ABSTRACT

Reinforced concrete requires steel bars in order to provide the tensile strength that is needed in structural concrete. However, when steel bars corrode, a loss in bond between the concrete and the steel bars occurs due to the formation of rust on the bars surface. Permeability of concrete is a fundamental property in perspective of the durability of concrete as it represents the ease with which water or other fluids can move through concrete, subsequently transporting corrosive agents. Nanotechnology is a standout amongst active research zones that envelops various disciplines including construction materials. The application of nanotechnology in the corrosion protection of metal has lately gained momentum as nanoscale particles have ultimate physical, chemical and physicochemical properties, which may enhance the corrosion protection in comparison to large size materials. The presented research aims to study the bond performance of concrete containing relatively high volume nano silica (up to 4.5%) exposed to corrosive conditions. This was extensively studied through tensile, bond strengths as well as the permeability of nano silica concrete. In addition micro-structural analysis was performed in order to evaluate the effect of nano silica on the properties of concrete at both the micro and nano levels. The results revealed that by the addition of nano silica, the permeability of concrete mixes decreased significantly to reach about 50% of the control mix by the addition of 4.5% nano silica. As for the corrosion resistance, the nano silica concrete is comparatively higher resistance than ordinary concrete. Increasing Nano Silica percentage increased significantly the critical time corresponding to a metal loss (equal to 50 μm) which usually corresponding to the first concrete cracking due to the corrosion of reinforcement to reach about 103 years instead of 23 years as for the normal concrete. Finally, increasing nano Silica percentage increased significantly the residual bond strength of concrete after being subjected to corrosive environment. After being subjected to corrosive environment, the pull out behavior was observed for the bars embedded in all of the mixes instead of the splitting behavior that was observed before being corroded. Adding 4.5% nano silica in concrete increased the residual bond strength to reach 79% instead of 27% only as compared to control mix (0%W) before the subjection of the corrosive environment. From the conducted study we can conclude that the Nano silica proved to be a significant pore blocker material.

Keywords: bond strength, concrete, corrosion resistance, Nano silica, permeability.

1. INTRODUCTION

Reinforced concrete uses steel bars in order to provide the tensile properties that are needed in structural concrete. However, when steel bars corrode, the formation of rust on the bars surface leads to a loss in bond between the concrete and the steel bars. The corrosion products on steel swell, and sometimes induce the cracking of concrete cover. So, corrosion rates are characterized by a time before first concrete cracking (tc). This time tc is arbitrarily defined, but it corresponds to real reinforced concrete structures. [1]Steel bars in concrete are usually in a non corroding (passive) condition. However, reinforced concrete is often used in severe environments where sea water or deicing salts are present. The movement of the chloride into the concrete leads to disrupt the passive layer protecting the steel. Moreover, another cause of steel corrosion is Carbonation of concrete. When concrete carbonates to the level of the steel rebar, the normally alkaline environment, which protects steel from corrosion, is replaced by a more neutral environment. Under these conditions, the steel is not in passive condition and rapid corrosion begins. Corrosion of steel is the chemical or electrochemical reaction between the steel and its environment that leads to deterioration in the material and its properties. For steel bars embedded in concrete, corrosion results in the formation of rust which has (2-4) times the volume of the original steel volume and none of its mechanical properties. Corrosion also produces pits in the surface of steel bars which lead to reduce strength capacity due to the reduction in cross-sectional area.[2]

Nano silica is one of the most important pozzolanic materials that attract the scientists’ attention. Different forms of Nano-sized amorphous silica have become available due to these developments in Nano technology. Due to the higher specific surface area of Nano silica in comparison with silica fume, a lot of studied have been made to investigate the different effects of Nano silica on the properties of cement based materials. Nano silica is a Nano material which has white powder spherical particles have a diameter below 100 nm and density equals to 2.12 kg/m3. Nano silica acts as nuclei for cement phases so it promotes cement hydration due to its pozzolanic reaction with CH especially at early ages and increases the production of C-S-H. In addition to the above, it acts as a filler material in the Nano pores because of its fine particle size, decreasing the water absorption and increasing the durability of the matrix. Finally, Nano silica helps replace the cement and reduce its content in concrete. Although a lot of studies have been made to investigate the influence of Nano silica on different
properties of cement composites (compressive, tensile and flexural strengths), some properties haven’t been studied well enough like bond strength and permeability while other properties haven’t been studied yet like corrosion resistance of Nano silica concrete. Nano silica concrete is a new discovery in the world of concrete technology. It has the ability to replace the normal concrete. A better investigation to understand its behavior under different normal and severe conditions (high temperature) will help to demonstrate its applicability. This paper reports the effect of Nano silica on tensile strength, permeability of concrete in addition to the bond strength of concrete before and after being subjected to corrosive environment. X-ray diffraction analysis and scanning electron microscopy will be introduced to help interpreting the behavior of Nano silica concrete.

2. EXPERIMENTAL PLAN

A. Materials

a) Cement

Portland Cement Type I was used. The grade used was CEM I 52.5 N. The chemical analysis and physical properties of cement are listed in Table-1.

b) Nano silica

The used commercial nano silica has particles of average size of 20 to 80 nm. (Fig. 1 and 2) show the TEM and XRD of nano silica respectively while the chemical analysis and physical properties of nano silica are listed in Table1. From the X-ray diffraction patterns of silica nanoparticles it is clear that the silica is observed at a peak centred at 2 Theta (Θ) = 23 °, which reveals the amorphous nature of the silica nanoparticles.

c) Fine aggregate

Natural available clean sand with particles size smaller than 0.5 mm and specific gravity of 2.58g/cm³ and fineness modulus of 2.25 was used as fine aggregate.

d) Coarse aggregate

Clean Crushed dolomite of maximum size of 12 mm and specific gravity of 2.96g/cm³ was used as coarse aggregate.

e) Mixed aggregate

The aggregates for the mixtures consist of a combination of crushed dolomite and fine sand with percentage of 65% and 35% by weight respectively.

f) Superplasticizer

The used polycarboxylate has a polyethylene condensate defoamed based admixture (Glenium C315 SCC). The chemical and physical properties of the used polycarboxylate admixture are shown in Table-2.
Table-2. Polycarboxylate admixture chemical and physical characteristics.

<table>
<thead>
<tr>
<th>Appearance Alkali content (%)</th>
<th>Off white opaque liquid Less than or equal to 2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride content (%)</td>
<td>Less than or equal to 0.10</td>
</tr>
<tr>
<td>PH-value</td>
<td>6.5 ± 1</td>
</tr>
<tr>
<td>Specific gravity @ 20°C</td>
<td>1.095 ± 0.02 g/cm³</td>
</tr>
</tbody>
</table>

B. Mixture proportions

The experimental work will be divided into five parts. The first part investigated the effect of using 1%, 3% and 4.5% (by wt.) Nano silica as partial replacement of cement on tensile strength of concrete while the second and third parts investigated the permeability and bond strength of Nano silica concrete using the same percentages of Nano silica respectively. The fourth part studied the corrosion resistance of Nano silica concrete and the effect of corrosive environments on its bond strength with the same percentages of Nano silica. The final part presented micro structure analysis of the mixes through SEM. The mix proportions and slump results of Nano silica concrete mixes are shown in Table-3.

Table-3. Mixes components (kg) per 1 m³.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Cement</th>
<th>Aggregate</th>
<th>Water</th>
<th>S.p.</th>
<th>N.s.</th>
<th>Slump cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Coarse</td>
<td>Fine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M0</td>
<td>450</td>
<td>1109</td>
<td>597</td>
<td>192</td>
<td>2.7</td>
<td>0</td>
</tr>
<tr>
<td>M1</td>
<td>443.25</td>
<td>1109</td>
<td>597</td>
<td>192</td>
<td>2.7</td>
<td>6.75</td>
</tr>
<tr>
<td>M3</td>
<td>436.5</td>
<td>1109</td>
<td>597</td>
<td>192</td>
<td>2.7</td>
<td>13.5</td>
</tr>
<tr>
<td>M4</td>
<td>429.75</td>
<td>1109</td>
<td>597</td>
<td>192</td>
<td>2.7</td>
<td>20.25</td>
</tr>
</tbody>
</table>

C. Methods

The mixtures are to be prepared with nano silica replacement ratios of 1.5%, 3% and 4.5% by weight of cement in the mix. For helping in the dispersion of nano silica particles, indirect sonicaiton using bath sonicator is to be applied. A modern ultra-sonication bath was used in nano silica dispersion with different times according to nano silica percentage, 9 mins for 1.5%, 12mins for 3% and 15 mins for 4.5%. The water cement ratio for all mixtures is to be 0.43. The aggregates for the mixtures will consist of a combination of crushed dolomite and fine sand, with sand percentage of 35% by weight.

- All mixtures are to be prepared by mixing the coarse aggregates, fine aggregates and cement in a laboratory concrete drum mixer in dry condition for 1.5 mins.
- Then adding nano silica after being sonicated in water using bath sonicator and continues the mixing for another 1.5 mins.
- Finally, adding the super-plastisizer with 1 lit. of mixing water to the mix and continue the mixing for the last 1.5 mins.

a. Specimen preparation

All specimens were cast and compacted on a vibrating table in two and three layers respectively. Each layer was vibrated for 10 seconds. After that the specimens were de-molded after 24 hours and cured at room temperature in normal pure water until the day of testing.

b. Splitting tensile strength

Cylinders of 100mm diameter and 200 mm in height were cast for 7 and 28 days tensile strength test. The test was carried out with rate of 0.25 N/mm²/sec using the universal testing machine SHIMADZU 1000 KN.

c. Pull out test

Concrete cubes of (150 mm*150mm*150mm) were cast for pull out test of 16 mm in diameter steel rebars. Half of the length of the embedded part of the bar was de-bonded using polyvinyl chloride tubing to avoid yielding of steel reinforcement. It is recommended to cast the bars into concrete cubes providing a clear cover of 4.5 times bar diameter from the bar to the center of each side of the horizontal cross section. [3] to avoid splitting behavior. Figure-3 contains details of the pullout test specimens.
d. Water permeability
Cubes of (150 mm*150 mm*150) mm were cast for permeability test. Lime solution was an alternative curing regime for better expected results with nano silica concrete.

For steady-state flow, the coefficient of permeability $K$ is determined from Darcy’s expression:

$$K = \frac{(Q \times L \times \nu)}{\Delta H \times A}$$

$Q$: the rate of fluid flow.
$\nu$: the viscosity of the fluid (water) = $8.90 \times 10^{-4}$ Pa·s.
$\Delta H$: the pressure gradient = 30 Bar
$A$: the surface area. = $(15 \times 15)$ cm
$L$: the thickness of the solid. = 15 cm

e. Corrosion resistance
The specimens were immersed in a 3% NaCl solution by weight of water. The impressed current direction is to be adjusted such that the reinforcing steel served as the anode while a stainless steel rod was positioned in tank to act as a cathode. In order to establish different levels of reinforcement corrosion, accelerated corrosion time was extended over 1, 7 and 15 days. A schematic representation of the electrochemical test set up is shown in Figure-4. The used instrument for corrosion measurements is “SP-150” which was produced by BioLogic SAS instruments, France. Figure-5 shows corrosion lap test. Bond strength test was made to investigate the performance of nano silica reinforced concrete after being subjected to corrosive environments.

f. Scanning electron microscope (SEM)
The microstructures of different concrete samples were examined on a Quanta FEG 250 (FEI, USA) with Image processor Up to 4096 x 3536 pixels (~14 MP).

3. RESULTS AND DISCUSSIONS

a. Tensile strength
Tensile strength of nano silica concrete has two main behaviors: the first one occurs when the nano silica particles are well dispersed which lead to more dense and homogenous C-S-H gel, better interfacial transition zone (ITZ) between aggregates and higher tensile strength. While the second behavior occurs when the nano silica particles are agglomerated, it cannot easily disperse within the cement matrix, and due to their high surface energy, they become more agglomerated during mixing process and a weak area of empty spaces such as voids appears. Consequently, the structure formed in such conditions cannot be compacted and homogenous [4]. It was found that C-S-H gels from pozzolanic reaction of the agglomerates cannot function as binder and there even existed ITZ between the large reacted agglomerates and the bulk paste. [5]

From Figures (6 and 7) it can be observed that:
Generally, increasing nano silica percentage increased slightly the 7 days tensile strength. The 7 days tensile strength value reached 34 Kg/cm² by the addition
of 3% nano silica instead of 30.5 Kg/cm² for the control mix (containing 0% nano silica).

The gain in 7 days tensile strength reached (2, 12, and 6.5%) by the addition of (1.5, 3, and 4.5%) nano silica respectively.

The same behavior was noticed in the 28 days results. The 28 days tensile strength value reached 41.5 Kg/cm² by the addition of 3% nano silica instead of 37 Kg/cm² for the control mix (containing 0% nano silica). This can be attributed to the action of nano silica as nuclei for cement phases to promote cement hydration due to its pozzolanic reaction with CH increasing the production of C-S-H gel. C-S-H gel is the bonding material in concrete, so it has a significant positive effect on the cohesion between aggregates and the mechanical properties of concrete.

Early and late age tensile strengths were improved by increasing nano silica percentage up to 3% then a significant decrease in strength was observed by the addition of 4.5% nano silica. It is worth noting here that the (4.5%) mix is still higher in strength than the control mix. This can be attributed to the fact that more the number of silica nano particles the higher the capability of these particles to gather around each other in the matrix. This can be contributed to the agglomeration of nano particles in concrete matrix (without happening of any chemical reaction) and subsequently strength decrease; since the newly formed agglomerations are weak.

The gain in 28 days tensile strength reached (3.5, 12, and 3.5%) by the addition of (1.5, 3, and 4.5%) nano silica respectively.

**Figure-6.** 7 days tensile strength and the gain in 7 days tensile strength as compared to control mix 0% W.

**Figure-7.** 28 days tensile strength and the gain in 28 days tensile strength as compared to control mix 0% W.
b. Permeability

Permeability of cement paste is a fundamental property in view of the durability of concrete. It represents the ease with which water or other fluids can move through concrete, thereby transporting aggressive agents. From Figure-8 the following can be observed:

Generally, increasing nano silica percentage decreased significantly the permeability of concrete. The coefficient of permeability reached (5.26, 4.35, 3.66 and 2.55) e-11 cm/sec using 0, 1.5, 3 and 4.5% nano silica respectively.

By using 1.5, 3 and 4.5% nano silica, the percentage of passing flow reduced to be 82.5, 69.5 and 48.5% of these passing through control mixes (containing 0% nano silica) respectively. This can be attributed to the filling effect of nano silica due to its particles small size as compared with cement particles even if Nano silica particles were agglomerated. In addition to the above, nano silica reacts with CH to form more C-S-H gel which makes the matrix more dense and homogeneous and decreases the permeability of concrete.

Nano silica can absorb the Ca(OH)₂ crystals and reduce the size and the amount of the Ca(OH )₂ crystals, thus making the interfacial transition zone (ITZ) of aggregates and binding paste matrix denser. Nano silica particles can fill the voids of the C – S – H gel structure and act as nucleus to tightly bond with C – S – H gel particles, densifying the microstructure, increasing the tortuosity of the pore system and making binding paste matrix denser.[6]-[7]-[8]

The reduction in concrete permeability reached (17.5, 31.5, and 51.5%) by the addition of (1.5, 3, and 4.5%) nano silica respectively.

Figure-8. Percentage of passing flow as compared to mix 0%W.

c. Bond strength

The results reveal that splitting occurred for all specimens either those containing nano silica or the control mix. Figure-9

From Figures (10 and 11) the following can be observed:

The bond strength was slightly improved by the addition of nano silica 3%, and then the gain in bond strength began to decrease by using 4.5% nano silica.

The results are in a good agreement with the tensile strength behavior since the failure occurred with the rebars was splitting due to the weak confinement provided by the covering concrete around the rebars (less than 4.5 bar diameter).

The bond strength value reached 164.5 Kg/cm² by the addition of 3 % nano silica instead of 151 Kg/cm² for the control mix (containing 0% nano Silica).

The gain in bond strength reached (3.5, 9, and 0%) by the addition of (1.5, 3, and 4.5%) nano silica respectively.

The optimum percentage of nano silica to improve bond strength is 3% (gain 9% as compared to control mix 0%W) due to the improvement in the tensile strength of 3% nano silica mixes.

Figure-9. 16 mm rebars splitting behavior.
d. Effect of corrosive environment on Nano silica concrete

Corrosion of steel is the chemical or electrochemical reaction between the steel and its environment that leads to deterioration in the material and its properties. For steel bars embedded in concrete, corrosion results in the formation of rust which has (2-4) times the volume of the original steel volume and none of its mechanical properties. Corrosion also produces pits in the surface of steel bars which lead to reduce strength capacity due to the reduction in cross-sectional area. Figure-12. The Corrosion Process may be represented as [2]:

\[ 2\text{Fe} \rightarrow 2\text{Fe}^2+ + 4\text{e}^- \]

The electrons remain in the bar and flow to cathodes, where they react with oxygen and water in the concrete. This cathodic reaction is called a reduction reaction.

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^- \]

To maintain electrical neutrality, the ions of ferrous migrate through the concrete pore water to these cathodic sites where they react to form iron hydroxides (rust):

\[ 2\text{Fe}^{2+} + 4\text{OH}^- \rightarrow 2\text{Fe(OH)}_2 \]

This initial precipitated hydroxide tends to react further with oxygen to form higher oxides. The increases in volume due to the reaction products react with dissolved oxygen which leads to internal stress within the concrete which may cause cracking then spalling of the concrete cover.
e. Effect of corrosive environment on Nano silica concrete corrosion resistance

Figure-14 shows a sample of the output of the Sp-150 instrument which was used in corrosion measurements showing the relation between potential (mV,SCE) and current density (mA/cm²). The results from the figure was processed and analysed to get the corrosion rate and current density (Table-4.1) using Ec-Lap software.

6Figure-14. Output of the corrosion test (relation between potential and current density.

From Tables (4, 5 and 6) and Figures (14, 15, 16, 17, 18, 19 and 20) the following can be observed:

Corrosion resistance property of nano silica concrete is comparatively higher than ordinary concrete.

Generally, increasing nano silica percentage increased significantly the corrosion resistance of concrete. This can be attributed to the lower permeability of nano silica concrete as compared to the ordinary concrete which reduces the capillary action and prevent chlorides and water to penetrate the specimens and subsequently higher protection to rebars embedded in concrete. Figure (4.48) shows the relation between permeability and corrosion rate of concrete mixes.

In addition to the above the higher bond strength of nano silica concrete as compared to ordinary concrete has an effect on the corrosion resistance of the mix due to the formation of more C-S-H gel which lead to more dense and homogenous matrix protecting the steel rebars.

Corrosion rate of ordinary concrete was (2.648, 2.56 and 2.229) e-3 mm/year after 1, 7 and 15 days of testing respectively.

Adding 1.5% nano silica led to corrosion rate of (1.539, 1.033 and 0.651) e-3 mm/year after 1, 7 and 15 days of testing respectively.

Adding 3% nano silica led to corrosion rate of (1.161, 0.983 and 0.544) e-3 mm/year after 1, 7 and 15 days of testing respectively.

Adding 4.5% nano silica led to corrosion rate of (1.031, 0.824 and 0.483) e-3 mm/year after 1, 7 and 15 days of testing respectively.

Adding 1.5% nano silica reduced the corrosion rate to be only (58, 40 and 29 %) of control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.

Adding 3% nano silica reduced the corrosion rate to be only (44, 38, 25.5 %) as compared with the control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.

Adding 4.5% nano silica reduced the corrosion rate to be only (39, 32, 21.5 %) as compared with the control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.

The percentage of 4.5% nano silica was the optimum percentage to enhance the corrosion resistance.

High and low percentages of nano silica have nearly the same effect on corrosion resistance, in late age. This can be attributed to the formation of a rust protection layer around the rebars that slow the corrosion process and subsequently decrease the effect of nano silica on corrosion resistance.

Generally, increasing nano silica percentage increased significantly the critical time corresponding to a metal loss equals to 50 μm which is usually corresponding to the first concrete cracking due to the corrosion of reinforcement.

Adding 1.5, 3 and 4.5% nano silica in concrete increased the critical time to be (77, 92 and 103.5) years respectively as compared to control mix (22.5 years).

Adding 1.5, 3 and 4.5% nano silica in concrete increased the critical time to be (32, 33.5 and 35) years respectively as compared to control mix (19.5 years) considering concrete deterioration.
Table-4. Corrosion rate and current density of concrete mixes.

<table>
<thead>
<tr>
<th>Days</th>
<th>Nano silica percentage</th>
<th>$I_{corr}$ (µA/cm²)*</th>
<th>Corrosion rate (mm/year) e-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>0%</td>
<td>9.051</td>
<td>2.648</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>5.261</td>
<td>1.539</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>3.970</td>
<td>1.161</td>
</tr>
<tr>
<td></td>
<td>4.5%</td>
<td>3.527</td>
<td>1.031</td>
</tr>
<tr>
<td>7 days</td>
<td>0%</td>
<td>8.750</td>
<td>2.56</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>3.533</td>
<td>1.033</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>3.361</td>
<td>0.983</td>
</tr>
<tr>
<td></td>
<td>4.5%</td>
<td>2.819</td>
<td>0.824</td>
</tr>
<tr>
<td>15 days</td>
<td>0%</td>
<td>7.621</td>
<td>2.229</td>
</tr>
<tr>
<td></td>
<td>1.5%</td>
<td>2.227</td>
<td>0.651</td>
</tr>
<tr>
<td></td>
<td>3%</td>
<td>1.860</td>
<td>0.544</td>
</tr>
<tr>
<td></td>
<td>4.5%</td>
<td>1.652</td>
<td>0.483</td>
</tr>
</tbody>
</table>

Table-5. Corrosion rate classification and critical time of corrosion [1].

<table>
<thead>
<tr>
<th>Corrosion rate</th>
<th>Value (mm/year)</th>
<th>Critical time $tc$ (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negligible</td>
<td>&lt;0.1</td>
<td>$tc&gt;50$</td>
</tr>
<tr>
<td>Low</td>
<td>0.1&lt; Value &lt;10</td>
<td>50&lt;$tc&lt;5</td>
</tr>
<tr>
<td>High</td>
<td>&gt;10</td>
<td>$tc&lt;5$</td>
</tr>
</tbody>
</table>

Critical time $tc$ is the time corresponding to a metal loss equal to 50 µm which usually corresponding to the first concrete cracking due to the corrosion of reinforcement.

Table-6. Critical time of corrosion $tc$ of concrete mixes.

<table>
<thead>
<tr>
<th>Nano silica percentage</th>
<th>Actual time to reach 50 µm metal loss (years)</th>
<th>Critical time $tc$ (years)(considering concrete deterioration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>22.5</td>
<td>19.5</td>
</tr>
<tr>
<td>1.5%</td>
<td>77</td>
<td>32</td>
</tr>
<tr>
<td>3%</td>
<td>92</td>
<td>33.5</td>
</tr>
<tr>
<td>4.5%</td>
<td>103.5</td>
<td>35</td>
</tr>
</tbody>
</table>

It is worth noting that $tc$ considering concrete deterioration was calculated from a logarithmic relation between corrosion rate and critical time.
Figure-15. Corrosion rate of all mixes after 1, 7 and 15 days of corrosion.

Figure-16. Effect of time on corrosion rate.

Figure-17. Effect of nano silica on corrosion rate after 1 day of corrosion as compared to control mix 0%W.
Figure-18. Effect of nano silica on corrosion rate after 7 days of corrosion as compared to control mix 0%W.

Figure-19. Effect of nano silica on corrosion rate after 15 days of corrosion as compared to control mix 0%W.

Figure-20. Relation between corrosion resistance and permeability of concrete.
Effect of corrosion on concrete-rebars bond strength

From Figures (21, 22 and 23) the following can be observed:

Generally, increasing nano silica percentage increased significantly the residual bond strength of concrete after being subjected to corrosive environment due to the improvement in the corrosion resistance of concrete by the addition of nano silica in addition to the relatively high bond strength of nano silica concrete as compared to ordinary concrete.

After being subjected to corrosive environment, the behavior of pullout was observed for all mixes instead of splitting behavior.

For ordinary concrete, the residual bond strength was 41 kg/cm² (27% of natural environment bond strength of 0% mix).

By the addition of 1.5% nano silica, the residual bond strength was 80 kg/cm² (51% of natural environment bond strength of 1.5% mix).

By the addition of 3% nano silica, the residual bond strength was 98 kg/cm² (60% of natural environment bond strength of 3% mix).

By the addition of 4.5% nano silica, the residual bond strength was 119 kg/cm² (78% of natural environment bond strength of 4.5% mix).

Adding 1.5, 3 and 4.5% nano silica in concrete increase the residual bond strength to be (53, 65 and 79)% as compared to control mix (0%W) respectively.

By using 4.5% nano silica, the residual bond strength was 79% while the control mix was only 27% of control mixes.
Figure-23. Effect of nano silica on bond strength after being subjected to corrosive environment as compared to natural environment bond strength.

Figure-24. Comparison between bond strength after being subjected to corrosive environment and natural environment bond strength of control mix 0% W.

g. Scanning electron microscopy

Scanning Electron Microscope images were taken to study the micro-structure for the materials. The SEM images are shown in Figures (23 to 27).

As for the SEM plates, the morphology structure in control samples, when compared with nano silica systems, is in agreement with the results.

Calcium silicate hydrate plates as well as calcium hydroxide crystals and Aft needles were clearly identifiable in the control specimen as well as the porous structure of paste. Figure-23.

While for low percentages nano silica (1.5%, and 3%) specimens, the calcium silicate hydrate plates were clearly dominating with a well compacted structure, as for the high volume nano silica (4.5%), calcium silicate hydrate plates can also be clearly found but with some agglomerated nano silica surrounding the hydration products. Figures (24, 25 and 27).

As a conclusion nano silica presence contributed to producing higher levels of calcium silicate hydrate [9]. As the nano silica’s high reactivity acted as a nucleating point [10] to bind the hydration products together [11]. This phenomenon may explain the high strength and performance of the specimens containing nano silica.

Nano Silica can absorb the calcium hydroxide crystals and reduce the size and amount of the Ca(OH)₂ crystals, thus making the interfacial transition zone of aggregates and denser. Nano silica particles can fill the voids of the C–S–H gel structure and act as nucleus to tightly bond with C–S–H gel particles, making binding paste matrix denser, durability and long-term mechanical properties of concrete are expected to be increased.

Micrograph of the nano silica concretes, which reached the highest strength, revealed that these samples have an interfacial transition zone (ITZ) denser than those on the control sample. The interfacial transition zone is denser because nano silica particles can fill the space...
between cement grains (Figure-26), so they can improve the behavior in two different ways: (i) due to packing effect, and (ii) due to reacting with Ca(OH)\textsubscript{2} to form more C–S–H. The observations from the SEM images showed also that the nanoparticles were not only acting as a filler, but also as an activator to promote hydration process and to enhance the cement paste microstructure if the nanoparticles were good and uniformly dispersed. The micrograph also showed that the microstructure of concrete with nano-silica was more homogeneous, uniform and compacted than that of the normal concrete.

The performed SEM examination verified the mechanism discussed in results and nano-silica particles were found to influence the hydration behaviour and lead to the differences in the microstructure of the hardened paste. The microstructure of the mixture incorporating nano silica revealed a dense, compact formation of hydration products and a reduced number of Ca(OH)\textsubscript{2} crystals.

Through SEM observation, a clear microstructure improvement of the hardened cement paste and the ITZ in concrete by adding nano-silica can be recorded regardless of its agglomerate size. It was revealed that C–S–H gels from pozzolanic reaction of the agglomerates cannot function as binder. The cement hydration gels did not penetrate into the pozzolanic gels nano-silica reduced the porosity of hardened concrete because of the super pozzolanic performance and the production of higher amounts of C–S–H gel. Moreover, the microstructure was considerably enhanced due to the micro and nano-filling effects. Portlandite crystals were reduced in size and quantity as a consequence of the pozzolanic reaction and the growth of crystal control by nano-silica. The agglomerated nano silica appearing in the micrographs of the 3% nano silica mix explains the filling performance of the nano silica. (Figure-26).

For 3% nano silica lime solution cured mixes the SEM results showed the best compacted mixes and a higher amount of the C-S-H than those found in the other mixes. This confirms the gain in tensile strength that was reported earlier by using 3% nanosilica Figure-25.
4. CONCLUSIONS

1. Tensile strength
   - Generally, late age tensile strength was improved by increasing nano silica percentage up to 3% then a significant decrease in strength was observed by the addition of 4.5% nano silica. It is worth noting here that the (4.5%) mix is still higher in strength than the control mix.
   - Optimum percentage of nano to improve late age tensile strength was 3% (41.5 kg/cm²) with gain equals to 12% as compared with control water mix 0%W (37 kg/cm²).

2. Permeability
   - The optimum percentage of nano silica to reduce the permeability of concrete was 4.5%. The reduction in permeability reached 51.5% as compared to control mix (0%W).
   - The filling effect of nano silica was the main reason of the reduction in nano silica concrete permeability using high percentages of nano silica, while the slight reduction in permeability using low percentages of nano silica was mainly because of the formation of more C-S-H gel.

3. Bond strength
   - Bond strength of 16 mm rebars has the same trend of the splitting tensile strength; the dominant behavior was splitting for all mixes.
   - The optimum percentage of Nano silica to improve bond strength of using 16mm rebars is 3% (gain 9% as compared to control mix 0%W) due to improvement in the tensile strength of 3% Nano silica mixes.

4. Corrosion resistance
   - Corrosion resistance property of the Nano silica added concrete is comparatively higher than ordinary concrete.
   - Generally, increasing Nano Silica percentage increased significantly the corrosion resistance of concrete.
   - Adding 1.5% Nano silica reduced the corrosion rate to be only (58, 40 and 29 %) of control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.
   - Adding 3% Nano silica reduced the corrosion rate to be only (44, 38, 25.5 %) as compared with the control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.
   - Adding 4.5% Nano silica reduced the corrosion rate to be only (39, 32, 21.5 %) as compared with the control mixes 0%W corrosion rate after 1, 7, and 15 days of testing respectively.
   - High and low percentages of Nano silica have nearly the same effect on corrosion resistance of concrete in late age.
   - Generally, increasing Nano Silica percentage increased significantly the critical time corresponding to a metal loss equal to 50 μm which usually corresponding to the first concrete cracking due to the corrosion of reinforcement.
   - Adding 1.5, 3 and 4.5% Nano silica in concrete increased the critical time to be (47.5, 48 and 48.5)years respectively as compared to control mix (40 years).
   - Generally, increasing Nano Silica percentage increased significantly the residual bond strength of concrete after being subjected to corrosive environment.
   - After being subjected to corrosive environment, the behavior of pullout was observed for all mixes instead of splitting behavior.
   - Adding 1.5, 3 and 4.5% Nano silica in concrete increase the residual bond strength to be (53,65 and 79)% as compared to control mix (0%W) respectively
   - By using 4.5% Nano silica, the residual bond strength was 79% while the control mix was only 27% of control mixes.
   - From the conducted study the Nano silica proved to be a significant pore blocker material.

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