EFFECT OF LIMESTONE FILLERS AND SILICA FUME POZZOLANA ON THE CHARACTERISTICS OF SULFATE RESISTANT CEMENT PASTES

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Characteristics of sulfate resistant cement pastes containing limestone as well as silica fume cured up to 90 days were studied. The results show that the addition of 5 wt.% of limestone as well as silica fume to the above cement improve its mechanical properties as well as give a lower porosity at 3-90 days curing times. In addition, the free lime contents give lower values (2.4 and 0.91 wt.%) in the pastes containing 8 and 10 wt.% silica fume, respectively.

INTRODUCTION

Limestone dust, which is produced in quarry operate possesses disposal and environmental problems. There is current interest, however, in the use of limestone as an addition to Portland cements. The addition of a small quantity up to 5 wt.% of unspecified filler such as limestone has been common practice in many European countries such as France, which has permitted such addition since 1979. The consumption of calcite, the formation of carbo-aluminates, the accelerating effect on the hydration of C_3A, C_3S, the change in the CSH and formation of transition zone between the filler and cement paste, are all facts specific of the reactivity of limestone fillers [1].

The development of new process and better quality control will lead to increase the reactivity of cement, i.e. cement which can be used in high performance concrete, but will need to be spread for the more common uses. The addition of filler is a possibility to achieve this in the most satisfactory way. The addition of 2-10 wt.% of limestone to low heat Portland cement was investigated [2-3]. The results show that the substitution of 4-6 wt.% of clinker by fine limestone (-76 μm) improves the rate of hydration up to 90 days. In addition, the amount of limestone increases the heat of hydration and the free lime contents slightly enhance. On the other side, the total porosity decreases and the compressive strength enhances at early age.

The characterization of high strength concrete using low heat Portland cement was studied [4]. The workability of the concrete is inferier to that of a concrete with ordinary Portland cement due to low water to cement ratio. Moreover, there are concerns about thermal cracking as the high strength concrete contains a great amount of cement. To solve this problem, the application of low heat Portland cement with the addition of limestone to high strength concrete was examined. The slump and long term compressive strength of low heat Portland cement concrete was higher than that of ordinary Portland cement concrete.

Substitution of 10 wt.% silica fume for Portland cement modifies the relative content in hydrates as well as the microstructure. The most important changes concern the formation of transition zone between the aggregate and the matrix paste [5]. On the other hand, pozzolanas increase the resistance of concrete against environmental attack since reduce permeability and absorption.

The resistance of concrete against pure and acid water is definitely increased by substitution of pozolanic materials for Portland cement. The silica fume reacts with free Ca $(OH)_2$ to produce calcium silicate hydrate. Thus, the amount of binder is increased, which both increases the strength and reduces the permeability by densifying the matrix of the concrete.

The objective of the present work is to study the influence of limestone fillers and silica fume pozzolanic on hydration properties of sulfate resisting cement paste. The physico-mechanical properties of the cement paste such as the water of consistency, setting time, total porosity, bulk density and compressive strength were determined. In addition, the kinetics of hydration such as free lime and combined water contents were estimated up to 90 days.

EXPERIMENTAL

The material used in this contribution were sulfate resistant cement, limestone and silica fume. Sulfate resistant cement supplied from Suez Cement Company, Egypt. The chemical oxide composition of the raw materials is shown in table 1. The plain surface area of sulfate resisting cement (SRC) was 310 m^2/kg, while the ground limestone pass through sieve No. 200, B.S. The mix compositions of the prepared batches are seen in table 2.

Table 1. Chemical oxide composition of starting materials, wt.%.

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	I.L.
SRC	21.88	4.11	4.74	64.72	1.91	1.69	0.98
Limestone	2.61	0.93	0.38	52.58	0.05	0.12	43.03
Silicafume	94.69	0.16	0.06	0.43	0.21	-	3.22

Table 2. Mix composition of the different prepared cements, wt.%.

Mix No.	SRC	Limestone	Silica fume
M_0	100	0	0
M_1	90	10	0
M_2	90	7.5	2.5
M_3	90	5.0	5.0
M_4	90	2.5	7.5
M_5	90	0	10

The ingredients were homogenized on a roller in a porcelain ball mill with few balls for 1 hr to attain complete homogeneity. The mixing and stopping of the hydration of the pastes were done as described elsewhere [7]. The water of consistency [8] and the setting time [9] were determined. The pastes were mixed under the water of consistency and molded in one inch cubes, cured in a humidity chamber at room temperatures for 24 hrs, then demolded and cured under water till the time of testing. The kinetics of hydration was followed by the determination of the free lime [10] as well as chemically combined water contents. The combined water contents was determined by the ignition loss at 1000°C of the dried paste on an ignited weight basis minus the amount of water held by free lime as well as the loss of the anhydrous cement. Also, the compressive strength was determined for each hardened paste up to 90 days.

RESULTS AND DISCUSSION

The water of consistency as well as initial and final setting time of the cement pastes are presented in figure 1. The results reveal that the water of consistency as well as the setting time of cement pastes slightly decreases with limestone content. This is because the addition of limestone increases the plasticity of cement paste. This may be attributed to the effect of limestone as an active component in the hydration of Portland cement, i.e. the rate of hydration increases and the amount of the hydration products enhances. The limestone acts a nucleating agents which increases the hydration rate of cement phases [2]. Also, the limestone forms monocarboaluminate hydrate that needs less water than that of ettringite. On the other hand, as the silica fume increases the water of consistency as well as setting times enhance. This is due to fact that, silica fume has a higher surface area which needs higher amounts of water during preparation of the cement paste.

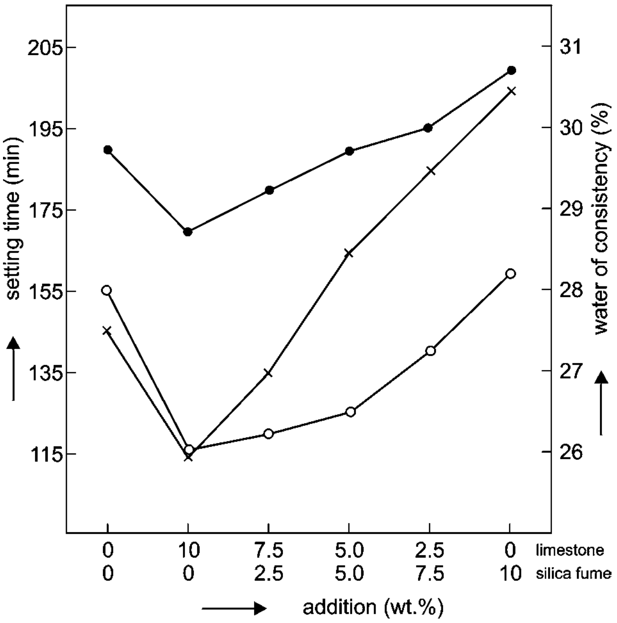

Figure 1. Water of consistency and setting time of the cement pastes (○ - initial setting time; ● - final; × - water of consistency).

The values of the combined water of cement pastes as a function of curing time are graphically plotted in figure 2. It is clear that the combined water increases with curing time for all hardened cement pastes. This is due to the continuous hydration with time The addition of 10 wt.% limestone shows higher combined water contents especially at early ages up to 7 days. As the silica fume content increases the combined water contents enhances at later ages of hydration. This is mainly due to the pozzolanic activity of silica fume. The addition of limestone accelerates the hydration reaction of cement phases especially at early ages. This accelerating effect may be related to a modification of the hydrating C_3S surface and nucleating effect. On the other side, as the silica fume content increases the combined water content enhances especially at 3-90 days. Also, the cement pastes containing 8 and 10 wt.% silica fume give a higher amount of combined water than the other pastes at all ages of curing time. 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. This indicates that the addition of 10 wt.% of limestone, silica fume or presence of them together plays an important role in the activation of hydration of sulfate resisting cement pastes.

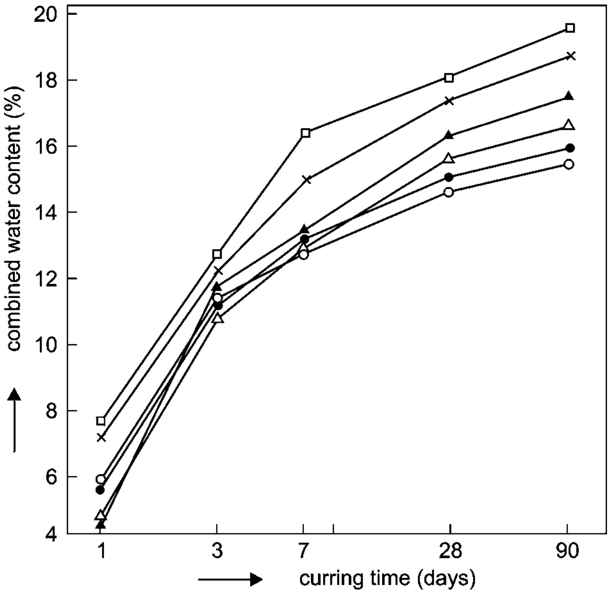

Figure 2. Chemical combined water of cement pastes cured for various periods of time (○ - M_0; ● - M_1; △ - M_2; ▲ - M_3; × - M_4; □ - M_5).

The free lime contents of hardened cement pastes are shown in figure 3. The results show that the cement pastes without addition (M_0) gives a higher amount of free Ca $(OH)_2$ than the other sample at 1-3 days, while the cement pastes (M_1) liberate free Ca $(OH)_2$ more than the cement pastes (M_0) at 7-90 days curing time. The increases of limestone till 10 wt.% is accompanied by a decrease in the clinker content. Therefore, the cement paste containing 10 wt.% limestone gives a lower amount of Ca $(OH)_2$ at early ages (1-3 days). The free lime of cement paste (M_1) sharply enhances at 7-90 days. This is attributed to the activated silicate phases especially C_3S which liberates more Ca $(OH)_2$ during the hydration. Also, as the amount of the silica fume increases the free lime sharply decreases especially at one day. This indicates the higher reactivity of silica fume towards reaction with Ca $(OH)_2$ liberated during the hydration. On the other hand, the cement pastes containing 7.5 and 10 wt.% of silica fume (M_4 and M_5) give lower amounts of Ca $(OH)_2$ than those other pastes at all ages. This is due to the pozzolanic reaction, silica fume reacts with lime during the hydration of the paste. Also, cement paste with 7.5 and 10 wt.% silica fume shows increase of the free lime up to 28 days and then decreases up to 90 days. This is mainly due to the fact that the clinker content decreases and consequently the free lime content diminishes. Also, the rate of liberation of free Ca $(OH)_2$ is lower than its consumption with silica fume. Therefore, the residual free lime in cement pastes with higher values of silica fumes (7.5 and 10 wt.%) decreases after 28 days up to 90 days.

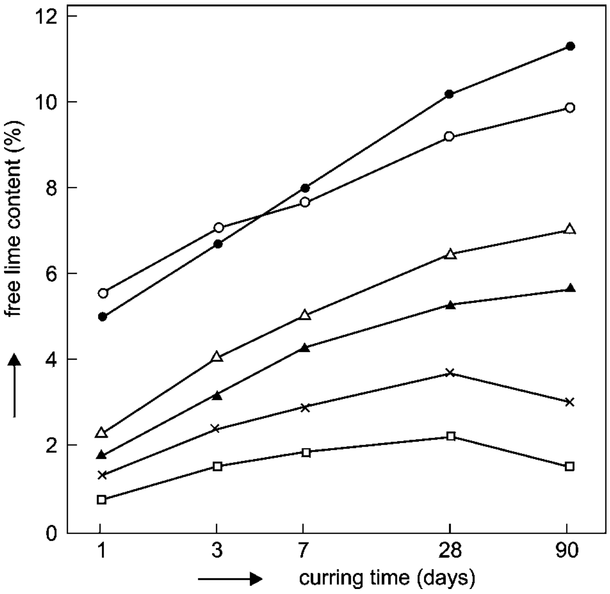

Figure 3. Free lime contents of hydrated sulfate resistant cement containing limestone and silica fume (○ - M_0; ● - M_1; △ - M_2; ▲ - M_3; × - M_4; □ - M_5).

The total porosity of the hardened cement pastes cured up to 90 days is illustrated in figure 4. The total porosity of all hardened cement pastes decrease with curing time due to filling up a part of the available pores with the hydration products. The cement paste without addition (M_0) exhibits higher values of porosity than those samples containing mineral admixtures at 3-90 days. On the other hand, as the silica fume content increases, the total porosity decreases, especially at 28-90 days. Cement pastes (M_2 and M_3) containing 2.5 and 5.0 wt.% limestone give the lowest values of porosity at all ages. This is attributed to the fact that the addition of limestone increases the plasticity and decreases the water of consistency of the cement paste [2]. Also, limestone 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. In addition, the silica fume reacted with free Ca $(OH)_2$ which liberates during hydration of silicate phases to produce CSH which deposits in the open pores of the cement paste and leads to decrease total porosity. It is evident that the addition of limestone/silica fume minerals admixtures to the sulfate resisting cement paste plays an important role in the activation of hydrated paste formation and crystallization of CSH as well as formation of a dense structure. The limestone acts as a filler which accelerates the hydration of cement paste in addition to filling some pores. On the other side, the silica fume is an active pozzolanic materials that reacts with free lime liberated during the hydration of cement paste forming hydrated calcium silicate hydrate which is precipitated in the open pores. Therefore, the total porosity decreases.

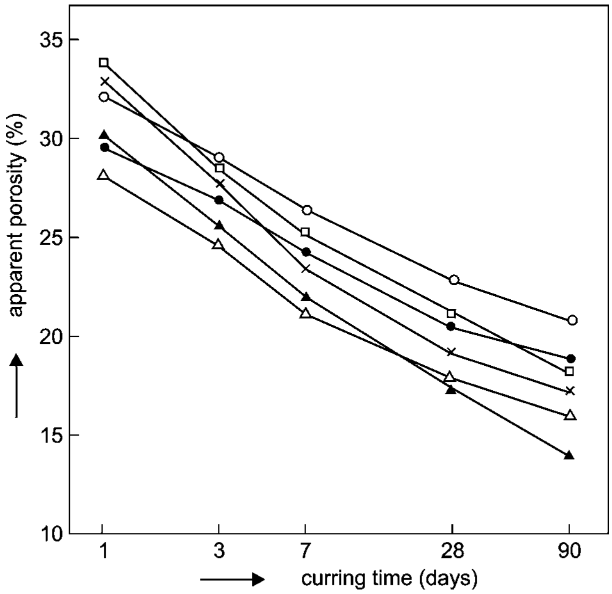

Figure 4. Apparent porosity of cement pastes versus curing time (○ - M_0; ● - M_1; △ - M_2; ▲ - M_3; × - M_4; □ - M_5).

The compressive strength of the hardened cement pastes cured up to 90 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 addition has lower values of compressive strength than those of other pastes at 28-90 days. The sample (M_3) gives the highest values of compressive strength at 3-90 days. This is attributed to two effects; (i) The presence of limestone in the pastes activates the cement phases especially silicate phases to form hydrates. (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 effects increase the compressive strength and densifying the matrix of cement paste. Moreover, as the silica fume reacts with free lime to produce calcium silicate hydrate, voids and pores within the cement paste are filled by the new hydration products and become more homogenous and dense. Thus, the addition limestone/silica fume mineral admixtures give greatly improved compressive strength.

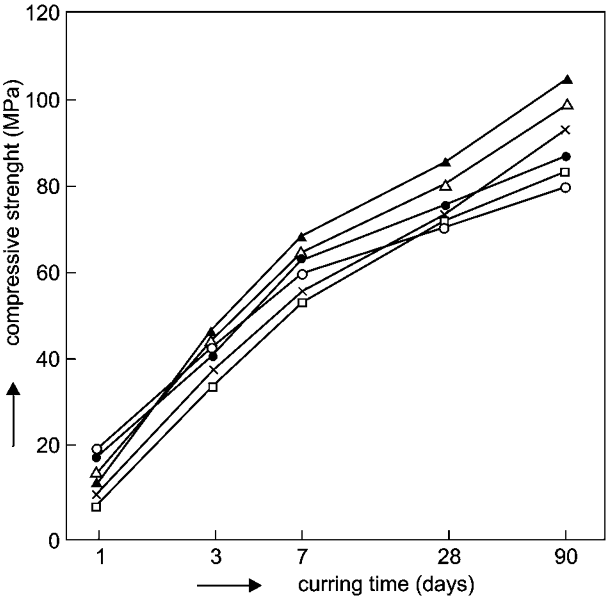

Figure 5. Compressive strength of cement pastes against curing time (○ - M_0; ● - M_1; △ - M_2; ▲ - M_3; × - M_4; □ - M_5).

CONCLUSION

The development of new process and better quality cement product will lead to a more reactive cement, i.e. a cement which can be used in high performance concrete. The additions of limestone/silica fume additives are a possibility to achieve this in the most satisfactory way. The main results obtained from this investigation are summarized as follows:

- The addition of 10 wt.% limestone to sulfate resistant cement increases the rate of hydration from 3 up to 90 days curing time.
- The addition 10 wt.% of silica fume to cement pastes reduces the liberated free Ca $(OH)_2$ to a minimum value (1.4 wt.%).
- As the silica fume increases till 5 wt.% the rate of hardening becomes a higher value than those other samples.
- The addition of 5 wt.% of both limestone and silica fume to cement paste gives good mechanical properties as well as the lowest porosity at all curing periods.

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VLIV VÁPENCOVÝCH PLNIV A KŘEMENNÉ PĚNY NA VLASTNOSTI PUCOLÁNOVÝCH CEMENTOVÝCH PAST ODOLNÝCH PROTI SÍRANŮM

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Byly studovány vlastnosti cementových past odolných proti síranům, obsahujícím vápno a křemennou pěnu, po zrání trvajícím až 90 dnů. Ukázalo se, že přídavek 5 hmot.% vápence a 5 hmot.% křemenné pěny k tomuto cementu zlepšil jeho mechanické vlastnosti a dále snížil jeho porozitu po zrání trvajícím 3 až 90 dní. Obsah volného vápna se snížil na 2,4 a 0,91 hmot.% v pastách obsahujících 8 a 10 hmot.% křemenné pěny.