# The Effect of Micro Silica on Permeability and Chemical Durability of Concrete Used in the Corrosive Environment

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**ABSTRACT:** *Micro silica (MS) is an extremely fine, spherical powder that is used as an additive for improving concrete performance. It is obtained as a by product of silicon metal and ferrosilicon alloy production. Due to its pozzolanic nature, micro silica can be used to enhance the qualities of both fresh and hardened concrete.*

*Addition of micro silica into the concrete as a cement replacement, decreases its permeability. As a result, it forms very dense and chemically durable concrete to withstand the harsh and corrosive chemical environments.*

*The results of detailed investigations on concrete made from type V cement with addition of micro silica as substituent and its curing by tap water shows dramatic increase is compressive strength (CS) of concrete after 7 days of hydration onwards. By repeating experiment in sodium sulfate solutions (50 gr/lit) prepared under ASTM C1012 requirements, the results were same as tap water but the extend of increase of compressive strength is lower. It is also confirmed that, micro silica modies pore size distribution and permeability of type V cement concreats in same way as reported for ordinary Portlant cement in various literature. By replacing micro silica as a substituent in type V cement composition, a concreat with high chemical durability and strength are formed, which easily can be used as suitable material for harsh environments such as marine and offshore structures or the places where the concentration of sulfate ions are high, such as concrete sewage pipe line networks.*

**KEY WORDS:** *Micro silica, Concrete made with type V cement, Sulfate resistant concretes, Sewages concrete pipe lines, Chemically durable concretes*.

## INTRODUCTION

Micro silica is a by-product of the Electric Arc furnaces used in the production of Ferrosilicon and silicon industries. Micro silica is in the amorphous state with the chemical composition of >90% silica and the grain size of < 0.1 microns. It is very fine active artificial pozzolanic and cementious material. It can be replaced

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as part of cement in production of pozzolanic cement [1].

When cement reacts with water, hydration takes place and a binding gel known as calcium silicate hydrate (CSH) is formed. At the same time, calcium hydroxide or free lime $Ca(OH)_2$ is released through the following chemical reaction. By adding pozzolanic materials such as steel slag, micro silica or fly ash which are mainly composed of amorphous silicon dioxide ($SiO_2$) in the concrete mixtures, the reactive silicon dioxide component reacts with calcium hydroxide to form additional calcium silicate hydrate which can be represented in the following chemical formulas.

$$\text{Cement} + H_2O \text{ --- } \text{CSH (cementing gel)} + Ca(OH)_2 \quad (1)$$

$$Ca(OH)_2 + SiO_2 \text{ ---- } \text{CSH (additional cement gel)} \quad (2)$$

The deterioration of concrete and its reinforcement material in corrosive environments has been a real problem over the years. In addition to carbonation of concrete and rusting of the steel reinforcements, the chloride and sulfate ions have imposed much deterioration to the structures. These can be prevented by reducing water to cement ratio (w/c) and proper curing of concrete that decreases its permeability which is the main cause of deterioration [2]. The penetration of corrosive ions such as chloride and sulfates, depends on the permeability of concrete; thus, greater water cement ratio the greater is penetration [3]. Resistance to the penetration of chloride and sulfate ions also could be achieved at relatively early ages by inclusion of slag or micro silica as a supplementary cementious material in a low water cement ratio [4]. Some researchers have found that chloride penetration into concretes with cement replacement of 3 % by Fly ash, 5 % by blast furnace slag and 10 % by micro silica; extremely low corrosive ion penetration values were obtained at one year [5]. Others investigated the effect of chloride and sulfate attack on concretes in the Persian golf countries. They found that chloride ions penetrate significantly faster than sulfates into the steel concrete interface, and influencing the corrosion mechanism in dependent of corrosion cause by sulfates [6]. The mechanism of chloride attack on the concrete has been investigated and concluded that, chloride ions saturates concrete structures, destroys the ferric oxide coating of steel bars by, penetrating into the body of reinforcement, and then corrosion starts [7].

The other sort of chemical attack that takes place in the body of concrete structures in the marine and salty environments is the sulfate attack. The sulfate ions react with free lime in the body of concrete and lead to the formation of calcium sulfate ($CaSO_4$) and Ettringite ($C_3A$, $CaSO_4$, $31H_2O$) in the presence of $C_3A$, thus the formation of Ettringite in concrete mostly depends on the presence of $C_3A$ and Sulfate ions. The expansion that is caused by the formation of Ettringite is about 227 % relatively higher in volume than the primary phases. The concrete that subjects to sulfate attack looks gray and white with lots of micro and macro cracks on the surface. Attack can lead to lower strength, expansion and ultimately disintegration [8]. The extent of chemical attack on the concrete mostly depends on the concentration of the salty solutions. The most severe attack takes place in the presence of 0.5 % Magnesium and 1% Sodium sulfate and also 1 % Sodium chloride solutions.

There are few ways, suggested by the other workers, to increase the chemical durability of concrete structures:

A) Decreasing the amount of $C_3A$ in the cement.

B) Decreasing the permeability of concrete.

Micro silica is one of the most reactive pozzolanic materials. In addition to the reaction of micro silica with lime leading to the formation of C-S-H gel, its fine grin size < 0.1 microns can decrease and block the capillary pores of concrete by formation of silica networks. Although there are number of reports about the effect of micro silica in ordinary Portland cement concretes [8-17], it looks, there is lack of information about this effect on concretes made from type V cement.

In this study the effect of Iranian produced micro silica has been investigated on concrete made with type V cement and gravel specially produced for sulfate environment to improve its chemical durability and produce a concrete more reliable for using in the sewage concrete pipe lines (in which diluted sulfuric acid is produced under the effect of bacterial oxidation of hydrogen sulfide). The effect of micro silica on the pore structure of concrete is graphically shown in Fig. 1.

## MATERIALS AND METHODS

The samples prepared by mixing type V cement, produced by Sepahan cement co. with proper gravel and sand aggregates. On a few samples 10 or 15 weight percent of cement replaced with Iranian produced micro silica. Its chemical composition is summarized in Table 1.

The water cement ratio (w/c) kept constant at 0.36. After proper mixing of cement, gravel, micro silica and water, the mix was placed in 10×10×10 cm molds and vibrated for 1 min. After 24 hours the samples were removed from the mold and surface of them was kept wet for additional 12 hours then some of the samples placed in tap water tank while the others left in the ASTM C1012 solution (50 grams sodium sulfate in one liter of solution). At required time intervals, concrete samples were removed from solution tanks, its surface dried and inspected for any changes in gray color of concrete and its length measured for any variations and used for mechanical testing. The test was repeated five times on each concrete sample. In order to investigate the effect of micro silica on pore size distribution and pore structure in body of concrete, two cores from the prepared slab at 45-55 and 67-75 mm dept from the surface was cut by derail. After removing of sand and gravel from the hardened cement of the cores, the pore structure through hardened cement paste was tested by mercury porosimeter under vacuum of 5-10 torr, mercury, then was intruded into sample under the pressure of 20000 PSI and results recorded based on the pore size distribution of the hardened cement pastes.

In this study emphasize has been on mechanical testing of samples because any changes in microstructure of concrete as a result of phase formation, mostly affects on mechanical strength of bonding phase which in this case is hardened cement paste.

## RESULTS AND DISCUSSIONS

### *(A) The effect of 15% Micro silica on the mechanical strength of concrete made with type V cement.*

The effect of 15% replacement was considered on the compressive strength of typeV concrete. For these experiments, 150 cubes of concrete were prepared, 75 with type V cement and the other 75 with type V cement+ MS. After setting and curing, samples put in tap water for different time periods (14, 28, 180, 360 days). At required times, samples removed from the bath and subjected to the compressive strength testing. Results are shown in Figs. 2 and 3. It seems from the results that compressive strength of concrete with 15 % micro silica is much higher than plain concrete in the ages up to 28 days. The difference between compressive strength of plain type V concrete and micro silica incorporating one

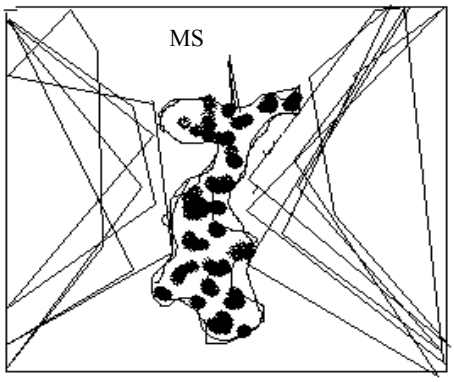


***Fig. 1: The effect of micro silica on the pore structure of concrete [15].***

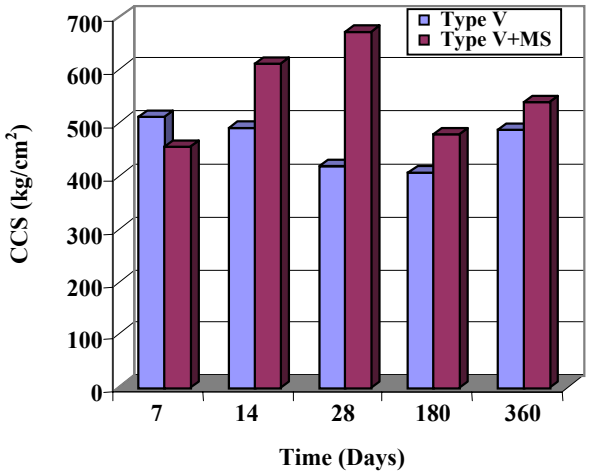


***Fig. 2: Effect of 15% micro silica addition on compressive strength of concrete prepared from type V cement.***

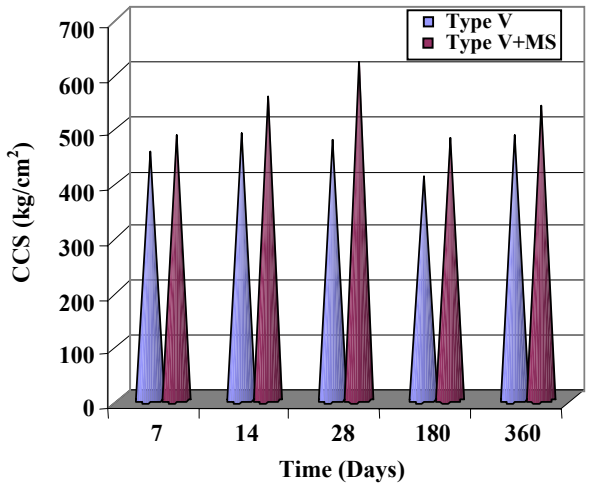


***Fig. 3: Effect of 15% micro silica addition on compressive strength of concrete prepared from type V cement.***

is about 100 kg/cm$^2$ at 14 days and 250 kg/cm$^2$ at 28 days. Comparison of results graphically shown in Figs. 2 and 3, reveals that the average trend of compressive strength and reproducible for all samples. The compression strength of samples hydrated for different time period (180, 360 days) shown reduction in strength as compare to 28 days one.

***(B) The effect of 10% micro silica on the mechanical strength of concrete made with type V cement***

Based on the previous experiments with 15 % Iranian micro silica replacement in concrete made with type V cement and the results not being reproducible, 150 other samples prepared with 10 % micro silica replacements and submerged in water bath. Samples removed from the water bath at required time intervals. The results of average amounts of compressive strength measurements of samples are shown in Table 2. Based on the result obtained, compressive strength of concrete made with type V cement is about 60 kg/cm$^2$ higher in the absence of micro silica after 7 days of hydration, but at longer ages like 14 and 28 days the compressive strength of samples with 10% micro silica additions increases up to 140 kg/cm$^2$ which is due to the chemical reaction of micro silica with free lime in concrete. When hydration time extended to 60days, the difference was about 100 kg/cm$^2$ and 140 kg/cm$^2$ at 180 days. Compared to the results of 15 % micro silica additions, results were reproducible and reliable in this part.

***(C) The effect of 10% micro silica additions on the sulfate resistance of concrete made with type V cement***

In order to investigate the effect of sulfate solutions on concrete made from type V cement with and without micro silica, the samples submerged in the 50 gr/lit sodium sulfate solution, made under the ASTM C1012 requirements. At various time intervals, samples removed from the water bath, surface of them dried and inspected for any changes in its gray color. Its length measured for any changes due to the formation of trace amounts of Ettringite due to the presence of sulfate ions in the solution. Then its compressive strength was tested under previously mentioned procedure.

Five samples were tested for each day and the results are shown in Fig. 4. It seems that the compressive strength of concrete made with type V cement was much

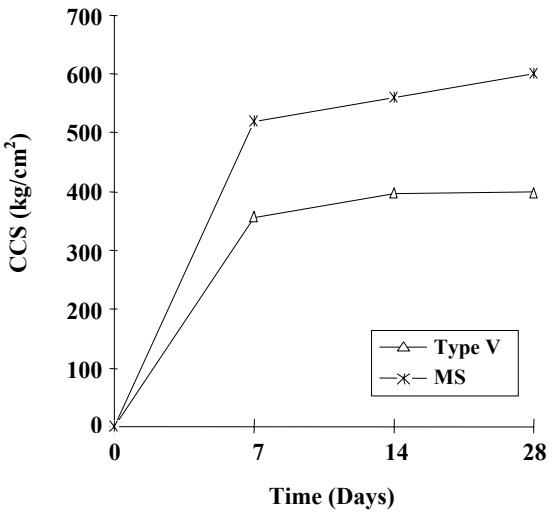


***Fig. 4: The Effect of $Na_2SO_4$ solution on the CCS of concretes with and without MS.***

lower than samples with 10 % micro silica replacement after 7 days of hydration, while it smoothly increases after 14 days onward in the parallel form compared to samples with micro silica. The investigation of a few other samples revealed that the strength development of concrete made with type V cement in sodium sulfate solution is much lower than when micro silica has been added to it. In another series of experiment run for 28 days, the result showed that the strength development of type V concrete in sodium sulfate solution is lower than the type V + MS. Based on these experiments one can say that micro silica addition improves sulfate resistance of concrete made with type V cement by changing the pore structure and prevention of sulfate ion penetration into the concrete and formation of Ettringite..

***(D) The effect of micro silica on permeability of concrete made with type V cement***

In order to investigate the effect of Iranian produced micro silica in comparison with values reported in the literatures on permeability of concrete made with type V cement, a few samples in the form of 500×250×100 mm slabs were prepared and used for nitrogen intrusion permeability measurement. The average results of the test showed that the rate of nitrogen intrusion into the concrete made with 10 % of micro silica permeability was reduced to 3 % cm$^2$/cm$^3$/hr as compare with 6 % cm$^2$/cm$^3$/hr of type V plain cement.

***Table 1: Chemical composition of Iranian produced micro silica.***

| $SiO_2$ % | $Fe_2O_3$ % | $Al_2O_3$ % | CaO % | MgO % | $Na_2O$ % | $K_2O$ % | C % | S % | LOI % |
|---|---|---|---|---|---|---|---|---|---|
| 94 | 0.03 | 0.06 | 0.5 | 1.1 | 0.04 | 0.05 | 1.0 | 0.2 | 2.5 |

***Table 2: Effect of 10% MS on the compressive strength of concrete made with type V cement.***

| No | Time/day | TypeV $kg/cm^2$ | Type V+ MS $kg/cm^2$ |
|---|---|---|---|
| 1 | 7 | 513 | 448 |
| 2 | 14 | 516 | 653 |
| 3 | 28 | 530 | 673 |
| 4 | 60 | 593 | 700 |
| 5 | 180 | 630 | 750 |

Based on this experiment can be concluded that, the permeability of concrete with addition of micro silica has decreased up to 50%.

***(E) The effect of micro silica additions on pore structure of concrete made with type V cement***

In spite of number of reports that are puldished on pore structure of concrete. It looks, there is lack of information about the effect of MS on pore size distribution and pore structure. In this study, we tried to investigate the effect of micro silica additions on pore structure of concrete made of type V cement with and without micro silica by mercury intrusion porosimeter. The cement was perforated from gravel and aggregates and dried in oven at 100 ºC for 24 hours to remove free water from capillary pores, the cooled samples inserted into the mercury porosimeter instrument for evaluating the pore size distribution and pore structure. The results are summarized in Table 3. The letter A and B are assigned for the depth of 45-55 mm and 65-75 mm respectively. The samples were numbered as S1 for type V and S6 for TypeV+10 %MS concrete. It seems from the results in table 3 that the porosity of concrete made with micro silica additions is much lower than the concrete made with type V cement. Also the pore size distribution varied with the addition of micro silica to the concrete. The amount of pores sized between 0.1 and 8 microns are much higher in plain type V concrete in comparison with the type V+ MS concrete. In this respect, the amount of pores in the size ranged between 0.01 – 0.1 μm also decreased in depth of concrete. While the amount of micro pores in the range 0.006 – 0.01 μm dramatically increased in type V+ MS concrete. These facts are due to the reaction of micro silica grains with free lime and block of the big pores and production of small pores in the body of concrete.

**CONCLUSIONS**

The following conclusions can be drawn from the experimental part of this paper:

A-When micro silica is added into the concrete composition, it reacts with free lime released as by product of hydration reaction and will improve the chemical durability of concrete.

B-Iranian produced micro silica increases the compressive strength of concrete in the same manner that has been previously reported in the literature.

C-Replacement of 15 % Iranian produced micro silica with type V cement in concrete, increased its compressive strength up to 28 days but it dramatically decreases at

***Table 3: Effect of MS on the pore size distribution of concrete made with type V cement.***

| Total pore volume | Porosity | Pore size distribution | | | | | |
|---|---|---|---|---|---|---|---|
| | | 0.1 – 8 μm | | 0.01 – 0.1 μm | | 0.006 – 0.01 μm | |
| ml/g | % | ml/g | % | ml/g | % | ml/g | % |
| 0.0289 | 6.48 | 0.0088 | 30.7 | 0.0161 | 55.7 | 0.004 | 13.8 |
| 0.0497 | 10.53 | 0.0173 | 34.8 | 0.0276 | 55.7 | 0.0052 | 10.5 |
| 0.0297 | 3.16 | 0.0088 | 26.9 | 0.0132 | 44.4 | 0.0077 | 25.9 |
| 0.0283 | 1.14 | 0.007 | 24.7 | 0.0151 | 53.3 | 0.0062 | 26.9 |

later ages. This behavior was not reproducible and did not produce reliable results.

D-The addition of 10 % micro silica (Iranian brand) improved compressive strength of concrete made with type V cement. The obtained reliable results are in good agreements with literature for Portland cement.

E-Micro silica improves chemical durability of concrete made with type V cement in sulfate environments.

F-Addition of 10 % micro silica modifies the pore structure of concrete made with type V cement as has been reported by other workers on ordinary Portland cement.

G-Based on the results of this paper 10 % micro silica addition is optimum amount for improving the properties of concretes made with type V cement.

H-The micro silica concretes with very high performance and chemical durability is the best suggestion for using in the harsh chemical environments such as marine and offshore structures or the places where the concentration of sulfate ions are high such as concrete sewage pipe line networks.

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