



INFLUENCE OF SILICA FUME ON CHLORIDE DIFFUSION AND CORROSION RESISTANCE OF CONCRETE - A REVIEW

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ABSTRACT

One of the most important durability indices affecting the reinforced concrete structures is corrosion of steel reinforcement. Investigations show that the main mechanism of corrosion distorting the long-term performance of such structures is Chloride-induced corrosion.

In order to challenge this problem, scientists offer utilizing supplementary cementitious materials. Silica fume is one of the most effective admixtures which control chloride diffusivity and initiation of steel corrosion.

The present literature, reviews recent studies on the influence of silica fume on permeability, chloride diffusion, electrical resistivity and reinforcement corrosion.

Keywords: Chloride diffusion; concrete; corrosion; silica fume.

1. INTRODUCTION

The chloride resistance depends on the permeability of concrete and the thickness of cover to the reinforcement. The integrity of the concrete cover under service load, in terms of cracking and crack width, also influences the resistance to penetrating chlorides. Corrosion of steel reinforcement is an electrochemical process. Hence electrochemical properties of concrete, such as resistivity, are important inherent properties affecting the corrosion rate of reinforcing steel [1].

Metha reconfirmed from a review of case studies that it is the permeability of concrete, rather than its chemistry, which is the key to overall durability. The causes of high permeability are not limited to poor concrete proportion but poor concreting practice, such as incomplete mixing, inadequate consolidation and curing after placement, insufficient cover to reinforcing steel, and poor constructed joints [2].

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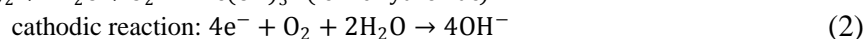
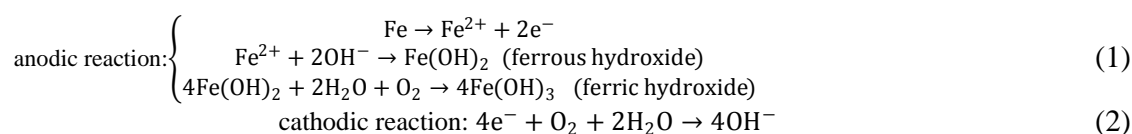
Supplementary cementitious materials (SCMs) are often incorporated in concrete to improve durability of concrete. These include fly ash, silica fume, ground granulated blast furnace slag (GGBFS), rice husk ash and other calcined natural pozzolanic materials such as metakaolin. The use of SCMs in concrete is increasing because they result in lower cost of construction and improve some mechanical properties and durability of concrete in aggressive environments [3].

2. MECHANISM OF CHLORIDE-INDUCED CORROSION

Embedded steel develops a protective passivity layer on its surface. This layer, which is self-generated soon after the hydration of cement has started, consists of $\gamma\text{-Fe}_2\text{O}_3$ adhering tightly to the steel. As long as that oxide film is present, the steel remains intact. However, chloride ions destroy the film and, in the presence of water and oxygen, corrosion occurs [4].

It may be useful to add that, provided the surface of the reinforcing steel is free from loose rust (a condition which is always specified), the presence of rust at the time the steel is embedded in concrete does not influence corrosion [5].

A brief description of the corrosion phenomenon is as follows. When there exists a difference in electrical potential along the steel in concrete, an electrochemical cell is set up: anodic and cathodic regions occur, connected by the electrolyte in the form of the pore water in the hardened cement paste. The positively charged ferrous ions Fe^{2+} at the anode pass into solution while the negatively charged free electrons e^- pass through the steel into the cathode where they are absorbed by the constituents of the electrolyte and combine with water and oxygen to form hydroxyl ions OH^- . These travel through the electrolyte and combine with the ferrous ions to form ferric hydroxide, which is converted by further oxidation to rust. The reactions involved are as follows [4]:



It can be seen that oxygen is consumed and water is regenerated, but it is needed for the process to continue. Thus there is no corrosion in dry concrete, probably below a relative humidity of 60%; nor is there corrosion in concrete immersed fully in water, except when water can entrain air, for example by wave action. The optimum relative humidity for corrosion is 70-80%. At higher relative humidities, the diffusion of oxygen through the concrete is reduced considerably [4].

The differences in electrochemical potential can arise from differences in the environment of the concrete, for example when a part of it is submerged permanently in sea water and a part is exposed to periodic wetting and drying. A similar situation can arise when there is a substantial difference in the thickness of cover to a steel system which is electrically connected. Electrochemical cells form also due to a variation in salt concentration in the pore water or due to a non-uniform access to oxygen [4].

For corrosion to be initiated, the passivity layer must be penetrated. Chloride ions

activate the surface of the steel to form an anode, the passivated surface being the cathode. The reactions involved are as follows:



Thus, Cl^- is regenerated so that the rust contains no chloride, although iron chloride is formed at the intermediate stage [4].

Because the electrochemical cell requires a connection between the anode and the cathode by the pore water, as well as by the reinforcing steel itself, the pore system in a hardened cement paste is a major factor influencing corrosion. In electrical terms, it is the resistance of the 'connection' through the concrete that controls the flow of the current. The electrical resistivity of concrete is influenced greatly by its moisture content, by the ionic composition of the pore water, and by the continuity of the pore system in the hardened cement paste [4].

There are two consequences of the corrosion of steel. Firstly, the products of corrosion occupy a volume several times larger than the original steel so that their formation results in cracking (characteristically parallel to the reinforcement), spalling or delamination of concrete. This makes it easier for aggressive agents to ingress towards the steel, with a consequent increase in the rate of corrosion. Secondly, the progress of corrosion at the anode reduces the cross-sectional area of the steel, thus reducing its load-carrying capacity. In this connection, it should be pointed out that chloride-induced corrosion is highly localized at a small anode, with pitting of the steel taking place [4].

3. SILICA FUME

3.1 Introduction

Silica fume (SF) is a byproduct of the smelting process in the silicon and ferrosilicon industry. It is also known as micro silica, condensed silica fume, volatilized silica or silica dust. Silica fume colour is either premium white or grey. Silica Fume consists of very fine vitreous particles with a surface area between 13,000 and 30,000 m^2/kg . Its particles are approximately 100 times smaller than the average cement particle. Because of its extreme fineness and high silica content, silica fume is a highly effective pozzolanic material. Silica fume is used in concrete to improve its properties. It has been found that silica fume improves compressive strength, bond strength, and abrasion resistance; reduces permeability; and therefore helps in protecting reinforcing steel from corrosion [6].

3.2 Applications of silica fume

Application of silica fume in mortars and concretes has been started in the late 1970s. It was first used for the production of high strength concrete. High strength concretes in the range of 70 to 80 MPa can be easily achieved by incorporating silica fume. Ultra high strength concretes in the range of 120 to 180 MPa have been produced with a special mix design using special aggregates, silica fume and sufficient high range water reducing agent. Construction of New Tjorn Bridge in Sweden in 1981 is believed to be the first industrial

use of silica fume to achieve a compressive strength of about 50 Mpa.

Another application of silica fume is in the projects where mortar or concrete is shotcreted. Silica fume increases the cohesiveness of fresh concrete and improves its bonding. Therefore it is a very useful material for both dry and wet shotcreting to reduce rebound.

As mentioned before, concretes containing silica fume have low permeability and are durable in the severe environments. Due to this advantage of silica fume in concrete mixtures, it is usually recommended to be applied in concretes where enhanced durability is required. This is usually referred to high performance concrete (HPC). The first known project on the use of silica fume in concrete where durability to erosion was important was for the repair of the stilling basin at the kinzu Dam in the USA. Tsing Ma Bridge in Hong Kong is an example of the large recent projects.

Silica fume has been recommended in the construction of concrete structures in the National Code of practice for concrete durability in the Persian Gulf and Omman Sea of Iran. Concrete structures in Assaloyeh gas refinery plant, Bandar Abbas port complex, Bandar Imam port complex, Bushehr port complex are among them [7].

3.3 Properties of silica fume

Silica fume particles are very small, with more than 95% of the particles being less than 1 micron. Most particles are in spherical shape with a mean diameter of 0.2 micron. Because the particles of silica fume are very small, the surface area is very large. The specific surface area of silica fume particles varies between 15000 and 30000 m²/kg [7]. Its typical physical properties are given in Table 1 [6]. Silica fume is composed primarily of pure silica in non-crystalline form. Silica fume has a very high content of amorphous silicon dioxide and consists of very fine spherical particles.

Small amounts of iron, magnesium, and alkali oxides are also found (Table 2) [6].

Table 1: Typical physical properties of silica fume (Silica fume association, 2005)

| Property | Value |
|--------------------------|--------------------------------|
| Particle size (typical) | <1 μm |
| Bulk density (produced) | 130-430 kg/m ³ |
| Bulk density (slurry) | 1320-1440 kg/m ³ |
| Bulk density (densified) | 480-720 kg/m ³ |
| Specific gravity | 2.22 |
| Surface area (BET) | 13000-30000 m ² /kg |

3.4 Reaction mechanism of silica fume

Because of its extreme fineness and very high amorphous silicon dioxide content, silica fume is a very reactive pozzolanic material. Mechanism of silica fume in concrete can be studied basically under three roles: Pore-size refinement and matrix densification. Reaction with free-lime (from hydration of cement). Cement paste-aggregate interfacial refinement.

Characteristics of the transition zone between the aggregate particles and cement paste plays a significant role in the cement-aggregate bond. Silica fume addition influences the thickness of transition phase in mortars and the degree of the orientation of the CH crystals in it. The thickness compared with mortar containing only ordinary Portland cement decreases and

reduction in degree of orientation of CH crystals in transition phase with the addition of silica fume. Hence mechanical properties and durability is improved because of the enhancement in interfacial or bond strength. Mechanism behind is not only connected to chemical formation of C-S-H (i.e. pozzolanic reaction) at interface, but also to the microstructure modification (i.e. CH orientation, porosity and transition zone thickness) as well [6].

It is worth noting that silica fume containing about 85 per cent of silica combines most of the available lime within 28 days while other natural pozzolans and fly ashes containing about 50-65 per cent silica are capable combining about 30 to 50 per cent of the lime in the lime-pozzolan mixture [7].

Table 2: Chemical composition of silica fume samples

| Oxides | Sandvik and Gj rv (1992) | Hooton and Titherington (2004) | Yazici (2008) |
|--------------------------------|--------------------------|--------------------------------|---------------|
| SiO ₂ | 92.1 | 96.65 | 92.26 |
| Al ₂ O ₃ | 0.5 | 0.23 | 0.89 |
| Fe ₂ O ₃ | 1.4 | 0.07 | 1.97 |
| CaO | 0.5 | 0.31 | 0.49 |
| MgO | 0.3 | 0.04 | 0.96 |
| K ₂ O | 0.7 | 0.56 | 1.31 |
| Na ₂ O | 0.3 | 0.15 | 0.42 |
| SO ₃ | - | 0.17 | 0.33 |
| LOI | 2.8 | 2.27 | - |

4. INFLUENCE OF SILICA FUME ON PERMEABILITY, CHLORIDE DIFFUSION AND DIFFUSION COEFFICIENT OF CONCRETE

Microstructure of concrete will be affected by the incorporation of silica fume in the mixture. The major influence is the refinement of the pore structure of cement paste. The total porosity may not alter by the addition of silica fume but the large pores are divided into smaller pores and hence changing the microstructure of the cement paste [7]. The effect of various amounts of silica fume on total porosity is shown in Fig. 1.

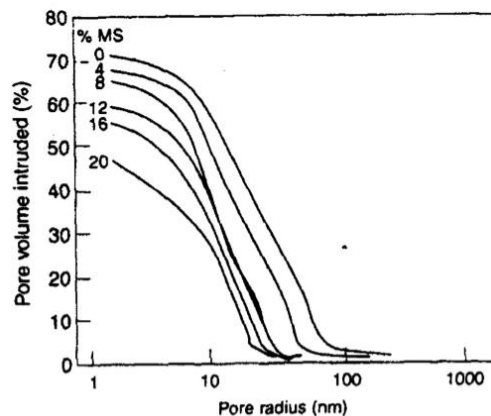


Figure 1. Effect of silica fume on total porosity

Permeability of concrete is also affected by the incorporation of silica fume in concrete mixtures. It is even more important than the effect on compressive strength. In a research work, a concrete mixture containing 100 kg/m³ portland cement, 20% silica fume, and a superplasticizer showed approximately similar permeability to the plain concrete containing 250 kg/m³ portland cement [7].

Gu et al. [8] investigated the performance of steel reinforcement in concrete slabs that were ponded with a 3.4% sodium-chloride solution for a period of 6 months. The concrete slabs were cast using Portland cement concrete with 10% silica fume and 55% blast-furnace slag with water-cementitious materials ratio (w/cm) of 0.32. OPC concrete slabs were made with water-cementitious materials ratio of 0.32, 0.43, 0.55, 0.76.

The concrete resistance to chloride-ion penetration was determined according to ASTM C 1202.

The test results showed that the silica fume concretes exhibited very low penetrability to chloride ions and approximately 3 times smaller than the slabs containing 55% blast-furnace slag (Table 3).

Table 3: Resistance of concrete slabs to chloride-ion penetration

| Mix No. | Type of SCM | SCM content, % | W/(C+SCM) | resistance to chloride-ion penetration (coulombs) |
|---------|-------------|----------------|-----------|---|
| 1 | silica fume | 10 | 0.32 | 235 |
| 2 | BFS | 55 | 0.32 | 670 |
| 3 | - | - | 0.32 | 1730 |
| 4 | - | - | 0.43 | 3970 |
| 5 | - | - | 0.55 | 5250 |
| 6 | - | - | 0.76 | 5970 |

Bleszynski et al. [9] expressed that additional of 8% silica fume can decrease RCPT results up to 80% (from 2290 coulombs to 450 coulombs).

Hou and Chung [10] studied the effect of admixtures, namely silica fume, on the corrosion resistance of steel reinforced concrete by measuring the corrosion potential and corrosion current density during immersion in Ca(OH)₂ and NaCl solutions. On the average, the E_{corr} of rebar in concrete with silica fume was 80 mV less negative than that of rebar in plain concrete. This indicates a greater chance for the rebar in plain concrete to become active than for the rebar in concrete with silica fume.

Hooton et al. [11] obtained multiple cores from 5 bridge decks and 4 parking garage decks between 6 and 15 years old in New York State, Ohio, Utah, and Wisconsin.

Slices from cores were tested for electrical conductance which integrated over a 6 hour test period (rapid chloride permeability) using ASTM C1202 (AASHTO T277), with results expressed in coulombs.

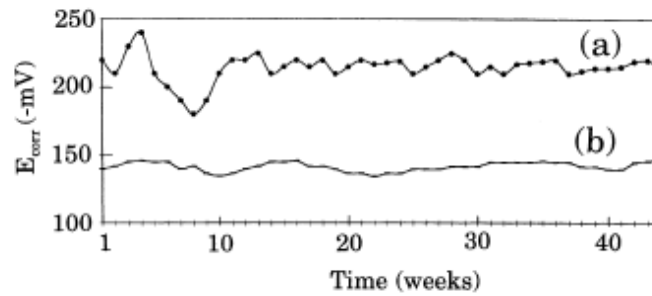


Figure 2. Effect of silica fume on the corrosion potential of rebar in concrete in saturated Ca(OH)_2 solutions. (a) Plain concrete, (b) concrete with silica fume

The non-silica fume, cores had bulk diffusion coefficients about 10 times higher than the silica fume decks and a much average higher coulomb values as well.

Parhizkar et al. [12] assessed the use of silica fume in a cementitious repair mortar, under laboratory and simulated Persian Gulf condition, to evaluate its durability performance in a hot and humid environment. The chloride penetration, permeability and porosity test results (obtained after 60 days immersion in chloride solution) showed that addition of 7% silica fume by weight of cement, increases the chloride penetration resistance of the repair mortar up to 25%. (in depth of 10mm of the specimens)

Poon et al. [13] studied chloride penetrability of HPC containing metakaolin (MK) and silica fume at water-to-binder (w/b) ratios of 0.3 and 0.5. When comparing the MK and SF concretes, it can be seen that a 5% SF replacement in concrete resulted in a lower total charge passed than a 5% MK replacement, but a 10% MK replacement resulted in a lower total charge passed than a 10% SF replacement, at both w/b = 0.3 and 0.5.

It was concluded that at a higher w/b ratio and percentage of replacement the use of MK is more effective than SF in improving the resistance of concretes to chloride ion penetration.

One of the factors affecting the permeability of concrete is Capillary porosity. Capillary porosity of cement paste can be divided into two categories. One is the capillary porosity of bulk paste and the other is the capillary porosity of ITZ. The capillary porosity would increase at the surface of aggregates because of wall effect [14,15].

Song et al. [14] reported that there was significant reduction in the capillary porosity of both bulk paste and ITZ with increase in silica fume contents (Fig. 3).

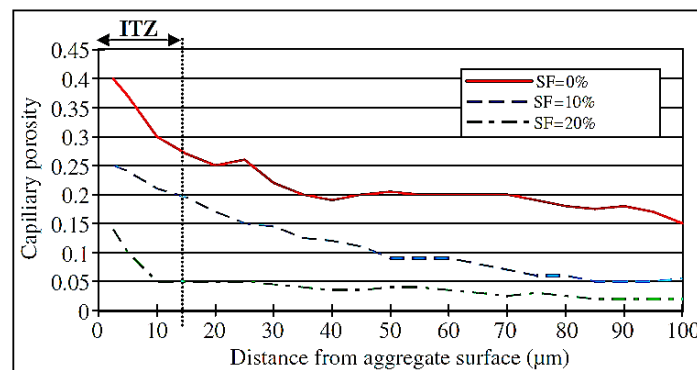


Figure 3. Capillary porosity vs. distance from aggregate surface for different silica fume contents

Gesoglu and Guneyisi [16] investigated the chloride permeability characteristics of plain and rubberized concretes with and without silica fume. For this purpose, they considered two types of tire rubber, namely crumb rubber and tire chips, were used as fine and coarse aggregate, respectively, in the production of rubberized concrete mixtures which were obtained by partially replacing the aggregate with rubber. Two water-cementitious material (w/cm) ratios (0.60 and 0.40), three moist curing periods (3, 7, and 28 days), four designated rubber contents (0, 5, 15, and 25 by total aggregate volume), two silica fume content (0 and 10% by weight of cement), and five different testing ages (3, 7, 28, 56, and 90 days) as experimental parameters.

The addition of silica fume to the concrete mixture, even as low as 10% by mass, improved the resistance of concrete against chloride penetration, irrespective of the amount of rubber used. The magnitudes of chloride penetration depth were remarkably decreasing with the use of silica fume, especially for the rubberized concretes.

The effect of silica fume on the chloride permeability of the concretes at varying rubber contents is well observed in Fig. 4. The figure indicated that the beneficial effect of silica fume was more pronounced at low rubber content (i.e., 5% by total aggregate volume), irrespective of w/cm ratio and moist curing period. However, as the rubber content increased up to 25% by total aggregate volume, the effect of silica fume had a tendency of decreasing. Interestingly, even at 3 days of moist curing period, the use of silica fume seemed to be more effective.

Ashrafi and Ramezaniapour [17] investigated the performance of concrete mixtures in the Persian Gulf. Ordinary and silica fume concrete mixtures containing various water to cementitious materials ratios were used. Rapid chloride permeability test and determination of diffusion coefficient of chloride ion penetration in accordance with bulk diffusion test under laboratory conditons simulated to Persian Gulf climate, and site investigation were performed. Test results show that silica fume reduces the chloride penetration and the diffusion coefficient in concrete mixtures (Fig. 5).

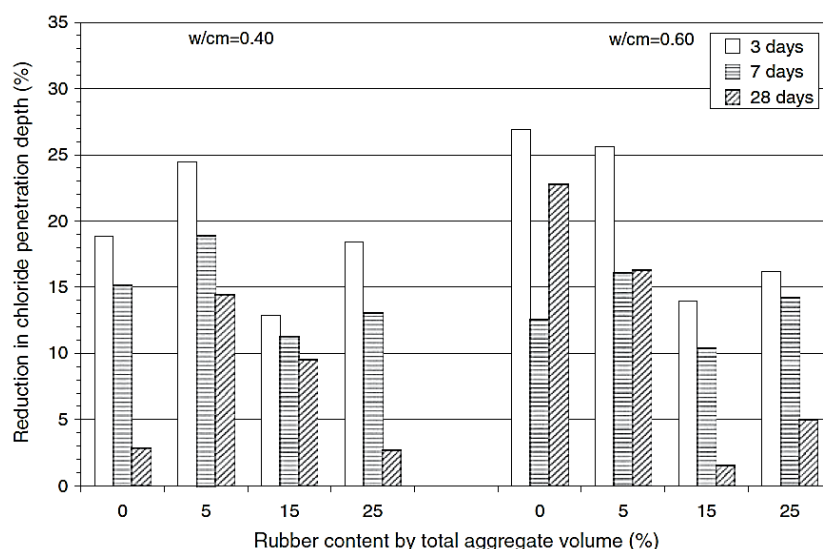


Figure 4. Percent reduction in chloride penetration depth of concretes containing different rubber replacement levels with the use of silica fume

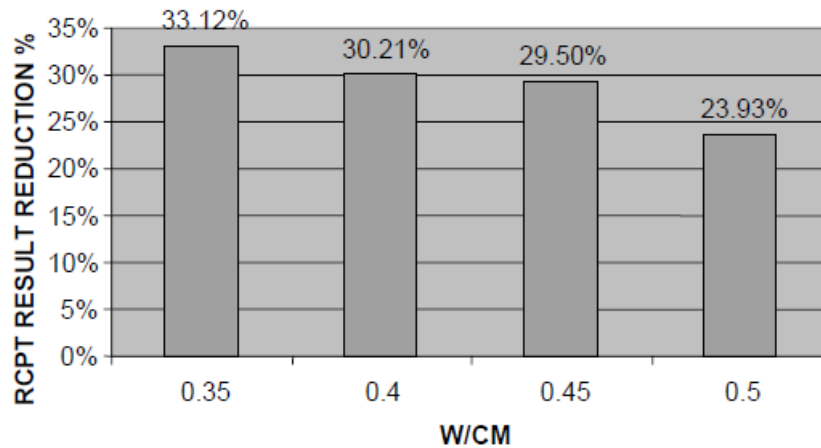


Figure 5. The effect of using silica fume (by cement mass) on decreasing RCPT results

Yazici [18] replaced cement with a Class C fly ash (FA) in various proportions from 30% to 60%. Durability properties of various self-compacting concrete (SCC) mixtures such as chloride penetration resistance have been investigated. Similar tests were carried out with the incorporation of 10% silica fume (SF) to the same mixtures.

Test results indicate that to improve the chloride penetration resistance, incorporation of FA and SF in SCC is very effective.

For example, chloride penetration depth of control mixture that has only Portland cement as a binder is 19 mm after 90 cycles. This value decreased to 17 mm with 60% FA and 9.5 mm with 60% FA and 10% SF replacement.

Shekarchi et al. [19] investigated the effects of silica fume on various properties of concrete specimens that were exposed to Persian Gulf conditions. Samples were taken at the ages of 3, 9 and 36 months and analyzed to determine the chloride diffusion coefficient. The results show that partial cement replacement with up to 7.5% silica fume reduces the diffusion coefficient significantly, e.g. about 500% reduction was observed in 3 months samples. Also time-dependent chloride diffusion of concrete containing silica fume is investigated by the following equation. [20]

$$D_{sf} = D_{pc} \times e^{-m(SF\%)} \quad (5)$$

Where D_{sf} represents diffusion coefficient of silica fume concrete; D_{pc} represents diffusion coefficient of Portland cement concrete; SF represents silica fume content (percent by weight of cement) and m is a time-dependent coefficient given in Table 4.

The effect of silica fume on performance of concrete against chloride ion ingress decreases with time. However, using silica fume at the earlier ages will decrease the diffusion coefficient significantly and thus a more durable concrete would be obtained. It can be seen that the coefficient m correlated better with silica fume content at earlier ages of specimens than at later ages.

Table 4: Values of m coefficient

| W/cm | chloride exposure period (months) | | |
|------|-----------------------------------|--------|--------|
| | 36 | 9 | 3 |
| 0.35 | -0.061 | -0.133 | -0.197 |
| 0.4 | -0.044 | -0.129 | -0.339 |
| 0.45 | -0.175 | -0.244 | -0.31 |
| 0.5 | -0.081 | -0.169 | -0.138 |

Ramezaniapour et al. [21] presented an experimental study on fresh and hardened properties of Self-Consolidating Concrete containing silica fume and volcanic pumice. Tests such as chloride-ion permeability were performed to evaluate durability of hardened concrete. Results showed that using silica fume and pumice significantly enhances the resistance to chloride penetration compared with the control concrete. At the age of 90 days, the control concrete specimens showed the highest value of 2675 coulombs while the charge passed through the SF and P concrete were 539 and 1457 coulombs, respectively. So the reduction of passing charge in SF specimens was more than P specimens.

Song et al. [22] presented a procedure for predicting the permeability of high strength silica fume cement concrete, developed by considering water-to-binder ratio, silica fume replacement ratio and degree of hydration as major influencing factors.

It was proposed that optimum silica fume replacement ratios that reduce the permeability of concrete is about 12 percent. If silica fume replacement ratio is over 12%, the permeability is marginal or, in some cases, increases for increased water-to-binder ratio.

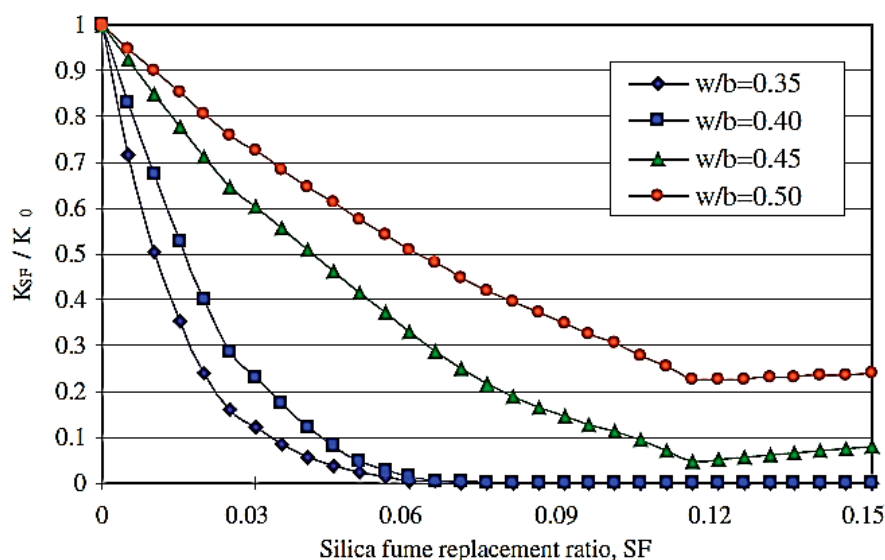


Figure 6. Reduction in permeability due to silica fume replacement for different w/c ratio

Ramezaniapour et al. [23] investigated the reduction of chloride penetration of silica fume mortars and concretes in rapid chloride penetration test (RCPT). Fig. 7 presents the RCPT values at 28 days for concretes containing 7% silica fume replacement with cement

and various cement contents. The charge passed through specimens has reduced from 3500 Columbs in control concretes to about 1000 Columbs for silica fume concretes.

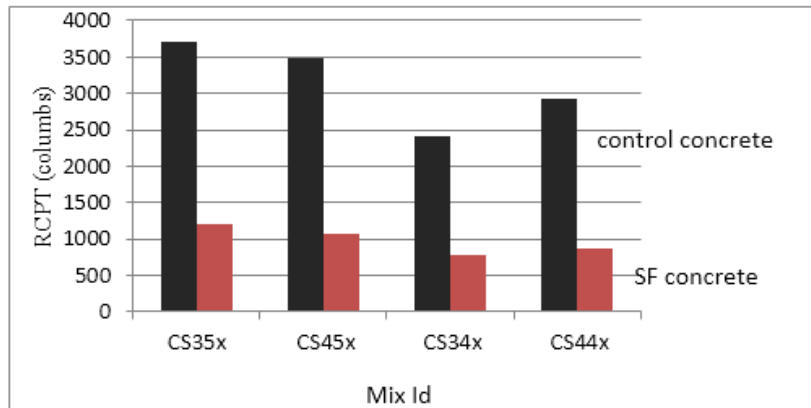


Figure 7. Influence of silica fume on rapid chloride penetration test results

Lee et al. [24] worked on effects of silica fume and fly ash on durability indices of cement-based composites. The results demonstrate that the addition of silica fume in cement-based composites resulted in a lower absorption, a lower critical pore size, a lower chloride diffusion coefficient, and a lower corrosion rate. Using 25% fly ash in concrete mixes decreased the 91-day total charge-passed from 2632 coulombs for the control mix to 1933 coulombs, whereas by replacing 10% SF, total charge-passed was 980 coulombs. Also results show that 10% SF replacement decrease diffusion coefficient 2 times higher than 25% FA replacement.

Jalal et al. [25] examined durability and microstructural properties of high performance self compacting concrete (HPSCC) incorporating SiO₂ micro and nanoparticles. For this purpose, a fraction of Portland cement was replaced by different amounts of microsilica, nanosilica and blend of micro and nanosilica as 10%, 2% and 10% + 2% respectively.

In depth of 0–5 mm of the samples containing 2% NS, Cl ion percentage decreased by 43, 40 and 43% for binder contents of 400, 450 and 500 respectively. The reductions in the samples containing 10% MS were obtained as 52%, 40% and 43% for the above-mentioned binder contents respectively. The samples containing 10%MS + 2%NS showed significant Cl ion percentage decrease as 62%, 60% and 56% for the above-mentioned binder contents respectively. As can be considered, mixtures containing both MS and NS with higher binder content show the best results in terms of Cl ions percentage and Resistivity.

Chahal et al. [26] examined the effect of silica fume on the rapid chloride permeability of concrete containing ureolytic bacteria (*Sporosarcina Pasteurii*). Three bacterial concentrations were optimized (103, 105, 107 cells/ml) and further designing of concrete mixes was done. In making concrete, cement was replaced with 5% and 10% of silica fume by weight. It can be concluded that replacement of 5% silica fume decreases the chloride permeability up to 50%. However for 10% replacement it does not decrease significantly.

Zhang and Ba [27] examined the effect of silica fume (SF) on the chloride diffusion coefficient of concrete subjected to repeated loading.

Portland cement was replaced by 5% and 10 % SF and the concrete specimens were

subjected to five cycles repeated loading, the maximum loadings were 40% and 80 % of the axial cylinder compressive strength (f'_c), respectively.

The diffusion coefficients were calculated from the steady state in the chloride migration test using the Nernst- Planck equation.

The results indicate that the diffusion coefficients of concrete containing 5 and 10 % SF replacements are lower than that of the control concrete at the age of 28 days. This trend increases with the increase of SF replacement. Five cycles repeated loading at 40 % f'_c or 80 % f'_c increase the diffusion coefficients (D_{28}) for all mixes investigated in this study. However, the effect of 80 % f'_c on D_{28} of concrete with 10 % SF is significantly lower than that of the control concrete without SF (Table 5).

The service life of concrete in chloride environment was predicted by Life-365 model. Compared with the control concrete without SF, 10 % SF replacements increase the service life of concrete by more than 10 times (Fig. 8).

Table 5: Diffusion coefficients calculated from the migration test ($10^{-13} \text{ m}^2/\text{s}$)

| Tension | C | SF5 | SF10 |
|-------------|------|------|-------|
| 0 % f'_c | 2.42 | 1.32 | 0.828 |
| 40 % f'_c | 2.77 | 1.39 | 0.873 |
| 80 % f'_c | 3.57 | 1.56 | 0.895 |

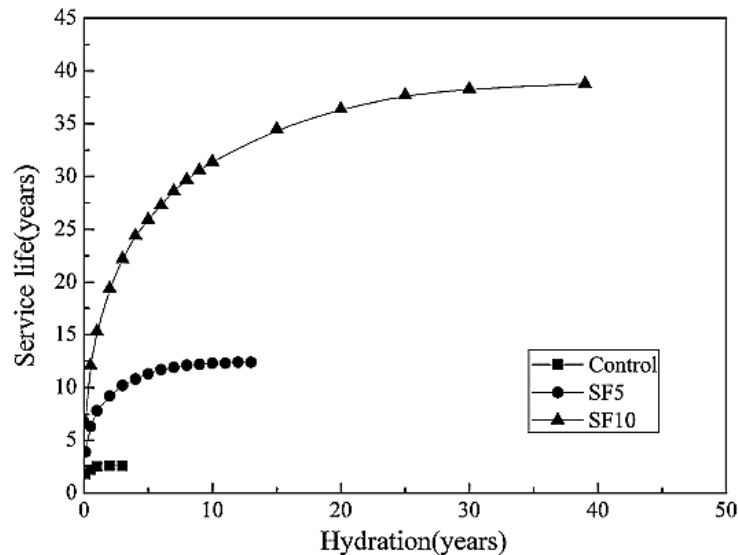


Figure 8. Effect of SF replacements on service life prediction for concrete subjected to 80 % f'_c

Sabet et al. [28] studied the effect of natural zeolite, silica fume and fly ash on the properties of concrete such as electrical resistivity and chloride permeability. The test results indicated that silica fume is more effective than natural zeolite or fly ash in improving durability properties of SCHPCs.

Using 10% and 20% natural zeolite or fly ash in concrete mixes increased the 90-day resistivity from 8.4 k Ω cm for the control mix to 30 and 50 k Ω cm. At this age resistivity of

specimens containing 10% and 20% SF were 54 and 231 k Ω cm, respectively.

It can be observed from Fig. 9 that the minimum amount of chlorides was in concrete containing 10% and 20% silica fume (0.07% weight of concrete).

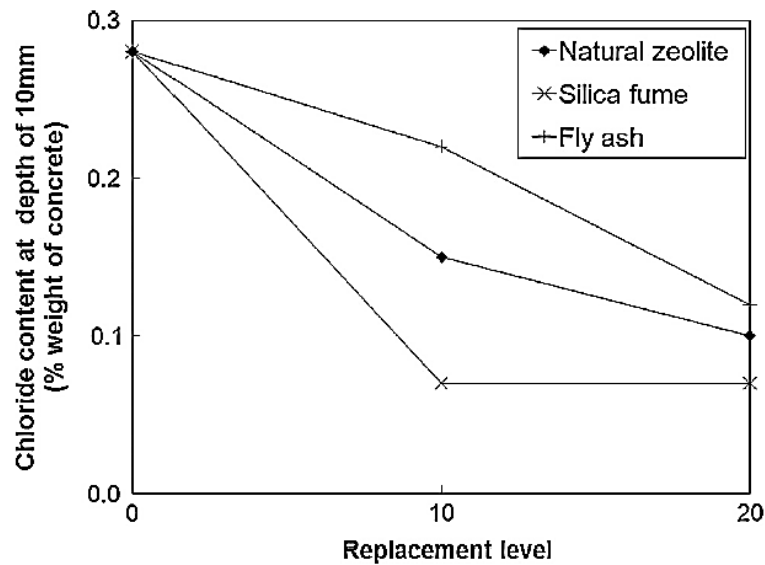


Figure 9. Chloride content at the depth of 10 mm for different concretes

5. INFLUENCE OF SILICA FUME ADDITION ON CORROSION

As mentioned earlier corrosion of steel reinforcement in concrete is the most common problem affecting the durability of reinforced concrete structures. Chloride-induced corrosion is one of the main mechanisms of deterioration affecting the long-term performance of such structures [1].

Chlorides lead to a local breakdown of the protective oxide film on the reinforcement in alkaline concrete, so that a subsequent localized corrosion attack (pitting) takes place [29]. Fig. 10 summarizes the factors involved in the initiation of this type of attack. Chloride penetration through the concrete cover produces in time profiles of chloride content, as shown by the grey lines in Fig. 10. Initiation of corrosion takes place at time t_i when the chloride profile is such that, as shown by the black line in Fig. 10, a chloride threshold value (Cl_{th}) is reached on the surface of the steel reinforcement, i.e. at a depth equal to the concrete cover thickness [30].

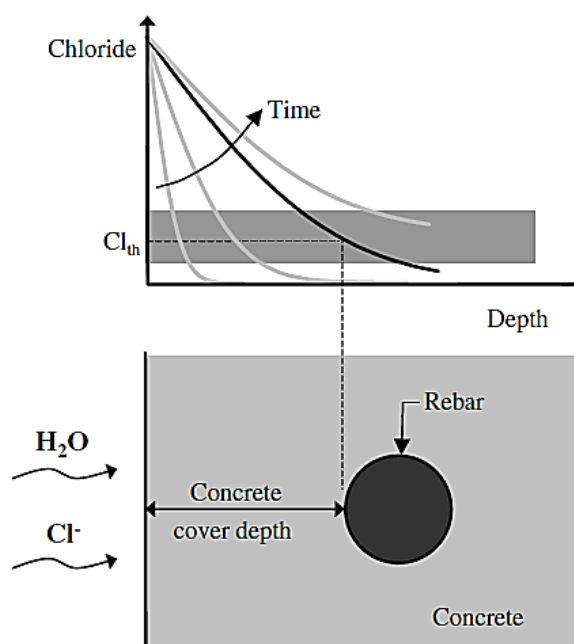


Figure 10. Factors involved in the initiation of chloride induced corrosion of steel in concrete

Marcotte and Hansson [31] examined the influence of silica fume on the corrosion behaviour of steel in high performance concrete (HPC) by comparing the behaviour of HPC concretes with and without a 10% by mass of cement addition of silica fume. Reinforced concrete prisms with embedded corrosion probes were loaded in three points bending to achieve a 0.3 mm crack and exposed to simulated sea water for up to four years. Corresponding prisms without induced cracks were also studied as controls. For the HPC with silica fume, pore size distribution measurements showed that after exposure to the simulated sea water, the hydration and pozzolanic reactions near the induced crack blocked almost all continuous pores in the 0.01 to 10 μm ranges. This affected the type and distribution of corrosion products that formed by restricting the access of chlorides and oxygen to the surface of the steel. Thus, only magnetite (Fe_3O_4) formed and was confined the space provided by the induced crack, effectively plugging the crack. In HPC without silica fume, oxygenated corrosion products such as goethite ($\alpha\text{-FeOOH}$) and akaganeite ($\beta\text{-FeOOH}$) formed in the induced crack region. Fig. 11. shows the mean corrosion rates measured for the two prisms of both concrete types, both cracked and uncracked, for up to four years of exposure to the simulated seawater. It also illustrates that silica fume has very good effect in reducing the corrosion rate.

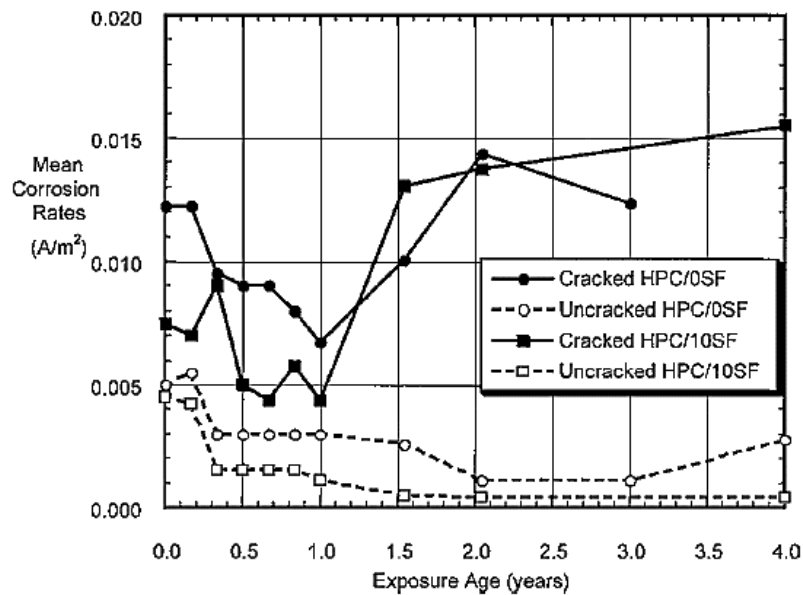


Figure 11. Comparison of the mean corrosion current densities of the steel probes intersected by the crack in the cracked specimens and in the centre of the beams for the uncracked specimens

Türkmen et al. [32] examined The corrosion current densities of the samples with steel reinforcement in 5% NaCl solution by the linear polarization technique after 28, 75, 150 and 250 days. The results showed a reduction in corrosion current density in samples containing 10% silica fume (Table 6).

Since no pronounced effect of time on the corrosion current density was observed between 75 and 250 days, it can be concluded that the passive protective layer started to form after 75 days.

Table 6: Reduction in corrosion current densities of experimental specimens compared to OPC (%)

| w/c | time(day) | | | |
|------|-----------|----|-----|-----|
| | 28 | 75 | 150 | 250 |
| 0.35 | 9 | 36 | 37 | 35 |
| 0.4 | 14 | 11 | 20 | 19 |
| 0.45 | 11 | 22 | 21 | 17 |

Dotto et al. [33] studied the influence of silica fume on the corrosion behaviour of reinforcement bars. Concretes with different water–binder ratio 0.50, 0.65 and 0.80 were used. Silica fume additions were 0%, 6% and 12% by weight of cement. Tests were conducted for electrical resistivity, and polarization curves. The results showed that the addition of 6% silica fume increases the electrical resistivity of concrete by 2.5 times and 12% silica fume increases it by 5 times. This suggests that the addition of silica fume can be effectively used in protecting steel reinforcement against corrosion [6].

Civjan et al. [34] conducted a long-term corrosion study to determine the effectiveness of calcium nitrite (CN), silica fume (SF), fly ash, ground granulated blast furnace slag (BFS),

and disodium tetrapropenyl succinate (DSS) in reducing corrosion of reinforcing steel in concrete. Mixture proportions included single, double, and ternary combinations of these admixtures. It was concluded that for optimal protection against corrosion in structural concrete, a ternary combination of CN, SF, and FA (or a double combination of CN and BFS), all at moderate dosages, is the best of all. A ternary combination of CN, SF, and BFS would also be effective, although the addition of SF may add cost without much improvement in minimizing corrosion [6].

Kayali and Zhu [35] did tests on high-strength reinforced silica fume–cement concrete slabs with a compressive strength of 70MPa for chloride diffusion and corrosion activity after partial immersion in a 2% chloride solution. It was found that high-strength concrete containing 10% silica fume possessed exceedingly high corrosion resistance [6].

According to half-cell potential test, after 50 days there was a more than 90% probability of corrosion initiation of OPC specimens subjected to salt solution, whereas after 550 days there was a less than 10% probability of corrosion initiation of specimens containing 10% SF.

Manera et al. [30] investigated the effect of silica fume on the chloride threshold value for the initiation of pitting corrosion of steel in concrete. Tests were carried out on concrete specimens made with ordinary Portland cement with 10% of silica fume. Chloride contents up to 2% by mass of cement were added to the mixes (internal source of chloride), in order to investigate the corrosion rate of embedded bars.

Results showed that the values of electrical resistivity for concrete without chlorides are almost one order of magnitude higher in concrete with silica fume (10%SF) compared to concrete without SF. However, addition of chloride caused a lower chloride threshold value in the bars which were embedded in concrete with silica fume compared to those embedded in concrete made of Portland cement.

For the initiation of pitting corrosion of embedded steel a range of 1.1–2% by mass of cement was detected for OPC concrete and a range of 0.6–1.2% by mass of binder for 10%SF concrete, i.e. the presence of silica fume may lead to a significant reduction in the chloride threshold value.

Ramezaniapour [36] investigated the effect of different supplementary cementing materials, namely; silica fume, slag and a natural pozzolan (trass) on properties of concrete. Other variables were cement types (type II and type V), water-cement ratio, cover thicknesses (3.5, 5 and 7cm) and environmental conditions of the Persian Gulf (submerged, tidal and dry). Durability tests such as corrosion of reinforcing bars were conducted at different ages.

In 4 year specimens subjected to tidal zone, the best performance was obtained for mixtures containing trass cement and ASTM Type II cement + silica fume.

Kelestemur and Demirel [37] analyzed the corrosion behavior of reinforcing steels embedded in concrete specimens obtained by substituting cement with finely ground pumice (FGP) at proportions of 5%, 10%, 15% and 20% by weight. Besides, with the purpose of determining the effect of silica fume (SF) additive over the corrosion of reinforcing steels embedded in concrete with FGP, SF has been entrained to all series with the exception of the control specimen, such that it would replace with cement 10% by weight.

In this study, it was observed that an increase in the corrosion rate of the reinforcing steel had taken place as a result of the FGP addition. However, it was determined that with the addition of SF into concretes supplemented with FGP, the corrosion rate of the reinforcing

steel has significantly decreased.

Results obtained from corrosion potential measurements of reinforcing steels embedded in the concrete specimens are displayed in Figs. 12 and 13.

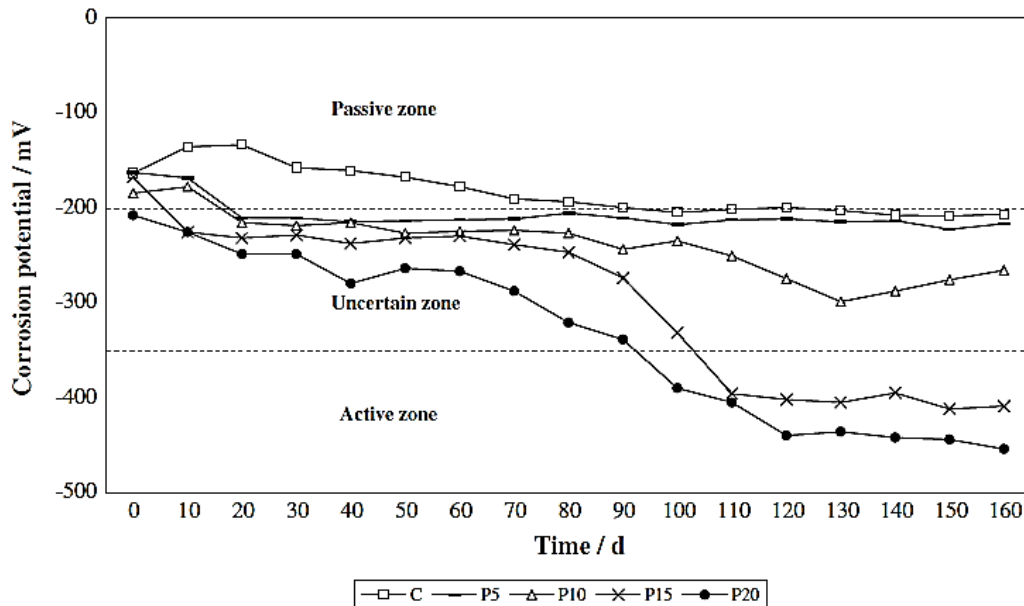


Figure 12. Change in corrosion potential on the specimens C, P5, P10, P15 and P20 (P20: specimens containing 20% FGP)

Dehwah [38] presented the results of a study conducted to evaluate the corrosion resistance of self-compacting concrete (SCC) prepared using quarry dust powder (QDP), silica fume (SF) plus QDP.

The variation of corrosion potentials with time on steel in all the SCC specimens exposed to 5% NaCl solution was obtained to evaluate the time of corrosion initiation, based on the ASTM C 876 criterion.

Results showed that the time to initiation of reinforcement corrosion in concrete containing SF is much more than that in all the other specimens.

The corrosion current density on steel in the specimens containing only 5% SF after 990 days of exposure was less than 0.3 A/cm^2 which means that the steel bars in these specimens were still in a passive condition.

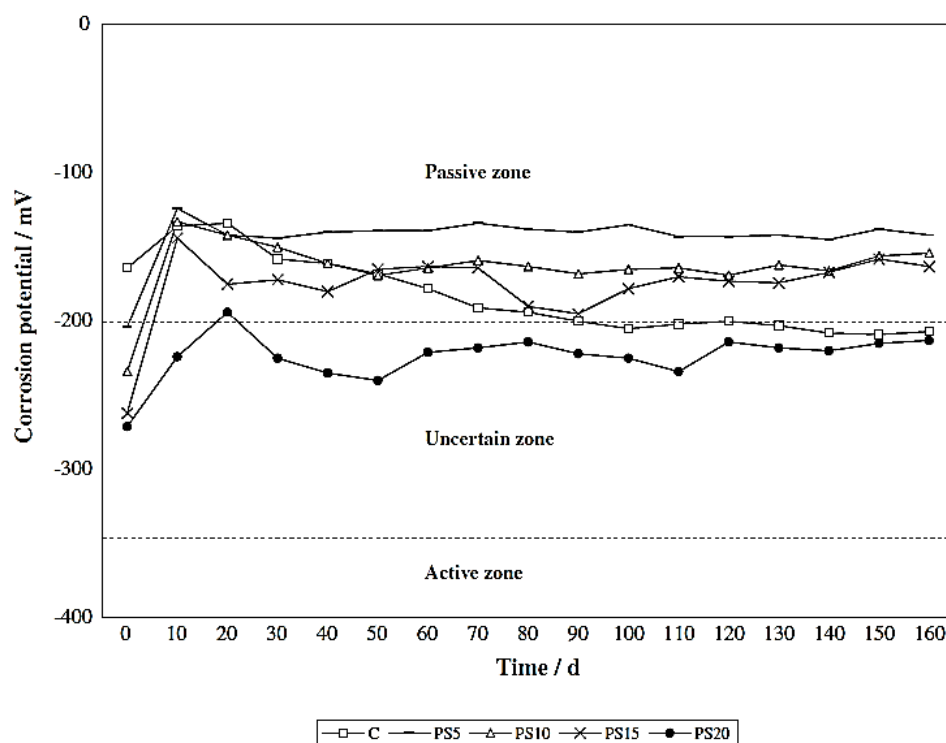


Figure 13. Change in corrosion potential on the specimens C, PS5, PS10, PS15 and PS20 P20 (PS20: specimens containing 20% FGP & 10% SF)

6. CONCLUSIONS

1. Addition of silica fume results in significant reduction in the permeability and chloride-ion diffusion. This could be attributed to the addition of silica fume causes considerable pore refinement i.e. transformation of bigger pores into smaller one due to their pozzolanic reaction concurrent with cement hydration.

2. In the design for durability of reinforced concrete structures, its contribution should be considered not only in relation to the penetration of chlorides, but also with regard to the chloride threshold. Specifically, for concrete with addition of silica fume, it is worth to consider that the great positive effect of this mineral addition due to the drastic reduction in the chloride penetration could be mitigated by the reduction in the chloride threshold. These two effects should be evaluated for any specific case.

3. The permeability of concrete is dramatically reduced as silica fume replacement ratio is beyond 8%, and the permeability is lowered until silica fume replacement ratio increases from 8% to 12%. However, if silica fume replacement ratio is over 12%, the permeability is marginal or, in some cases, increases for higher water-to-binder ratio.

4. The reduction in diffusion coefficient is not proportional to the increase in silica fume content. The addition of 7.5% silica fume resulted in a significant reduction in chloride diffusion into concrete. However, an increase of silica fume content from 7.5% to 12.5% exhibited little effect on the reduction in permeability.

5. Electrolyte resistance and resistance against charge transfer of concrete increase considerably by use of silica fume especially at later ages.

6. SF addition of 5 % may increase the service life of concrete by more than 3 times, and a SF addition of 10 % increase by more than 10 times. Concrete containing SF as a partial replacement for cement exhibits an increased service life because of the significant decrease of chloride diffusion coefficient.

7. The chloride diffusion coefficient of a concrete is time dependent. It will typically decrease as time passes since the capillary pore system will be altered as hydration products continue to form.

8. The effect of silica fume on performance of concrete against chloride ion ingress decreases with time. However, using silica fume at the earlier ages will decrease the diffusion coefficient significantly and thus a more durable concrete would be obtained.

9. The addition of SF, in a way that would replace with the cement 10% by weight, has dramatically reduced the corrosion rate of the reinforcing steels embedded in concretes.

10. The source of chloride ion is an important point in studying the corrosion of reinforcement in concrete containing silica fume. It has been investigated that if the chloride ion has an external source, silica fume will be very effective in reducing the corrosion rate. However, in case of internal source of chloride ion, the presence of silica fume will expedite the corrosion of reinforcement.

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