates are ill crystalline.

Figure 5 illustrates the DTA thermograms of SRC with various proportions of SF as well as HAC at 90 days. It is clear that as the silica fume increases on the expense of HAC, the peak of CSH increases and the peak of CAH decreases and completely disappear at zero HAC. Also, the endothermic effect at  $320^\circ\text{C}$  due to the formation of  $\text{C}_4\text{AH}_{13}$  decreases with SF and completely disappears in  $\text{M}_3$ . On the other side, the endothermic peak at  $\approx 500^\circ\text{C}$  due to the decomposition of  $\text{Ca}(\text{OH})_2$  decreases with silica fume content. In addition, the endothermic peaks of the carbonate decrease also with silica fume content. For the addition 15 wt.% silica fume, an exothermic peak at  $900\text{-}1000^\circ\text{C}$  is due to the recrystallization of wollastonite [16]. This is indication from the decomposition of CSH from silica fume. These results of free lime are in a good agreement with those of chemical analysis.

The total porosity by blended cement pastes cured for 3, 7, 28 and 90 days are graphically plotted in figure 6. It is clear that the total porosity decreases with curing

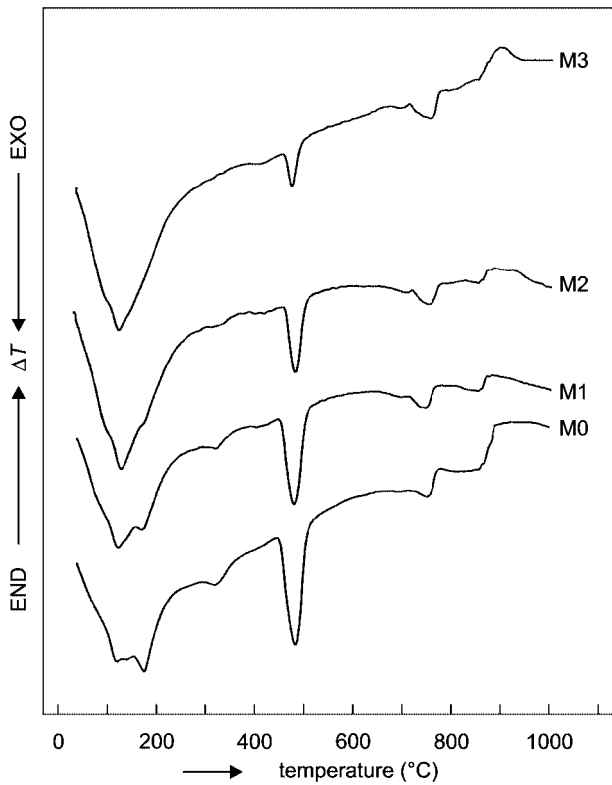


Figure 5. DTA thermograms of SRC pastes with various proportions of silica fume and HAC up to 90 days.

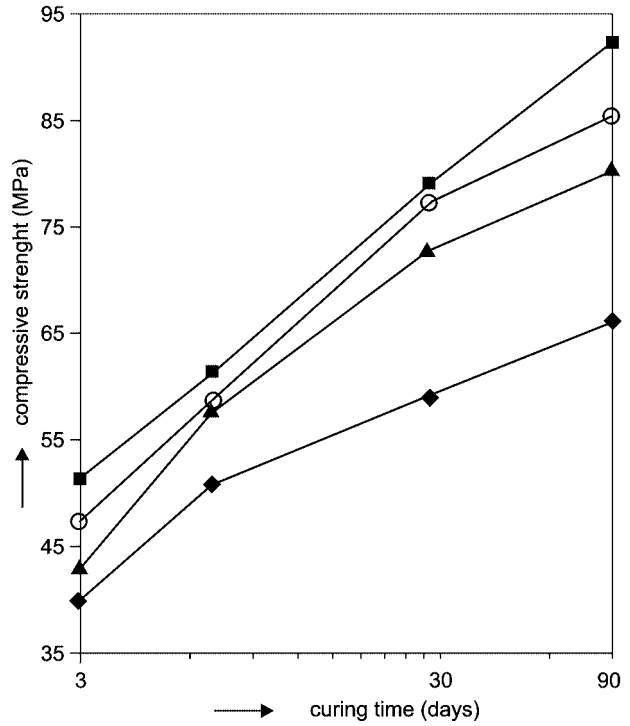


Figure 7. Compressive strength of SRC pastes with various proportions of silica fume and HAC up to 90 days.

■ M0; ○ M1; ▲ M2; ◆ M3

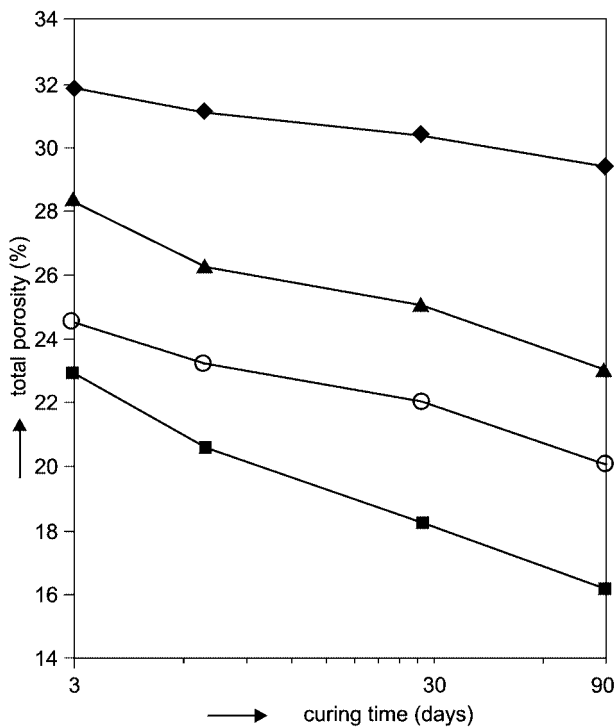


Figure 6. Total porosity of SRC pastes with various proportions of silica fume and HAC as a function of curing time

■ M0; ○ M1; ▲ M2; ◆ M3.

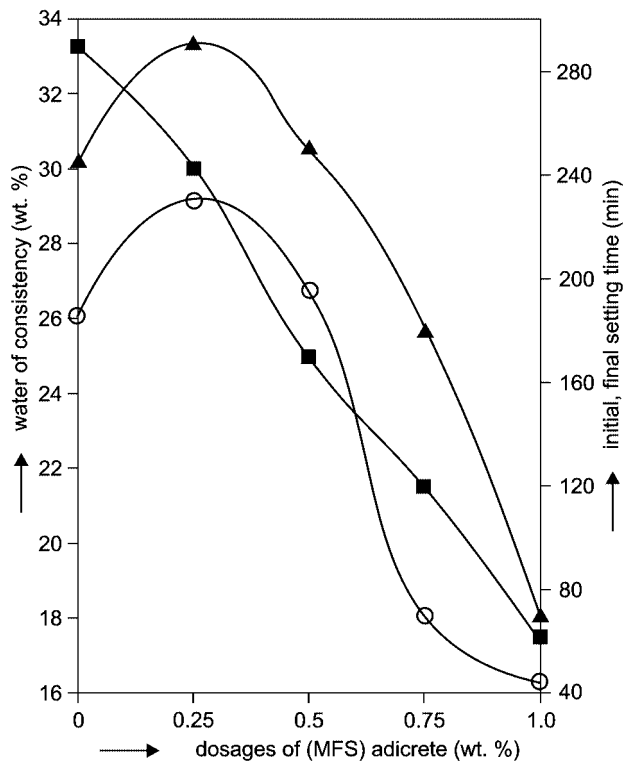


Figure 8. Water of consistency, initial and final setting time of SRC with HAC and silica fume in presence of different dosages of admixture.

■ water of consistency; ○ initial setting times; ▲ final setting times

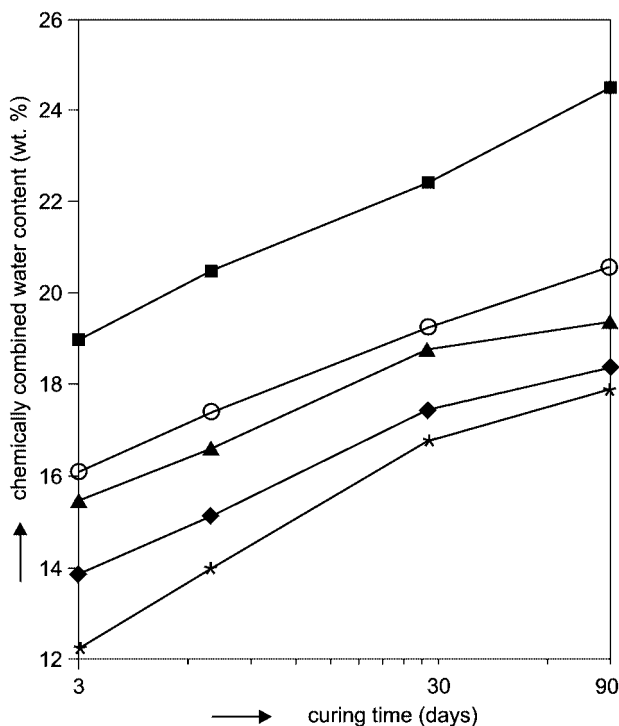


Figure 9. Combined water content of SRC with HAC and silica fume cured up to 90 days in presence of different dosages of MFS admixture.

■ 0 wt.%; ○ 0/0.25 wt.%; ▲ 0.50 wt.%;  
◆ 0.75 wt.%; ★ 1 wt.%

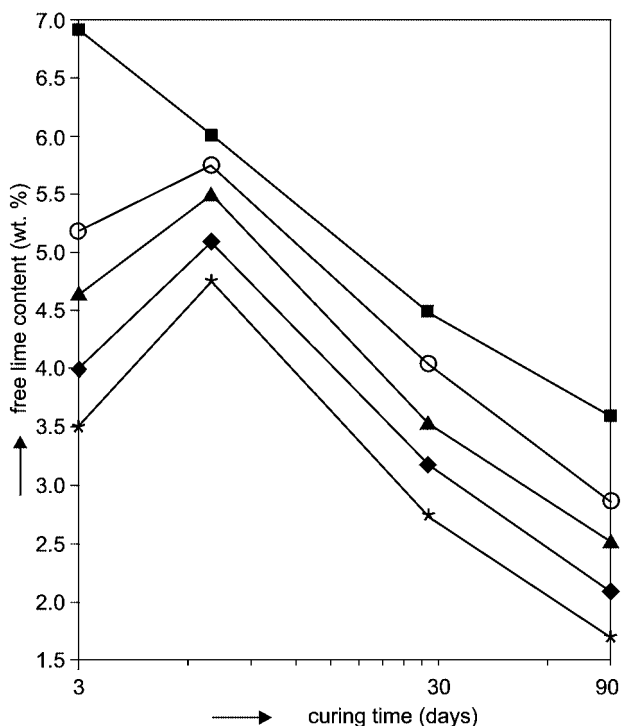


Figure 10. Free lime content of SRC with HAC and silica fume cured up to 90 days in presence of different dosages of MFS admixture.

■ 0 wt.%; ○ 0/0.25 wt.%; ▲ 0.50 wt.%;  
◆ 0.75 wt.%; ★ 1 wt.%

time for all hardened cement pastes due to the filling up a part of the available pore volume with hydration products. On the other hand, the increase of silica fume the total porosity increases due to the increase of the water of consistency.

The compressive strength of blended cement pastes is graphically plotted in figure 7. The compressive strength for all cement pastes increases with curing time. This is mainly due to the increase of the amount of hydration products such as tobermorite-gel, calcium sulphoaluminate, calcium aluminate and gehlenite hydrate. As the hydration proceeds, more hydration products are formed; this leads to the accumulation of these hydrates in the pores and the compressive strength increases with curing time.

Obviously, the increase of silica fume, decreases the compressive strength of cement pastes. This is mainly due to the increase of water of consistency. Therefore, MFS superplasticizer must be added to the silica fume blended cements to decrease the water of consistency which affects the total porosity and also the compressive strength. The effect of different dosages of melamine formaldehyde sulphonate (MFS) admixture as 0.25, 0.50, 0.75 and 1.00 wt.% of cement on the blended cement of 85 wt.% SRC with 5 wt.% HAC and 10 wt.% SF was studied.

The water of consistency, initial and final setting times of cement pastes with MFS are plotted in figure 8. The water of consistency of cement pastes without MFS is higher than that with MFS admixture. The addition of MFS superplasticizer decreases the water of consistency of cement pastes. Also, the increase of MFS superplasticizer decreases the water of consistency due to the coating effect of these admixtures. The adsorption of the admixture appears to be linearly related to its amount up to the optimal dose, at high dosage than the optimal, the excess admixture appears to inhibit the influence of water reduction and strength production capabilities. The admixture does not react with cement to form crystal type [17].

The initial and final setting times of blended cement pastes are accelerated with the dosage of MFS admixture due to the decrease of water/cement ratio. This is also due to the dispersing action of the admixture and to the decrease of water of consistency. It can be concluded that MFS at lower dosages as 0.25 acts as retarder and then the increase of the dose acts as accelerator.

The combined water contents for cement pastes in presence of different dosages of MFS admixture cured up to 90 days are graphically represented in figure 9. It is clear that the combined water contents increase with curing time for all cement pastes. On the other side, the

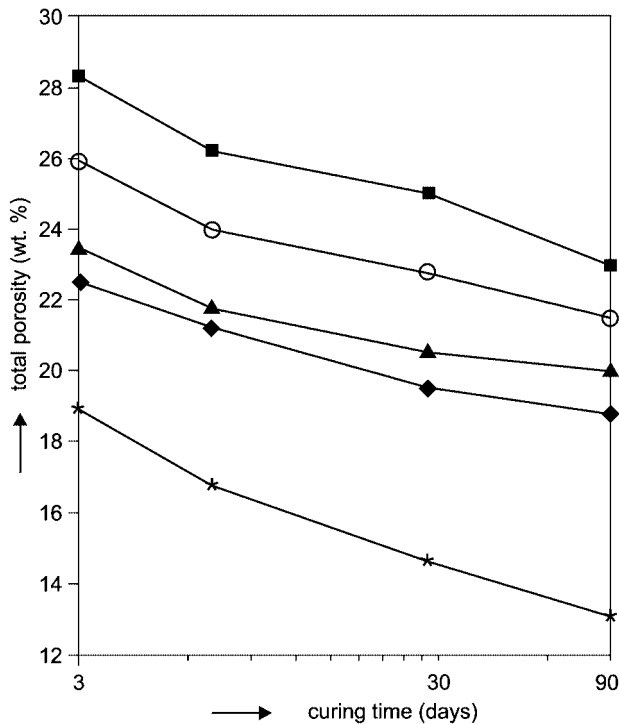


Figure 11. Total porosity of SRC with HAC and silica fume cured up to 90 days in presence of different dosages of admixture.

■ 0 wt.%; ○ 0/0.25 wt.%; ▲ 0.50 wt.%;  
◆ 0.75 wt.%; ★ 1 wt.%

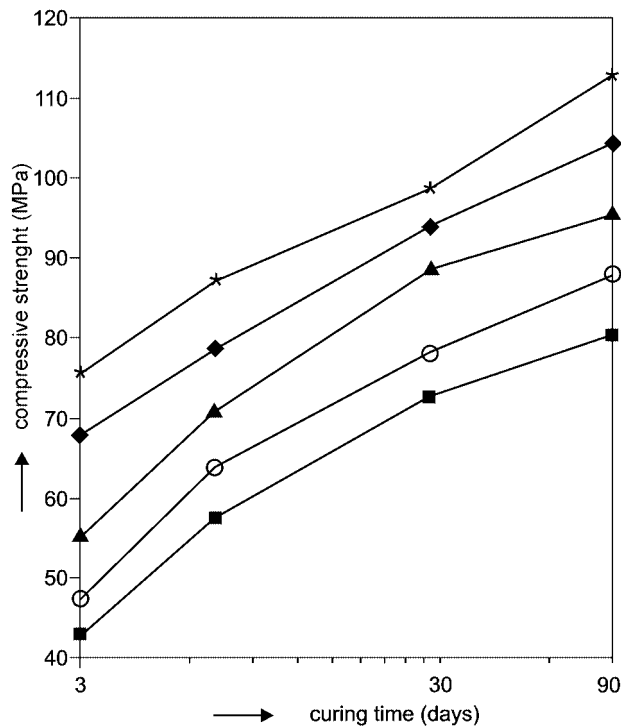


Figure 12. Compressive strength of SRC with HAC and silica fume cured up to 90 days in presence of different dosages of admixture.

■ 0 wt.%; ○ 0/0.25 wt.%; ▲ 0.50 wt.%;  
◆ 0.75 wt.%; ★ 1 wt.%

combined water content decreases with the dosage of MFS super-plasticizer due to the decrease of mixing water, which retards the hydration of cement paste.

The free lime content of cement pastes in presence of MFS cured up to 90 days are plotted in figure 10. The results indicate that the free lime content of cement paste without MFS decreases linearly with curing time. The SF and HAC consume some of liberated portlandite during the hydration of cement paste. On the other side, the free lime content of cement pastes with MFS increases up to 7 days followed by gradual decrease up to 90 days. The initial increase of free lime content up to 7 days is mainly due to that the rate of liberation of  $\text{Ca}(\text{OH})_2$  is higher than its consumption at early ages in the presence of superplasticizer. Also, the decrease of free lime content after 7 days is mainly due to the consumption of liberated  $\text{Ca}(\text{OH})_2$  with HAC as well as SF forming hydrated  $\text{C}_4\text{AH}_{13}$  and  $\text{C}_2\text{AH}_8$  as well CSH. The decrease of  $\text{Ca}(\text{OH})_2$  with the admixture content may be due to the reduction of porosity which leads to approaching the grains of silica fume from the liberated lime as well as the low water content which retards the hydration.

The total porosity of cement pastes containing 10 wt.% SF and 5 wt.% HAC with different dosages of MFS cured up to 90 days are graphically represented in figure 11. As the curing time proceeds, the total porosity decreases. This is due to continuous filling up of a part of the available pore volume with the hydration products. It is clear that as the dosage of MFS admixture increases the total porosity decreases due to the reduction of the water of consistency.

The compressive strength of cement pastes in presence of different dosages of MFS cured up to 90 days are graphically represented in figure 12. The compressive strength for all cement pastes increases with curing time due to the increase of the amount of hydration products especially tobermorite-gel. As the hydration proceeds, more hydration products and more cementing materials are formed, this leads to the accumulation of these hydrates in the pores then the compressive strength increases. On the other side, the compressive strength increases with the dosage at all ages due to the decrease of water of consistency, which tends to increase the compressive strength. The addition of superplasticizer enhances the workability and improves the degree of compaction [18,19]. The increase of the dosage of MFS admixture causes the reduction of total porosity that leads to approaching the grains of condensed silica fume from the liberated lime that forming additional amounts of calcium silicate hydrates with low  $\text{CaO}/\text{SiO}_2$  [20]. The calcium silicate hydrate is the main source of compressive strength.

## CONCLUSION

From the above findings it can be concluded that:

- The substitution of alumina cement in SRC and HAC composite with SF the water of consistency increases and the initial as well as final setting times are elongated.
- The apparent porosity increases and the compressive strength decreases with the substituted silica fume content.
- MFS was used as superplasticizer to decrease the mixing water and accelerate the setting time. By using MFS superplasticizer, the mechanical properties were improved, i.e. the total porosity is decreased and the compressive strength is increased.
- MFS at an addition of 0.25 wt.% acts as retarder and at higher values behaves as accelerator.

## References

1. Tkemoto K., Uchikawa H.: Proc. 7<sup>th</sup> Int. Congr. Chem. Cem., Vol. 1, Theme IV-2/1-29, Paris 1980.
2. Tkalcec E., Zelic, J.: Zement-Kalk-Gips 40, 574 (1987).
3. Kasselouri V., Ftikos Ch., Parisakis C.: Cem.Concr. Res. 13, 649, (1983).
4. Traetteberg A., Asgerission: il Cemento 75, 349 (1978).
5. Malhotra V.M., Ramachandran V.V., Feldman R.F., Aitcin P.C. in: *Condensed Silica Fume in Concrete*, pp. 53-81, CDC Press Inc., Boca Raton, Florida 1987.
6. El-Didamony H., Amer A.A., Ebied E., Heikel M.: il Cemento 90, 221 (1993).
7. El-Didamony H., Helmy I.M., Amer A.A., Heikel M.: Zement-Kalk-Gips 502, 123 (1995).
8. Bentsen S., Seltveit A., Sandberg B. in: *Calcium Aluminate Cements*, pp. 294-319, Editor Mangabhai R.J., E & FN Spon, London 1990.
9. Marcdargent S., Testud M., Bayoux J.P., Mathieu A.: Proc. 9<sup>th</sup> Int. Congr. Chem. Of Cement, Vol. IV, pp. 651-7, New Delhi 1992.
10. Ding J., Fu Y., Beaudoin J.J.: Cem.Concr.Res. 25, 1331 (1995).
11. Ding J., Fu Y., Beaudoin J.J.: Cem.Concr.Res. 7, 171 (1995).
12. ASTM Standards, ASTM Designation, C187-83, 195 (1983).
13. ASTM Standards, ASTM Designation, C191-82, 208 (1983).
14. Kodo R., Abu-El-Enein S.A., Diamon M.: Bull Chem.Soc.Japan 48, 222 (1975).
15. El-Didamony H.: Thermochim.Acta 35, 201 (1980).
16. Ramachandran V.S.: *Application of Differential Thermal Analysis in Cement Chemistry*, pp. 213-221, Chemical Publ. Co. INC., New York 1969.
17. Sweeltand D.: *Civil Engineering*, p. 33, Acad. Press Inc., London 1976.
18. Taylor H.F.W.: *Cement Chemistry*, pp. 345-376, Acad. Press Inc., London 1990.
19. Okafor F.O.: Cem. Concr. Res. 21, 551 (1991).
20. Ramachandran V.S., Feldman R.F., Beaudoin J.J.: *Concrete Science*, pp.61-166, Hyden, London 1981.

---

### VLIV KŘEMIČITÉHO ÚLETU NA VLASTNOSTI SMĚSI SÍRANOVZDORNÉHO A HLINITANOVÉHO CEMENTU

IVON HELMY, HAMDY EL-DIDAMONY, ALI HASSAN ALI\*,  
TAREK EL-SOKKARY\*

*Faculty of Science, Zagazig University, Zagazig, Egypt*

*\*Housing and Building Research, Centre, Dokki, Cairo, Egypt*

Cílem práce je studium účinku křemičitého úletu na vlastnosti směsi síranovzdorného a hlinitanového cementu během devadesátidenní hydratace. Náhrada hlinitanového cementu křemičitým úletem zvyšuje množství záměsové vody a prodlužuje dobu tuhnutí. S přidavkem křemičitého úletu dále roste zdánlivá porosita a klesá pevnost v tlaku. Jako plastifikátor byl použit sulfonát melaminformaldehydu (MFS) s cílem snížit vodní součinitel, který ovlivňuje vlastnosti cementové kaše.