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Scientific paper
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Effect of silica fume on the corrosion performance of reinforcements in concrete

The influence of silica fume on the corrosion resistance and strength of concrete was studied. The aim of this investigation mainly focused on how the silica fume was involved in the strength of concrete and also in the corrosion property of steel rebar embedded in mortar and concrete. Compressive strength measurements were made on various silica fume addition for the different curing period. Potential-time behavior studies were carried out to determine the status of rebars inside the mortar. Weight loss measurements were adopted to quantify the corrosion of rebars embedded in silica fume admixed concrete. Anodic polarisation studies were carried out to understand the optimum level of silica fume with better corrosion resistant properties. Alkalinity and free chloride contents were analysed at the initial and final exposure periods. All these studies showed that additions of silica fume up to 8 percent by weight of Ordinary Portland cement (OPC) improved the corrosion resistance properties of steel in mortar and concrete. Silica-fume has both positive and negative effects on the different factors governing the steel reinforcement corrosion. However, the positive factors by far dominate over the negative factors. Silica fume has a positive effect on the risk of corrosion and rate of corrosion, provided that normal good workmanship is carried out and that silica fume is not used in very low-quality concrete to reduce the cement content.

Key words: *Corrosion; Reinforcements; Mortar; Concrete; Silica fume*

1. INTRODUCTION

The use of silica fume was prompted by air pollution emission limitations that were placed on the silicon metal production industry. The material is called “fume” because it is an extremely fine particulate material that constitutes the emissions of the ferrosilicon manufacturing process. The fume is essentially composed of amorphous silicon oxide (silica) with a high surface area. As such, the material can be used to considerable advantage as a supplementary cementing material with an average diameter of about 0.1 micron and a bulk density to 250 kg/m3 in combination with Portland cement to form a so-called “pozzolanic” concrete. The fume particles are perfectly spherical in shape and are about 50 to 100 times finer than cement particles [1]. Silica fume has been in use in the concrete industry for over 20 years. An Indian standard for silica fume is not available but international standards include ASTM C- 1240:97, CSA A 3000:989 (Canada) and AS 3582 (Australia). The addition of silica fume to concrete is recognized in IS 456:2000. The fume reacts with calcium hydroxide in the presence of water to form cementing compounds consisting of calcium silicate hydrate. The in-corporation of silica fume in concrete improves its strength and durability characteristics. Typically 5 to 10% silica fume addition is utilized for bridges and short-crete applications. Since silica fume is more expensive than cement, it is rarely utilized for concrete pavements. Concrete incorporating more than 10% silica fume becomes sticky and in order to improve workability the initial slump should be increased. It has been found that silica fume reduces ‘bleeding’ because of its effect on the rheologic properties of the concrete. It is also reported that silica fume has been successfully used to produce very high strength, low permeability and chemically resistant concrete. It has been shown by several researchers that the addition of silica fume significantly reduces permeability [2-4]. Practical application of silica fume commenced in

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the late 1970's. At that time, and in subsequent years, opinions on the effect of silica fume on reinforcement corrosion were inconsistent. The corrosion process of reinforcement steel in concrete may be divided into two stages i.e. the initiation period and the propagation period. It has been reported that silica fume affects both the stages. In the initiation period, carbonation is taking place and/or chlorides may be transported into the concrete [5-7]. However, in the propagation period, the electrical resistivity of the concrete and oxygen diffusion within it is the factors, which governs the corrosion rate. It is considered that the first processes are very much increased by the incorporation of silica fume, but its impact on the second mechanism is less certain. Based on corrosion activity measurements, silica fume may have an inhibiting effect [8-10]. The scope of the present investigation was to study the strength and the corrosion performance of concrete blended with silica fume in chloride environments.

2. EXPERIMENTAL DETAILS

2.1. Materials Used

The following materials were used for the present study:

Ordinary Portland cement: Conforming to IS 456 – 2000

Graded fine aggregates: Local clean river sand (fineness modulus of medium sand equal to 2.6) conforming to a grading zone III of IS-383 – 1970, was used as fine aggregate.

Graded coarse aggregates: Locally-available well-graded aggregates of normal size greater than 4.75 mm and less than 10 mm, having a fineness modulus of 2.72, was used as coarse aggregate.

The composition of OPC used was given in Table 1. The mix design used for casting was as shown in Table 2.

Table 1 - Compositions of ordinary Portland cement

Constituent %)	
SiO_2	21.04
Fe_2O_3	3.35
Al_2O_3	9.93
CaO	60.68
MgO	1.30
Na_2O	0.20
K_2O	0.90
Loss on Ignition	2.60

Table 2 - Mix design (1: 3.3: 6.9, W/C = 0.50)

Constituent	Quantity used (kg/m^3)
Ordinary Portland cement	215
Fine aggregates	710
Coarse aggregates	1485
Silica fume	2 %, 4 %, 6 %, 8 % and 10 % addition level used

2.2. Methods used

2.2.1.pH measurements

The pH values measured for extracts of plain cement and cement containing various silica fume addition levels namely 2%, 4%, 6%, 8%, 10% and 15%. The pH was measured using standard calibrated pH meter.

2.2.2. Compressive strength measurements

100 mm × 100 mm ×100 mm concrete cubes were cast using 1:3.3:6.9 mix proportion with w/c ratio of 0.50. Specimens with OPC (plain) and OPC with various silica fume level were cast. During moulding, the cubes were mechanically vibrated. After 24 hrs the specimens were demould and subjected to curing in distilled water for 7 and 28 days. After curing, the specimens were tested for compressive strength using a compression testing machine of 2000 kN capacity. The tests were carried out on six specimens and average compressive strength values were obtained.

2.2.3. Measurement of open circuit potential (OCP)

The OCP of carbon steel anodes embedded in the mortar specimens was monitored periodically against a saturated calomel electrode (SCE) as reference electrode.

2.2.4. Anodic Polarization

Carbon steel rods were embedded in cylindrical mortar (1:3) specimens of size 58 mm dia and 60 mm height using W/C ratio 0.45. The mortar specimens containing only ordinary Portland cement (control) and OPC with various silica fume addition levels of 2%, 4%, 6%, 8% and 10% were subjected to anodic polarization studies using a three-electrode system. The embedded steel acted as a working electrode, cylindrical stainless steel acted as the counter electrode and a saturated calomel electrode (SCE) served as reference electrode. The samples were immersed in 3% NaCl solutions. The currents flowing at +300 mV and +600 mV vs. SCE from the OCP values were recorded for all the specimens at ambient temperature of 32+1^{o}C.

2.2.5. Weight loss measurements

Concrete cubes of size 10 x 10 x 10 cm were cast using OPC and OPC was blended with various silica fume additions of 2, 4, 6, 8 and 10%. Rebar of size 1.2 cm diameter and 6 cm in length were embedded centrally. Initially the rebars were cleaned in inhibited HCl solution having the following composition: (HCl): 100%, $SnCl_2$: 35 gms, Sb_2O_3: 25 gms. The samples were then degreased with acetone and washed with double distilled water and dried. The initial weight of the rebar samples were taken using a Metler balance to allow gravimetric weight loss measurement to be obtained. Concrete cube specimens were prepared using 1:3.3:6.9 mix with a w/c ratio of 0.50. The specimens were mechanically vibrated. After 24 hours of curing, the specimens were demould and cured for 28 days in distilled water in order to avoid any contamination. After the curing period, all of the specimens were completely immersed in 3 % NaCl solution. The specimens were maintained in the same condition for 15 days and then subjected to drying for another 15 days. One alternate wetting and drying cycle consists of 15 days immersion with 3% NaCl solution, followed by a 15-day drying in the open air at room temperature. In order to induce the accelerated corrosion, a 3% NaCl solution was used. All of the concrete specimens were subjected to 12 complete test exposure cycles. Tests were conducted on a minimum of six replicate specimens and the average values were reported. At the end of the exposure period the concrete specimens were split open and visual observation data on corrosion were made and expressed in terms of percentage of area rusted. The corrosion rate of carbon steel anodes embedded in control (OPC) and various silica fume addition levels were measured by gravimetric weight loss method and expressed in millimeter per year (mmpy).

The corrosion rate is calculated using the following equation:

$$\text{Corrosion rate} = \frac{87.6 \times W}{D \times A \times T}$$

where,

W = Weight loss in milli grams

D = Density of the material used

A = Area of the specimen (cm^2)

T – Time duration in hrs

2.2.6. Estimation of fee chloride contents

The core samples collected near the anode were crushed mechanically and powdered. Then 100 gm of powdered sample was shaken with 100 ml of double distilled water in a conical flask using microid flask shaker for one hour. The extract was then filtered through a whatman filter paper No.42. The extract prepared from the powdered sample was then analyzed for free chloride contents as per the standard procedures. 20 cc of filtered solution was taken and the free chloride was estimated by standard silver nitrate solution using potassium chromate as an indicator. The amount of chloride present was expressed in terms of parts per million (ppm) on the basis of weight of sample taken for analysis.

3. RESULTS AND DISCUSSIONS

3.1. pH measurements

The pH values measured for plain cement extracts and various silica fume addition levels are given in Table 3. From the Table, it was observed that pH of the plain cement extract was 13.8. The pH values measured for various silica fume systems were in the range from 13.63 to 12.0. There was no appreciable change in pH values for silica fume addition upto 8 %. After that, there was a slight reduction in pH values at 10 % silica fume addition. At 15 % silica fume addition, pH value was drastically reduced to 12. During the chemical reaction between silica fume and components in the pore water, the content of components keeping a high pH value is reduced, especially calcium hydroxide and potassium.

Table 3 - pH for plain cement extracts and with various silica fume addition levels

S.No	System	pH
1	OPC (plain)	13.80
2	OPC + 2 % SF	13.63
3	OPC + 4 % SF	13.62
4	OPC + 6 % SF	13.50
5	OPC + 8 % SF	13.29
6	OPC + 10 % SF	12.75
7	OPC + 15 % SF	12.00

The reason for pH reduction above 10 % silica fume level may be due to the fact that, the amount of calcium hydroxide is depleted gradually when silica fume content is increased. However the pH value is still higher than 12.5 possibly due to minor amounts of alkali silicates or to an alkaline calcium silicate hydrate (CSH) composition. It has been reported that silica fume has a much higher effect on pH reduction when compared to other mineral admixtures like fly ashes or natural pozzolans. The type of cement also plays an important role and the reaction of calcium hydroxide has a decisive influence on the scope and rate of reaction of silica fume. A high level of alkali content in the cement accelerates the reaction rate of silica fume. Even when the calcium hydroxide is depleted, the pH of the pore water may still exceed 12.5. This is enough for protecting the passivity of steel in concrete.

3.2. Compressive strength measurements

The average compressive strength for OPC control and OPC blended with various silica fume levels is given in Table 4. From this table it was inferred that, as the curing time increased the compressive strength of concrete also increased. The same trend was observed in these studies also irrespective of amount of silica fume added. In the case of OPC control, a two fold increase in compressive strength was observed at the end of 28 days. At 7 and 28 days the compressive strength was 20.2 and 43.8 MPa, respectively. On the other hand, silica fume systems showed comparable compressive strength with OPC. At the end of 28 days it showed slightly higher compressive strength than control system. These data clearly illustrated that addition of silica fume did not affecting the strength of concrete. Since the silica fume accelerates the growth of CSH gel, which is more advantageous to enhance the strength development.

Table 4 - Compressive strength measurements for various systems (MPa)

S. No	System	Compressive strength (MPa)	
		@ 7 days	@28 days
1	OPC	20.2	43.8
2	OPC + 2 % SF	21.2	44.2
3	OPC + 4 % SF	22.3	43.9
4	OPC + 6 % SF	21.9	44.1
5	OPC + 8 % SF	21.2	44.0

3.3. Anodic polarization technique

The results of anodic polarization data for steel embedded in 1:3 mortar specimens in 3 % NaCl solution is given in the Table 5. The relation between open circuit potential (OCP) vs. various silica fume addition levels are shown in Fig 1. It was inferred from Figure that, OCP of OPC was –468 mV vs. SCE. But the OCP was shifted to more positive side, when silica fume level was increased from 2% to 10 %. At 10 % level, it showed potential of –420 mV vs. SCE. Interestingly upto 8 % silica fume level, the current was maintained constant and above 8 % the current was drastically increased indicating the better performance of corrosion-resistance properties upto 8 %. This observation was noticed both at +300 mV and +600 mV vs. SCE. At 10 % silica fume level the current was almost doubled indicating the lesser corrosion-resistance properties at this level.

Table 5 - Anodic polarization data for steel embedded in 1:3 mortar specimens in 3 % NaCl solutions

Sl. No	System	OCP	Current (mA)	
			+300 mV	+ 600 mV
1	OPC	-468	8	13
2	OPC + 2 % SF	-463	8	13
3	OPC + 2 % SF	-457	8	13
4	OPC + 2 % SF	-448	8	13
5	OPC + 2 % SF	-440	10	15
6	OPC + 2 % SF	-420	20	30

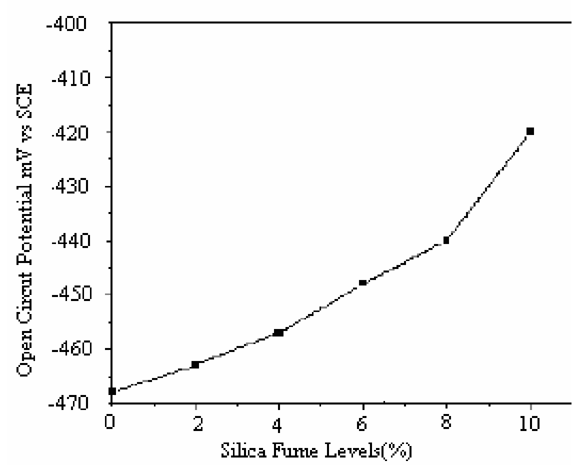

Fig. 1 - Potential with respect to various silica fume for rebar embedded in mortar

3.4. Weight loss measurements

The weight loss data for rebar embedded in OPC and OPC blended with various silica fumes addition level are reported in Table 6. From this Table it was observed that, the corrosion rate for OPC system was found to be 0.0015 mmpy. In the case of silica fume system, as the percentage of silica fume increases, corrosion rate was also found to be increased. But comparable results with OPC were obtained upto 8 % silica fume addition, which represent the tolerable limit of addition with better corrosion-resistance properties. The percentage reduction in corrosion rate calculated with reference to OPC also indicated the similar behaviour. Beyond 8 % the corrosion rate was drastically increased. The reason for better property of silica fume blended with OPC may be due to the pore-filling effect. The silica fume particles are smaller than OPC the pore refinement takes place. These results were concordant with results obtained from anodic polarization and weight loss measurements.

Table 6 - Corrosion rate for steel embedded in OPC and with various silica fume addition levels

S. No	System	Corrosion rate (mmpy)
1	OPC	0.0015
2	OPC + 2 % SF	0.0015
3	OPC + 4 % SF	0.0016
4	OPC + 6 % SF	0.0016
5	OPC + 8 % SF	0.0028
6	OPC + 10 % SF	0.0058

3.5. Free chloride contents

At the end of the test period, CTD anode embedded in OPC and various silica fume system were subjected to qualitative estimations. The data calculated were reported in Table 7. From this Table, it was revealed that in 100 % OPC system no rust was observed at any of the surface of carbon steel. For silica fume system, upto 8 % silica fume negligible red rust (less than 1 %) was observed. Beyond 8 % more than 5 % red rust was observed. The free chloride contents estimated were reported in Table 6. Interestingly upto 8 % addition level the penetration of chloride ion was found to be in the range 100 to 200 ppm. As the silica-fume addition level increases the penetration of chloride ion is also increased. Due to reduced pH values in concrete with silica fume, it is expected that the chloride binding capacity also should be reduced. Chloride binding in cementing materials is dominated by the content of C3A (tricalcium aluminate) and C4AF (tetra calcium alumino ferrite) no matter the chloride source, both forming Fridels salts. Sulphates in the cement however, form stronger bonds than the chlorides so only a fraction of the C3A and C4AF is accessible for chloride binding capacity; since these materials form additional calcium aluminate hydrates in their reaction. Silica fume will decrease the chloride binding capacity.

Table 7 - Qualitative estimation of SF blended System

S.No	Systems	Percentage of area rusted %	Free Chloride Content (ppm)
1	OPC	No rust	100
2	OPC+ 2 % SF	Negligible (1)	100
3	OPC+ 4 % SF	Negligible (1)	100
4	OPC+ 6 % SF	Negligible (1)	100
5	OPC+ 8 % SF	2	200
6	OPC+ 10 % SF	8	300

The important pre-requisite for good admixed system are: (i) to increase the corrosion-resistance of steel embedded in concrete (ii) should not significantly affect the strength properties of the concrete. In this aspect, silica fume was found to be more effective in controlling the corrosion of steel in concrete and did not reduce the compressive strength, particularly when used upto 8% addition level.

4. CONCLUSIONS

The following conclusions can be drawn from the present investigations:

- Silica fume up to 8 % does not affect the pH of the concrete.
- Comparable results on corrosion rates with OPC were obtained upto 8 % addition of silica fume, from weight loss measurements.
- Anodic polarization data showed that, more anodic current was observed beyond 8 %.
- Silica fume is not very effective beyond 8 % for chloride binding capacity.
- Silica fume has both positive and negative effects on the different factors governing the steel reinforcement corrosion. However, the positive factors are dominating by far over the negative factors. Silica fume has a positive effect on the risk of corrosion and rate of corrosion, provided that normal good workmanship is to be carried out and that silica fume is not used in very low concrete qualities to reduce cement.

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