



## **Increasing of the Cement Strength and Corrosion Resistance of Rebar Inside it using Silica Nanoparticles**

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### **Abstract**

In this work, silica nanoparticles were added to the mortar with one percent by weight of cement. To investigate the effect of these nanoparticles on the strength of cement, 7-day and 28-day strength according to ASTM C109 standard was obtained and compared with the results of the control sample. The results showed that these nanoparticles increase the compressive and bending strengths. To investigate this nanoparticles effect on the corrosion resistance of the rebar inside the cement, polarization and EIS tests were performed in 3.5% salt solution. The results of the polarization test showed that the sample with silicon dioxide nanoparticles has more corrosion potential and less corrosion current, which indicates less corrosion rate and less corrosion tendency of this sample compared to the control sample. EIS analysis showed that samples with the presence of silicon dioxide nanoparticles have higher electrical impedance than the other. By simulating the equivalent circuit, the reason for the higher electrical impedance of the mortar in the presence of SiO<sub>2</sub> nanoparticles was investigated. The results showed that the reason for the increase in corrosion resistance and electrical impedance is the increase in electrical resistance, increase in ion diffusion and the decrease in capacitance of mortar.

**Keywords:** Cement, Compressive strength, bending strength, Electrical impedance, Corrosion resistance.

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## **Introduction**

Cement is one of the widely used materials in the construction industry. The very small holes in the cement play a key role in the quality of this product. Cement-based materials have poor mechanical properties and are permeable to chemicals and water, which reduce the strength and durability of this product. The cement industry also increases carbon dioxide in the world and 5 or 6% of the world's carbon dioxide is related to this industry. Using of nanotechnology into the cement industry, significant changes occurred in this product and their quality was greatly improved [1-6]. The results show that nanotechnology reduces the propagation of carbon dioxide [7], and increases the resistance of cement to cracking [8]. Also, the results show that when small amounts of nanoparticles are evenly dispersed in the cement paste, in addition to filling pores and reducing the spread of water, they act as cores to bond tightly to the hydrate of the cement and expand the hydration of the cement. These nanoparticles also prevent the growth of crystals such as  $\text{Ca}(\text{OH})_2$  by being among the hydrated products, and these fine crystals make the cement stronger [9].

In recent years, the use of nanoparticles in improving the properties of concrete and cement has greatly increased. Many researchers have investigated the effect of various nanoparticles such as carbon nanotubes [10], ZnO [11-13],  $\text{Fe}_2\text{O}_3$  [14,15],  $\text{TiO}_2$  [16,17],  $\text{Al}_2\text{O}_3$  [18,19], CuO [20],  $\text{ZrO}_2$  [21],  $\text{SiO}_2$  [22-38] and  $\text{CaCO}_3$  [39] were investigated in the properties of cement mortar. Meanwhile, the use of nanosilica is more than other nanoparticles. Studies have shown that nanosilica reacts much faster with calcium hydroxide and very small amounts of this nano particle have a very high pozzolanic effect. In other words, the use of nanosilica in cement not only improves the structure due to the filling of pores but also makes the pozzolanic reactions more active. This nanoparticle participates in the hydration process by forming C-H-S by reacting with  $\text{Ca}(\text{OH})_2$  [40-42].

One of the uses of concrete is to build offshore structures. Therefore, corrosion of rebars inside these concretes by chlorine ions of salt water is also one of the problems that should be considered. Because matter is corroded when it loses electron, the tendency and speed of electron loss must be reduced to corrosion protection of the material. For this purpose, the electrical impedance must be increased [43, 44]. Given that the electrical impedance is an imaginary quantity and depends on elements such as capacitance, electrical resistance, etc., to increase the electrical impedance of the mortar, its electrical resistance must be increased. In addition, its capacitance must be reduced.

The use of oxide nanoparticles can be useful to increase electrical resistance. The smaller the dielectric constant of these nanoparticles, the smaller the capacitance of the mortar, and thus the higher the electrical impedance and the better the corrosion protection. Because  $\text{SiO}_2$  nanoparticles have a suitable dielectric constant for this purpose, in this work, by adding  $\text{SiO}_2$  nanoparticles to

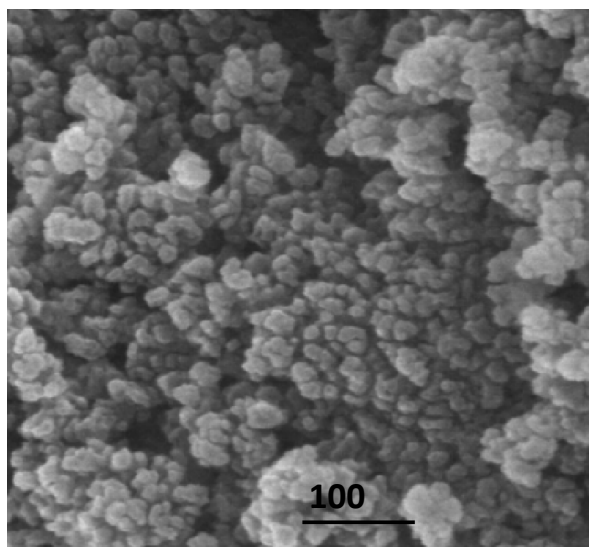
cement, its effect on the strength of cement and in the protection of corrosion of the rebar inside it has been investigated. In this paper, the effect of SiO<sub>2</sub> nanoparticles in addition to the strength of concrete, in the protection of corrosion of the rebar inside it has been investigated.

### Experimental

To investigate the effect of SiO<sub>2</sub> nanoparticles on the strength of cement and protection against corrosion of the inside rebar, the nanoparticles were purchased with the characterization given in Table 1 and added to the cement mortar with 1% of cement weight. Figure 1 shows the SEM images of SiO<sub>2</sub> nanoparticles used in this work. It is clear from the figure that the average diameter of nanoparticles is about 40 nanometers.

**Table 1.** Chemical composition of SiO<sub>2</sub> nano particle used in this work.

| Element (wt %) |        |         |         |                  |
|----------------|--------|---------|---------|------------------|
| Fe             | Na     | Ca      | Ti      | SiO <sub>2</sub> |
| >0.2ppm        | >63ppm | >0.6ppm | >100ppm | <99              |



**Figure 1.** SEM image of SiO<sub>2</sub> nanoparticles used in this work.

To prepare this mortar, 450 gr of cement with the characterization given in Table 2, 1350 gr of standard sand (ASTM C778), 4.5 gr of SiO<sub>2</sub> Nanoparticle and 1250 ml of distilled water were used. After preparing the mortar, it was poured into a standard three-part mold, the dimensions of each part of which were 40 × 40 × 160 mm.

**Table 2.** Chemical composition of Portland cement II (wt %, determined using X-ray fluorescence).

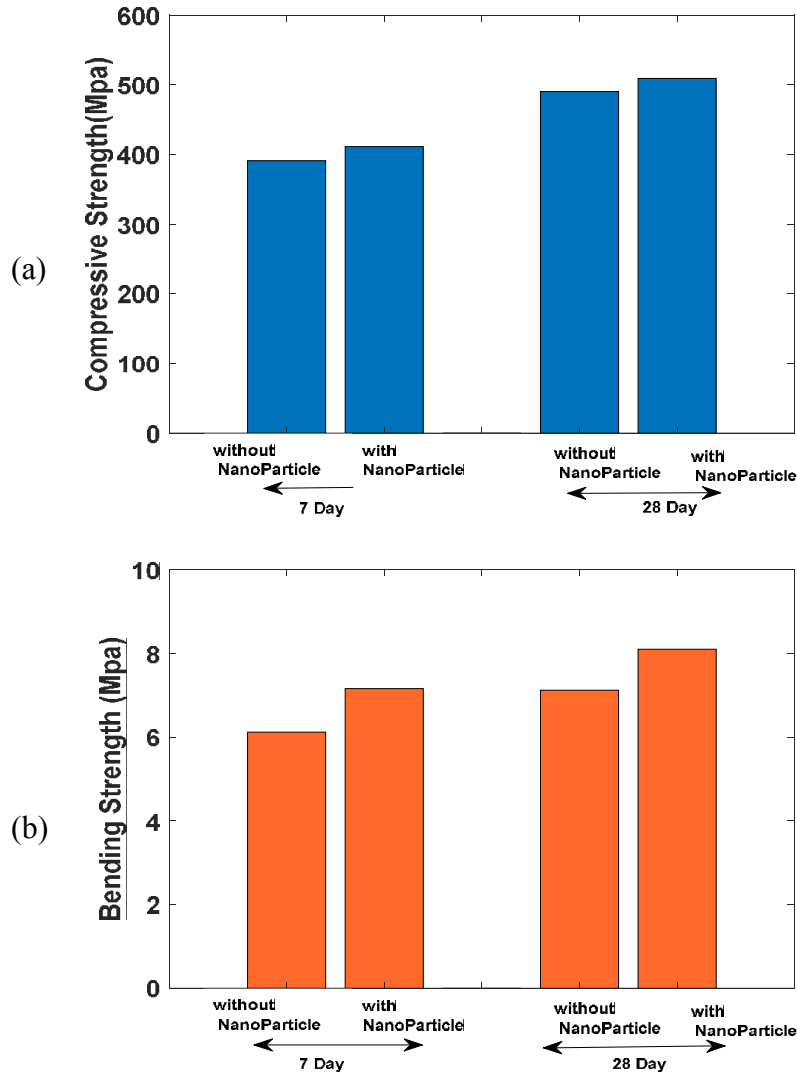
| Element (wt %)   |     |                   |                  |                 |       |                                |                                |      |
|------------------|-----|-------------------|------------------|-----------------|-------|--------------------------------|--------------------------------|------|
| SiO <sub>2</sub> | MgO | Na <sub>2</sub> O | K <sub>2</sub> O | SO <sub>3</sub> | CaO   | Fe <sub>2</sub> O <sub>3</sub> | Al <sub>2</sub> O <sub>3</sub> | LOSS |
| 21.9             | 1.5 | 0.3               | 0.5              | 1.5             | 65.00 | 4.20                           | 4.00                           | 1.1  |

Inside the mortar of one of these three sections, a cylindrical rebar with the specifications given in Table 3 was placed. This rebar had a diameter of 1 cm and a length of 10 cm, which was bent in an L shape and was placed inside the rebar so that it is 8 cm inside the mortar and 2 cm bent outside the mortar. These samples were considered for measuring corrosion resistance and the other two samples were measured for bending and compressive strengths of 7 and 28 days. After smoothing the surface, the samples were placed in a hammer machine to be denser. Then it was placed in a humidity chamber for 24 hours and finally the 7-day and 28-day compressive and bending strength of the samples were measured according to ASTM C109 standard. To measure the corrosion resistance of rebar in mortar, after 28 days of sample with rebar, in lime water, polarization and EIS tests in 3.5% salt solution were performed using a potential acetate device. The sample was placed in solution so that only two centimeters of rebar were out of solution. These two centimeters of rebar were considered for connection. Polarization measurements were performed starting with potential from -4 V to 4 V with a speed of 50mV/s and EIS test was measured in the frequency range of 0.001 to 1000 Hz and with a voltage amplitude of 0.01V. Before measurement, the samples were immersed in the solution for half an hour to stabilize the ocp potential. All of these steps were performed three times to maintain reliability. Once again, the same thing was done without the presence of nanoparticles so that the results could be compared with the presence and without the presence of nanoparticles.

## Results and discussion

### *Compressive and bending strength*

Figure 2a shows the results of 7-day and 28-day compressive strength measurements. Figure 2b shows the 7-day and 28-day bending strength with and without the nanoparticles in the cement mortar. It is clear from the results that by adding one percent of SiO<sub>2</sub> nanoparticles to the cement mortar, the bending and compressive strengths are improved. This is due to the filling of cement pores with SiO<sub>2</sub> nanoparticles as well as increasing the hydration reaction. However, the most important purpose of this paper is to investigate the effect of nanoparticles on increasing the corrosion resistance of rebar in cement, which we will discuss below.



**Figure 2.** 7-day and 28-day a) compressive strength and b) bending strength of mortar with and without SiO<sub>2</sub> nanoparticles.

### Electrochemical analyses

Figure 3 shows the result of the polarization test. It is clear from the results that the sample with SiO<sub>2</sub> nanoparticles has more corrosion potential and less corrosion current than the control sample. The corrosion current and corrosion potential of this sample and the control sample are listed in Table 4. Considering that the corrosion potential and corrosion current indicate the corrosion tendency and corrosion speed, respectively, it can be concluded that by adding the nanoparticles to the cement, the corrosion tendency and corrosion speed are reduced.

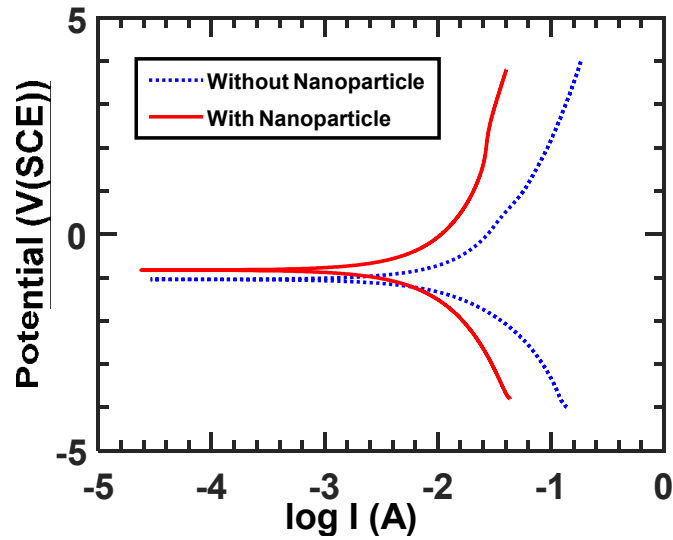


Figure 3. Polarization test results of samples in the 3.5% NaCl solution.

Table 4. Polarization test results.

|                     | Without Nano Particle  | With Nano Particle    |
|---------------------|------------------------|-----------------------|
| $I_{corrosion} (A)$ | $8 \times 10^{-3}$     | $4 \times 10^{-3}$    |
| $V_{corrosion} (V)$ | $-1046 \times 10^{-3}$ | $-829 \times 10^{-4}$ |

The results of the EIS analysis shown in Figure 4 indicate that the electrical impedance of the rebar in the cement containing nanoparticles is higher than the electrical impedance of the control sample. The high electrical impedance of this sample indicates that the rate of electron loss of the rebar in a mortar containing nanoparticles is slower than that of another sample. The sample is corroded by losing electrons, and the faster the electron loss, the more the sample is corroded. As a result, to increase the corrosion resistance, the rate of electron loss must be reduced, or the electrical impedance must be increased. The results show that by adding nanoparticles to the cement mortar, the electrical impedance can be greatly increased and thus corrosion can be prevented. This can be very useful for offshore structures.

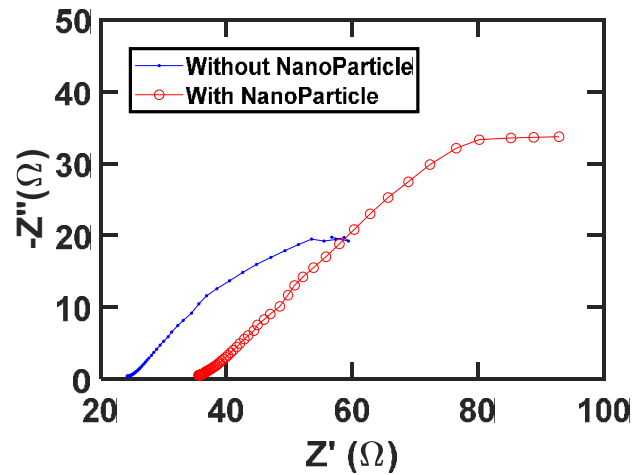


Figure 4. EIS test results of samples in the 3.5% NaCl solution.

By simulating the equivalent circuit, the reason for the increase in electrical impedance of this sample was investigated. The equivalent circuit obtained is shown in Figure 5.

Figure 5. Equivalent circuit of mortar with and without SiO<sub>2</sub> nanoparticles.

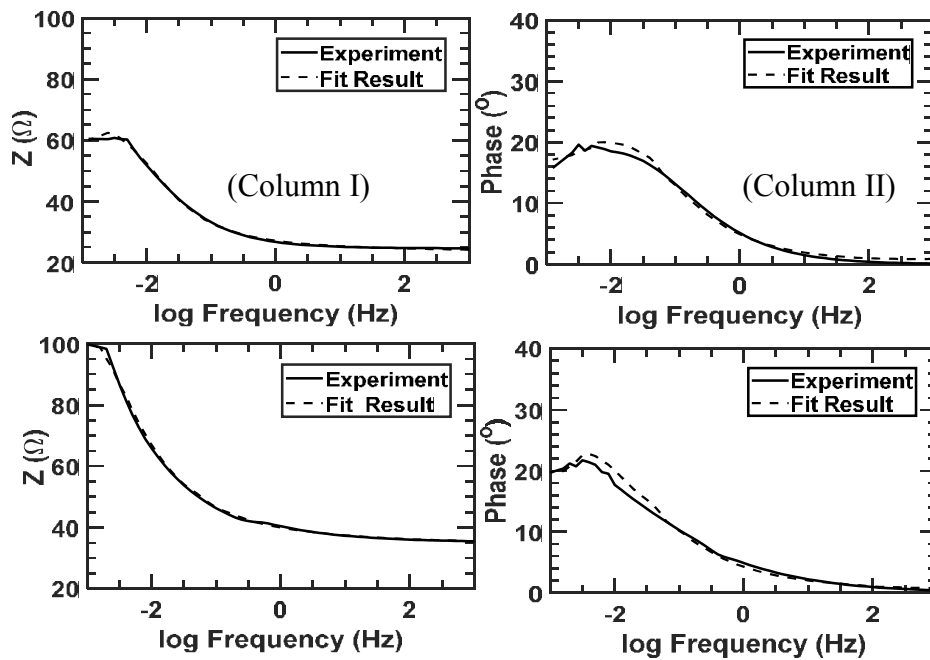


Figure 6. Bod (column I) and phase (column II) diagrams of mortar with and without SiO<sub>2</sub> nanoparticles. Experiment: solid line and simulation: dashed line.

The bod-phase diagrams of the samples, which show the best fit between experimental and simulation, are shown in Figure 6. In the equivalent circuit, R1 is the ambient resistance and Ws is the short Warburg impedance that represents the finite diffusion of ions. In this circuit, C is the capacitance related to the mortar and is shown by the following equation [43]:

$$C = \varepsilon \frac{A}{d} \quad (1)$$

Where d is the distance between the rebar to the corrosive solution A is the area exposed to the solution and  $\varepsilon$  is the dielectric constant of the mortar. Due to the heterogeneity and roughness of the surface and being far from the ideal state, the capacitor is displayed with CPE. The quantity  $\alpha$  indicates how far it is from the ideal capacitor. In this circuit, R represents the electrical resistance of the mortar. The results of this simulation are given in Table 5. The results show that the addition of SiO<sub>2</sub> nanoparticles to cement increases the electrical resistance of the mortar. It is also clear from the results that because SiO<sub>2</sub> has a small dielectric constant, adding this nano particle to the cement reduces the capacitance. Increasing the electrical resistance along with decreasing the capacitance increases the electrical impedance of the mortar. The results also show that by adding this nanoparticle to cement mortar, the diffusion of ions at high frequencies also increases, which further increases the electrical impedance.

**Table 5.** Equivalent circuit quantities.

|               | Without Nanoparticle  | With Nanoparticle  |
|---------------|-----------------------|--------------------|
| $R_1(\Omega)$ | 25                    | 35                 |
| $W - R$       | 121                   | 647                |
| $W - T$       | 324                   | 3727               |
| $W - P$       | 0.43                  | 0.39               |
| $CPE(F)$      | $1071 \times 10^{-4}$ | $5 \times 10^{-4}$ |
| $\alpha$      | 0.9                   | 0.9                |
| $R_2(\Omega)$ | 54                    | 97                 |

Considering that the corrosion resistance is obtained from the difference between infinite frequency impedance and zero frequency impedance, it can be concluded that the corrosion resistance of rebar inside the mortar with SiO<sub>2</sub> particles is higher than the corrosion resistance of the control sample.



## Conclusions

In this work, to increase the cement strength and to increase the corrosion resistance of the rebar inside the cement, SiO<sub>2</sub>nanoparticles were added to the mortar with one percent by weight of cement. Investigation of bending and compressive strengths of cement showed that the mortar with silica nanoparticles has more strength than the control sample. The cause was attributed to the porosity filling by these nanoparticles investigation of corrosion tests which showed that the addition of silica nanoparticles to the mortar reduces the corrosion speed and corrosion tendency of the rebar inside the mortar. The results also indicated that the reason for the increase in corrosion resistance is the increase in the electrical impedance of the mortar. By equivalent circuit simulation, it was found that the reason for increasing the impedance of the mortar and consequently increasing the corrosion resistance of the rebar inside it is to increase the electrical resistance, increase the ion diffusion and decrease the capacitance of the mortar.

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