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Effect of silica fume or granulated slag on sulphate attack of ordinary portland and alumina cement blend

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Abstract

The effect of silica fume or granulated slag as high alumina cement (HAC) substitutes, on sulphate attack of ordinary Portland and alumina cement blend up to complete substitution and up to 12 months, was studied. The results indicate that the cement pastes with silica fume give higher combined water and lower free lime contents than those containing granulated slag. The increase of HAC substitution by silica fume or granulated slag in the OPC–HAC blend decreases the aggressive attack of sulphate ions on the hardened cement pastes, yet the granulated slag is more effective than the silica fume.

Keywords: Ordinary Portland cement (OPC); High alumina cement (HAC); Silica fume (SF); Granulated slag (GS); Sulphate attack; Free lime; Combined water; Porosity; Compressive strength

1. Introduction

Aggressive attack of sulphate ions is one of the factors responsible for damage to Portland cement concrete [1]. Sulphate ions can react with some constituents of cement pastes producing sulphoaluminate hydrates (ettringite or monosulphate) and gypsum, which cause expansion and cracking of concrete. The supersulphated Portland blast- furnace slag or pozzolanic cements increase the chemical resistance to sulphate attack, and possess impermeability and lower heat of hydration [2].

Condensed silica fume is a by-product of the manufacture of silicon or silicon alloys which are produced in the submerged arc electric furnaces. Silica fume particles appear to be formed by the oxidation and condensation of the gaseous silicon sub-oxide SiO that is formed in the reaction zone. The silica fume is mainly amorphous and has about 20–25 m^2/g surface area, therefore it has a good pozzolanic activity [3].

Granulated blast furnace slag is hydraulically very weak, due to its glassy structure. A highly alkaline medium is required in order to disintegrate the silicate aluminate net work of the slag glass. Portland cement clinker is normally used to provide this alkalinity [4].

Resistance of silica fume-sulphate resisting blended cement pastes to sulphate attack was studied by Ali et al. [5]. These blended cements have a good resistance to sulphate attack due to the fine pore structure and reduction of lime content.

Helmy et al. [6] studied the role of silica fume on the chloride and sulphate attack on the composite of 85% SRC and 15% high alumina coment (HAC). It was found that the substitution of HAC with SF improved the attack of chloride and sulphate ions on cement pastes. Helmy and El-Sokkary [7] showd the effect of silica fume and granulated slag on the hydration characteristics of sulphate resisting (SRC) and alumina cement composite.

The objective of the present work is to study the effect of the 4% solution of Mg SO4 on the composite of 85% ordinary Portland and 15% high alumina cement, respectively. Also, the effect of substitution of high alumina cement by silica fume or granulated slag on the hydration kinetics and the aggressive attack of cement pastes up to one year were studied.

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2. Experimental procedure

The materials used in this work were OPC, supplied from Helwan Portland Cement company, silica fume from Egyptian company producing ferrosilicon alloys, Edfo, granulated slag from the iron and steel company Helwan Egypt, and HAC, Secar 40% Al_2O_3, imported from Lafarge company, France. The chemical analysis and surface area of the materials are given in Table 1.

Different mixes were made from the ordinary Portland cement, alumina cement, silica fume and granulated slag as seen in Table 2. Each dry mix was homogenized for 1 h in a porcelain ball mill using two balls to assure complete homogeneity. The mixing of cement pastes was carried out with the water required for normal consistency [8], that in the case of OPC and HAC composite, with 0, 5, 10 and 15% silica fume or granulated slag was 28.75, 32.00, 34.50 and 37.00% or 28.75, 26.25, 26.75 and 27.25%, respectively. The increase of the mixing water with silica fume content is mainly due to its high surface area.

The mixing of cement with the required water amount was completed by continuous mixing by hand for 4 min by gauging trowels. Immediately, after mixing the cement paste was poured in cubic moulds 2×2×2 cm and pressed until homogeneous specimen was obtained. The moulds were manually shaken to remove any air bubbles, and then smoothed by spatula. The moulds were cured in a 100% R.H. chamber at 23 ± 2 °C for 24 h, then demolded and cured under tap water for 28 days. After 28 days (0 time) curing in tap water, hardened samples were immersed in 4% $MgSO_4$ solutions for 1, 3, 6, 9 and 12 months. The solution was renewed every month to keep the concentration of SO_4^{2-} as much as possible constant. The progress of the attack was determined through the measurements of compressive strength, total sulphate, free lime content [9], and total porosity [10]. After the compressive strength determination, a representative sample, of about 10 g was taken, ground in alumina mortar with 50 ml solution [(1:1v) methanol/acetone] and then filtered through sintered glass funnel G4. The paste was washed for two times with the stopping solution and finally with 50 ml fresh diethyl ether and dried at 70 °C for 1 h then kept in an airtight bottle [11]. The sulphate content was determined as described elsewhere [12]. Some selected samples were examined by X-ray diffraction to identify the products in the cement pastes.

3. Results and discussion

Different blended cement pastes were prepared starting from a mixture of 85% ordinary Portland cement and 15% alumina cement, the latter was substituted by 0, 5, 10 and 15% of silica fume or granulated slag, Table 2.

The combined water contents of different blended cement pastes immersed in 4% $MgSO_4$ solution for one year are graphically represented in Fig. 1. Generally the combined water content increases gradually with curing time for all hardened 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 the calcium silicate hydrate. The cement pastes with silica fume give higher values of combined water than those containing granulated slag.

On the other side, as the granulated slag increases, the combined water content decreases. This is due to that the granulated slag has poor hydraulic properties in comparison with alumina cement.

3.1. Free lime content

The free lime contents of different blended cement pastes immersed under 4% $MgSO_4$ solution up to one year are graphically plotted in Fig. 2. The results show that the free lime content of all cement pastes decreases with curing time up to one year. This is mainly due to the reaction of $Ca(OH)_2$, which is liberated during the hydration of Portland cement with silica fume and HAC. Also, the decrease of free lime of cement pastes in $MgSO_4$ solution is mainly due to the reaction of $Ca(OH)_2$ with $MgSO_4$ to give gypsum and $Mg(OH)_2$, therefore the amounts of free lime content decreases with curing time up to one year.

On the other hand as the amount of silica fume increases the free lime decreases due to the reaction of

Table 1
The chemical composition and surface area of starting materials (mass%)

Materials	Oxides										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	LOI	Na_2O	K_2O	Cl	Surface area cm^2/g
OPC	21.05	5.45	3.42	63.41	2.09	2.39	1.90	0.18	0.09	0.020	3370
HAC	7.92	39.81	1.81	44.88	2.61	0.00	2.50	0.25	0.20	0.003	2300
SF	94.64	0.97	0.93	0.55	0.35	0.10	2.01	0.20	0.25	0.000	20 m^2/g
G.Slag	35.94	13.56	0.72	39.06	3.80	0.06	3.50	1.02	0.68	0.010	3350

Table 2
The mix composition of the different blends

Mix No.	OPC (%)	HAC (%)	SF (%)	G. slag (%)
M0	85	15	0	0
M1	85	10	5	0
M2	85	5	10	0
M3	85	0	15	0
M4	85	10	0	5
M5	85	5	0	10
M6	85	0	0	15

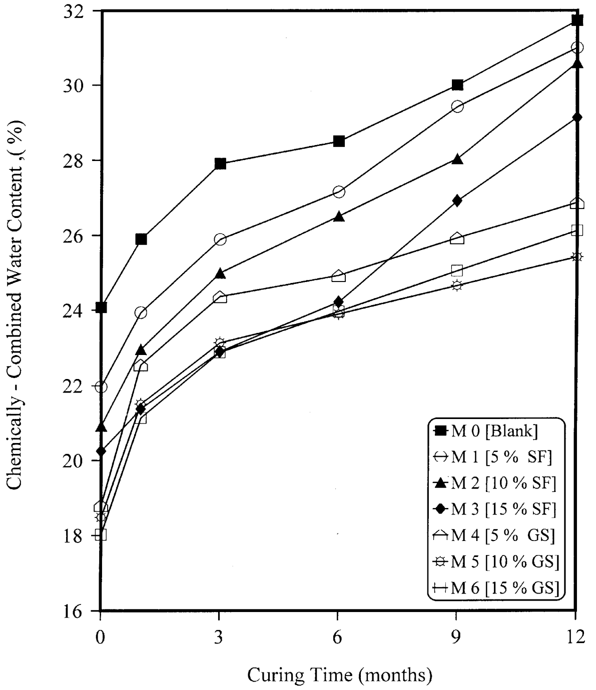

Fig. 1. Combined water contents of SF–GS–HAC–OPC pastes immersed in 4% $MgSO_4$ solution up to 1 year.

more silica fume with $Ca(OH)_2$. Generally the hardened cement pastes containing silica fume give lower values of free lime than those without silica fume.

The free lime contents of cement pastes with granulated slag are lower than those with alumina cement, but they are higher than those with silica fume. As the amount of granulated slag increases the free $Ca(OH)_2$ decreases. The decrease of free lime content is due to the activation of granulated slag with lime forming hydrated CSH or calcium aluminosilicate hydrates. Also, the free lime reacts with $MgSO_4$ to give gypsum and $Mg(OH)_2$.

3.2. Total sulphates

The total sulphate contents of cement pastes immersed in 4% $MgSO_4$ solution up to one year are graphically plotted in Fig. 3. It is clear that the total sulphate contents increase with curing time up to one year. This is due to the migration of sulphate ions from the aggressive medium ($MgSO_4$ solution) to the cement pastes which react with aluminate and ferrite or Ca(OH)2 forming hydrated calcium sulphoaluminates as ettringite and/or monosulphate hydrate [13]. Also, $MgSO_4$ reacts with calcium silicate hydrate to produce gypsum, silica gel and $Mg(OH)_2$ [14–16]. Gypsum reacts furtherly with C_3AH_6 to form calcium sulphoaluminate hydrate (ettringite) and/or monosulphate hydrate. On the other hand, the total sulphate of the silica fume blended cement pastes shows higher values than those of blended cement pastes without silica fume. As the silica fume increases, the total sulphate increases. This is due to the reaction of free lime with sulphate ions. Also, the mixing water increases with silica fume therefore, the porosity increases. As the porosity increases the sulphate ions are penetrated in the open pores then the sulphate content increases. On the other side, the alumina cement can not react with sulphate ions and $Ca(OH)_2$, therefore, the silica fume blended cement pastes show higher values of total sulphates.

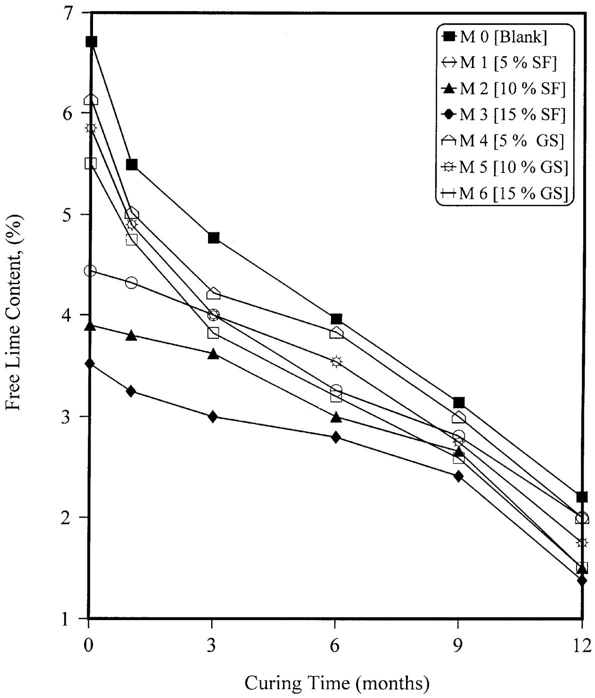

Fig. 2. Free lime contents of SF–GS–HAC–OPC pastes immersed in 4% $MgSO_4$ solution up to 1 year.

The total sulphates of the granulated slag blended cement pastes show higher values than those without slag in $MgSO_4$ solution. As the granulated slag content increases the total sulphate increases. This is due to the reaction of alumina from slag with sulphate ions in comparison with the alumina cement. The alumina cement does not react with sulphate ions and reacts with free lime faster than granulated slag.

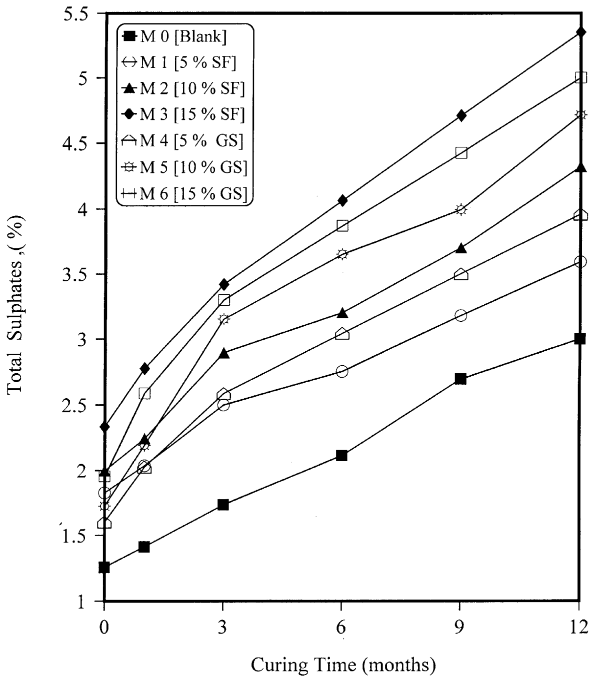

Fig. 3. Total sulphate of SF–GS–HAC–OPC pastes immersed in 4% $MgSO_4$ solution up to 1 year.

3.3. XRD-patterns

The XRD patterns of the composite 85% OPC + 15% HAC with 5, 10 and 15% silica fume substitutions, and immeresed in 4% $MgSO_4$ solution for one year, show the presence of gypsum, brucite $Mg(OH)_2$ and calcite as the main phases in the composite without silica fume substitution. Substitution of 5% HAC with SF tends to increase the hydrated lime as well as ettringite, gypsum and CSH (I). As the substitution of HAC with silica fume increases up to complete substitution, the gypsum increases-as it is the main hydration product-with small amount of hydrated lime and ettringite. Also, 15% SF substitution leads to the increase of CSH (I), calcite and brucite. The presence of CSH (I) in the blend 85% OPC and 15% SF is due to the reaction of silica fume with the hydrated lime.

The XRD patterns of hydrated OPC with 15% SF immersed in 4% $MgSO_4$ up to 12 months illustrates the presence of small amount of hydrated lime with calcium silicate hydrate and carbonate in the sample hydrated for 28 days in tap water (zero time). Sample immersed in $MgSO_4$ for 3 and 6 months shows no difference in the hydration products. After 12 months, the gypsum seems to be the predominant phase with the presence of sulphoaluminate hydrates and hydrated lime. $MgSO_4$ corroded the CSH with the formation of gypsum and the increase CH content. [13]. Mg $(OH)_2$ (brucite) is also detected due to the reaction of $MgSO_4$ with $Ca(OH)_2$.

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2$$

The increase of immersing time of OPC–15% SF composite in $MgSO_4$ solution up to 12 months tends to increase calcite and β-C_2S formation, too.

The XRD patterns of the composite 85% OPC + 15% HAC, with 5, 10 and 15% granulated slag substitutions and immersed in 4% $MgSO_4$ solution for one year, shows the presence of gypsum, brucite and calcite as the main phases in the composite without granulated slag substitution. Substitution of 5% HAC with granulated slag illustrates the presence of hydrated lime as the predominant phase with sulphoaluminate hydrates (ettringite and monosulphate) and gypsum. At 10% of granulated slag, the hydrated lime and gypsum peaks decrease whereas the sulphoaluminate hydrates show the same intensity. As the amount of slag increases up to 15%, the hydrated lime, sulphoaluminate hydrates and gypsum decrease.

The complete substitution of slag shows also the decrease of calcite, β-C_2S, CSH (I), and brucite. It can be concluded that the granulated slag is more suitable for durability than silica fume in the OPC + HAC composite in $MgSO_4$ solution.

The XRD patterns of 85% OPC with 15% granulated slag immersed in 4% $MgSO_4$ solution up to one year show that there is no effect on the durability of this cement paste up to 6 months. Sample immersed for 12 months shows the presence of small amount of gypsum. Therefore, granulated slag improves the durability of OPC in $MgSO_4$ solution. The increase of immersing period of OPC–15% slag composite in $MgSO_4$ solution tends also to a small increase of sulphoaluminate hydrates and brucite, as well as a low decrease of portlandite, calcite and β-C_2S.

3.4. Total porosity

The total porosity of cement pastes immersed under 4% $MgSO_4$ solution up to one year are shown in Fig. 4. The total porosity decreases with curing time for all hardened cement pastes as the hydration products fill part of the available volume of pores.

At a given time, the total porosity increases with silica fume or granulated slag content. This is due to the high water demand of silica fume and the low hydraulic property of granulated slag. Also, the total porosities of cement pastes containing granulated slag are lower than those containing silica fume, except the cement paste with 5% silica fume, which is lower than that of 15% granulated slag substitutions. This is due to the increase of the water/cement ratio of silica fume blended cement pastes.

3.5. Compressive strength

The compressive strength of cement pastes immersed in 4% $MgSO_4$ solution up to one year is shown in Fig. 5.

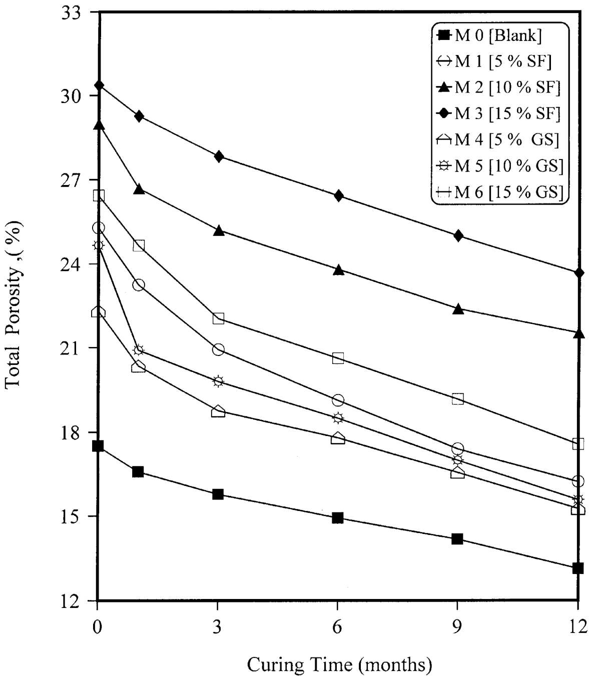

Fig. 4. Total porosity of SF–GS–HAC–OPC pastes immersed in 4% $MgSO_4$ solution up to 1 year.

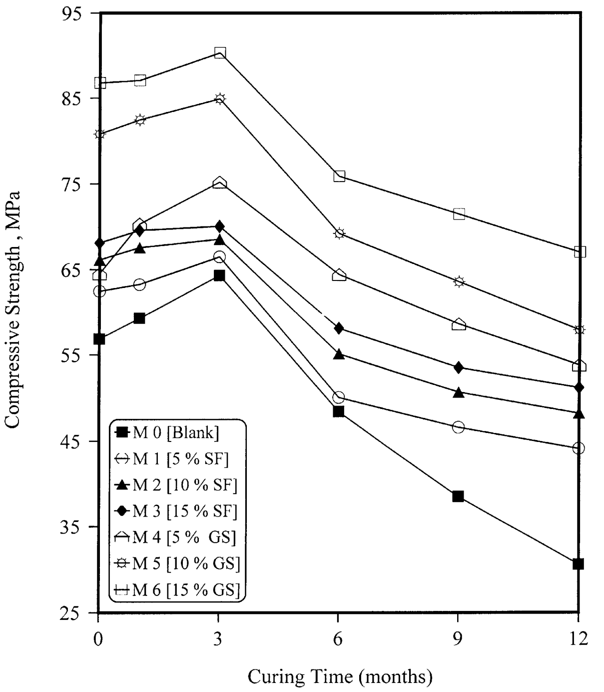

Fig. 5. Compressive strength of SF–GS–HAC–OPC pastes immersed in 4% $MgSO_4$ solution up to 1 year.

The compressive strength of all cement pastes increases for the first 3 months, then decreases till 1 year. The increase of compressive strength in the first 3 months, of all hardened cement pastes in $MgSO_4$ solution, is mainly due to the activation of hydration of cement pastes by sulphate ions, and the formation of calcium silicate hydrate (tobermorite like phase) and calcium sulphoaluminate (ettringite). The calcium silicate hydrate is the major factor of the compressive strength, therefore, the compressive strength increases up to 3 months. Obviously, the decrease of compressive strength after 3 months up to one year of all hardened cement pastes is mainly due to that sulphate ions attack most of the constituents of all cement pastes. $MgSO_4$ reacts with the liberated $Ca(OH)_2$ and deposits $Mg(OH)_2$ and gypsum. Also, CSH can be decomposed by $MgSO_4$ solution [14–16] forming $Mg(OH)_2$ and gypsum. These two reactions tend to decrease the compressive strength after 3 months up to 1 year, due to the reaction of gypsum with C_3A forming ettringite and monosulphate hydrate, which grow and expand resulting an internal stress which cause cracking and deterioration of cement pastes. On the other side, with the increase of the amount of silica fume in blended cement pastes, the compressive strength increases due to the formation of additional amounts of calcium silicate hydrate (tobermorite like phase) which gives higher strength than calcium aluminate and sulphoaluminate hydrates inspite of the increase of water/cement ratio with silica fume content.

On the other hand, with the increase of the amount of granulated slag in blended cement pastes, the compressive strength increases. This is mainly due to the formation of additional amounts of calcium silicate hydrates that give higher strength than calcium sulphoaluminate hydrates and also due to the decrease of mixing water. It can be said that the pozzolanic cement containing slag has higher values of calcium silicate hydrates in comparison with OPC and alumina cement. Generally the compressive strengths of cement pastes with granulated slag are higher than those with silica fume,due to the increase of water/cement ratio of silica fume blended cement pastes.

4. Conclusions

From the above findings, it may be concluded that:

1. The cement pastes with silica fume give higher values of combined water and lower values of free lime than those containing granulated slag.
2. The Compressive strength of all cement pastes increases with immersing time in 4% $MgSO_4$ solution, for the first 3 months, then decreases up to 12 months. The compressive strength increases with the silica fume or granulated slag up to 15%, at all immersing times, yet the granulated slag is more effective in this respect than the silica fume.
3. The increase of HAC substitution by silica fume or granulated slag, up to complete substitution in

the 85% OPC–15% HAC composite decreases the aggressive attack of sulphate ions on the hardened cement pastes.

4. The granulated slag is more suitable than silica fume as HAC substituent in the 85% OPC–15% HAC composite immersed in 4% $MgSO_4$ solutions.

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