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Increasing the strength of cement and improving the corrosion resistance of rebar inside it using Fe_2O_3 nanoparticles

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Abstract

In this work, Fe_2O_3 nanoparticles were used to increase the cement strength and to increase the corrosion resistance of the rebar inside it. For this, the nanoparticles were added to the cement mortar with one percent of the cement weight. According to the ASTMC109 standard, bending and compressive strengths of 7 days and 28 days were obtained and compared with the control sample. The results showed that by adding this nanoparticle to cement, the bending and compressive strengths of cement mortar have been increased. To investigate the corrosion resistance of the rebar inside the cement mortar, polarization and Electrochemical Impedance Spectroscopy (EIS)tests in 3.5% sodium chloride solution were measured and evaluated. The results of the polarization test showed that by adding this nanoparticle to cement mortar, the corrosion current decreases and the corrosion potential increases. EIS measurements confirmed the increased corrosion resistance of rebar inside the cement. Finally, the reason for increasing the corrosion resistance is investigated by equivalent circuit simulation.

Keywords: Nano Particle, Fe_2O_3, Cement, Impedance, EIS, Polarization.

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Introduction

Concrete is a stone-like material that is obtained by mixing cement, sand, water, and other additives. The chemical interaction between water and cement causes the aggregates to integrate and adhere to each other. These aggregates form the main structure of the concrete and withstand the force on the concrete. The water in this mixture causes a chemical reaction in the cement which hardens the concrete mixture after a period of about twenty-eight days and reaches the final strength of the concrete.

Today, the use of concrete in buildings has increased more than ever because concrete buildings have advantages over metal buildings, such as greater resistance to fire and atmospheric factors (corrosion), easy to prepare due to the abundance of composite materials, and insulation against heat and sound. These reasons have led the increasing development of concrete buildings.

One of the major disadvantages of concrete buildings is their very high weights which are directly related to the amount of earthquake damages. Therefore, providing lightweight concrete can solve the problems. In other words, by using lightweight concrete, the destruction of the building by the earthquake is greatly reduced. However, the low strength of lightweight concrete has been an important factor in limiting the scope of application of this type of concrete and taking advantage of it. Therefore, increasing the strength of concrete is very important. Researchers have shown that the use of nanoparticles in the structure of concrete increases the compressive and bending strength of concrete. This has led to an increase in the use of nanoparticles in improving the properties of concrete and cement in recent years. Researchers have examined the effects of various nanoparticles such as carbon nanotubes [1], zinc oxide [2-4], Iron Oxide [5,6], titanium dioxide [7,8], alumina [9,10], copper oxide [11] Zirconium oxide [12], silica [13-29] and $CaCO_3$ [30] on the strength of cement.

In addition to use in urban buildings, one of the uses of concrete is the construction of offshore structures. In the sea environment, many structures such as bridge piers, breakwaters, submarine tunnels, etc. are made of concrete. The concrete used in these cases must be of high strength concrete, otherwise the structure will be destroyed after a while. Corrosion of the rebar inside concrete is one of the main causes of destruction of concrete structures in the sea environment. Corrosion of the rebars inside concrete is often not uniform. Corrosion can usually be seen at both ends of a concrete structure or in the middle of concrete. Over time, this corrosion increases and eventually leads to the collapse of the structure. In general, corrosion makes concrete less resistant to stresses.

Most corrosions are in environments where structures are in contact with corrosion agents. The three main causes of corrosion are oxygen, moisture, and chlorides. Therefore, the use of concrete that protects the rebar inside it is also a basic need. Given that when matter loses its electrons, to prevent corrosion, the tendency and speed of electron loss must be reduced, which means an increase in electrical impedance [31,32].

Given that electrical impedance is quantitative, it is imaginary and depends on elements such as capacitance, electrical resistance, etc. To increase the electrical impedance of the mortar, its electrical resistance must increase and the capacitance must decrease. 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 iron oxide nanoparticles are materials with small dielectric constant, in this work, the effect of adding these nanoparticles to the strength of cement and concrete impedance has been investigated.

Experimental

In this work, Fe_2O_3 nanorods were purchased with the specifications given in Table 1 and mixed with one percent by weight of cement. The XRD spectrum of these nanoparticles is given in Figure 1. This figure shows that the diffraction pattern has 13 peaks, all of which represent the α-Fe_2O_3 phase (JCPDS: 33-0664), and the Fe_2O_3 nanoparticles used in this work have a crystalline structure. TEM images of these nanoparticles are shown in Figure 2. This figure shows that these nanorods have an average length of 200 nanometers and an average diameter of 70 nanometers.

Table1. Specifications of Fe_2O_3 nanoparticles used in this work.

Sample	**powder**
Morphology	Nano Rod
Purity (%)	>0.99
Nano particle Size (nm)	Length:100-300 Diamete:50-80
Structure	Crystalline

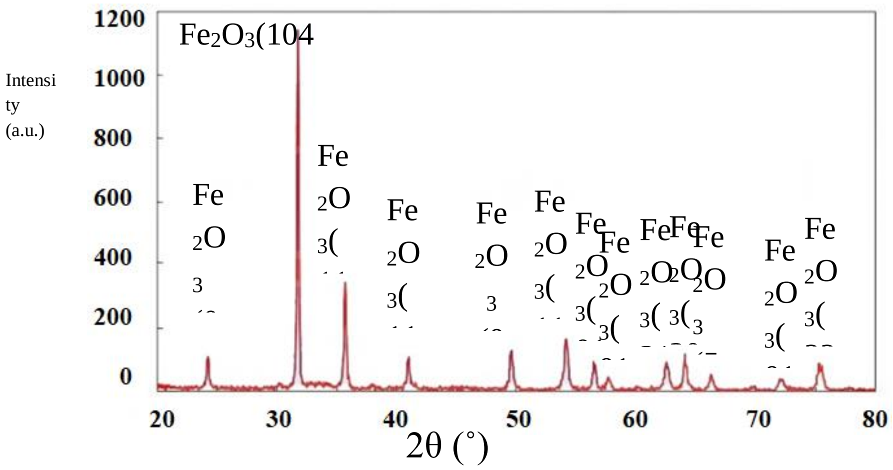

Figure 1. XRD pattern of Fe_2O_3 nanoparticles.

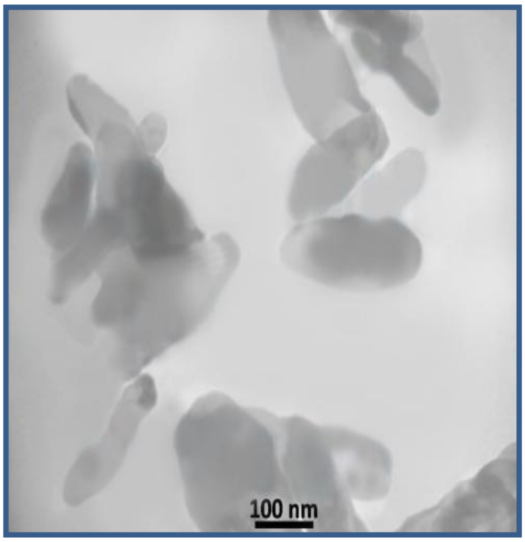

Figure 2. TEM of Fe_2O_3 nanoparticles.

To prepare the mortar, 4.5 g of these nanoparticles were mixed with 450 g of Portland cement type 2. The resulting mixture was mixed with 1350 g of standard sand (ASTM C778) and 1250 ml of distilled water. The composition of used cement is given in Table 2.

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

SiO2	MgO	Na2O	K2O	SO3	CaO	Fe2O3	Al2O3	LOSS
21.۹	۱.۵	0.۳	۰,۵	۱,۵	6۵.۰۰	۴.۲۰	۴.00	۱,۱

The prepared mortar was poured in a three-part standard mold, the dimensions of each part of which were 40 × 40 ×160 mm, in two stages. Inside the mortar of one of these three sections, a cylindrical rebar with the specifications given in Table 3 was placed. The rebar was 1 cm in diameter and 10 cm long, which was bent in an L shape and placed inside the mortar so that it was 8 cm inside the mortar and 2 cm bent out of the mortar. This sample was used to measure corrosion resistance and the other two samples were used to measure flexural and compressive strengths of 7 and 28 days.

After smoothing the surface, the samples were placed in a hammer machine to expel the air inside and make the mortar denser. All three samples were then placed in a humidity chamber for 24 hours. Then the samples were transferred to lime water and finally their 7-day and 28-day compressive and flexural strengths were measured according to C109 standard.

Table 3. Chemical composition of used rebar.

Si	Mn	C	P	S	N
0.65	1.66	0.4	0.05	0.5	-

To measure the corrosion resistance of rebar inside the mortar, after 28 days of soaking the rebar sample in lime water, polarization, and EIS tests were performed in 3.5% salt using the potentiodynamic method with a potentiostat coupled to PC (Ivium, De Zaale 11, 5612 AJ Eindhoven, Netherlands). In order to carry out this analysis, the sample was placed in the solution so that only two centimeters of the rebar that was bent for connection were out. Potentiodynamic polarization measurements were performed by sweeping the potential from -4 V to 4 V with a scan rate of 50mV/s. Before starting the test, the samples were immersed in the solution for 30 min so that the open circuit potential (OCP) was stabilized.

Electrochemical impedance spectroscopy (EIS) was performed in the frequency range of 1000Hz to 0.001 Hz with a voltage amplitude of 0.01 volts. To ensure all these steps were performed three times, and the results were compared with the results of the control sample without nanoparticles. Figure 3 shows how the sample is placed in sodium chloride solution for polarization and EIS tests.

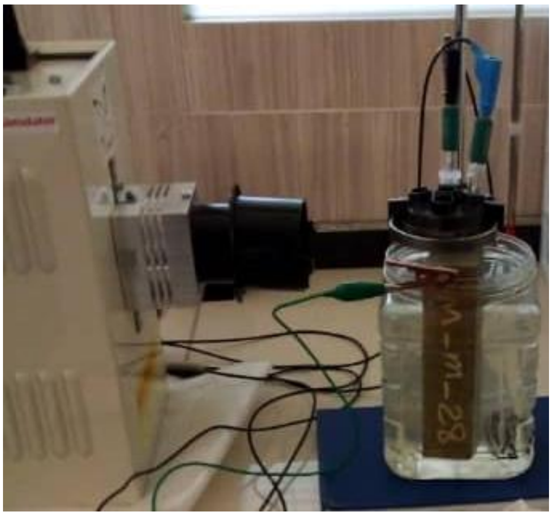

Figure 3. Placing the sample in sodium chloride solution for polarization and EIS tests.

Results and discussion

Strength results

Figures 4a and b show the results of compressive and flexural strengths, respectively. In these figures, it is clear that the addition of this nanoparticle to the cement mortar increases the flexural and compressive strengths of 7 days and 28 days. The main reason for increasing the strength of cement by adding these nanoparticles to cement mortar can be attributed to the filling of cavities by these nanoparticles. These nanoparticles prevent water from penetrating and spreading into the concrete. In addition, the uniform distribution of nanoparticles in the cement mortar prevents the growth of calcium hydroxide crystals. Calcium hydroxide produces calcium carbonate when reacted with carbon dioxide. These chemical reactions acidify the water that penetrates the concrete. For this reason, carbonation of cement reduces the strength of cement, corrosion of the rebar inside it and finally the destruction of the structure.

(a)

(b)

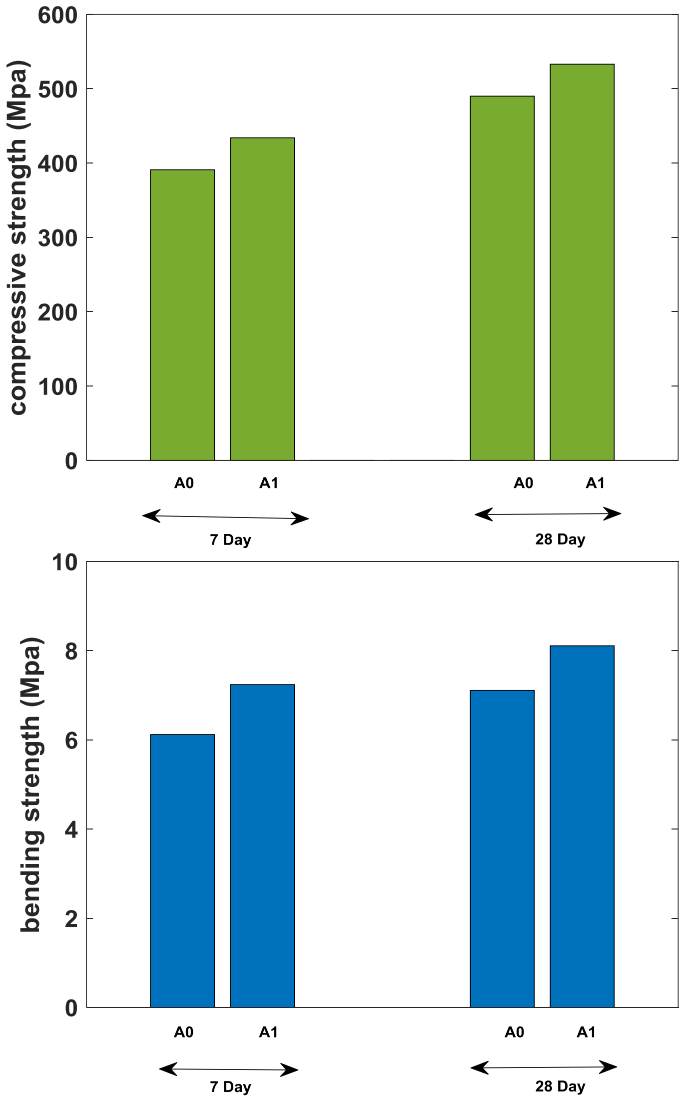

Figure 4. 7-day and 28- day, a) compressive strength and b) bending strength.

Corrosion results

The results of polarization test with and without Fe_2O_3 nanoparticles in cement mortar are shown in Figure 5 and Table 4. These results show that with the presence of this nanoparticle, the corrosion current decreases sharply and the corrosion potential increases, which indicates a decrease in the velocity and tendency of electron loss for the rebar in the presence of this nanoparticle.

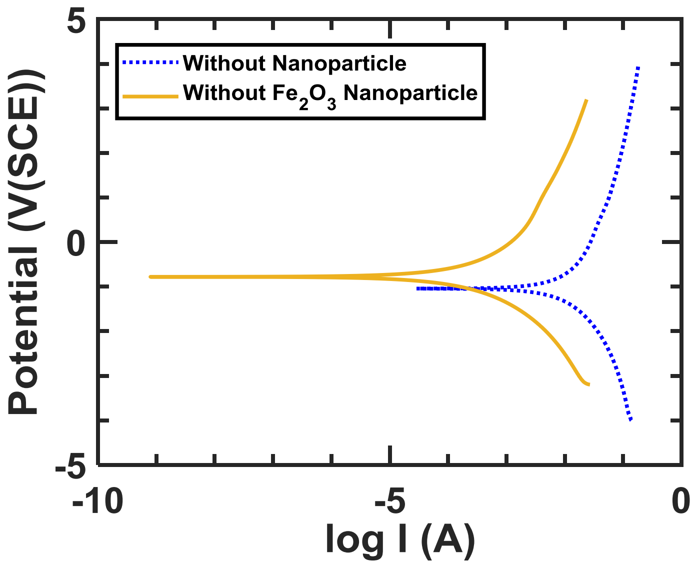

Figure 5. Polarization test results with and without Fe_2O_3 nanoparticles.

Table 4. polarization test results.

	Without NanoParticle	With NanoParticle
$I_{corrosion}\ (A)$	8×10^{-3}	1×10^{-3}
$V_{corrosion}\ (V)$	-1046×10^{-3}	-780×10^{-4}

Figure 6 shows the EIS test results with and without presence of the nanoparticles in the cement mortar. It is clear from the figure that the presence of Fe_2O_3 nanoparticle increases the electrical impedance well. Using equivalent circuit simulation, the reason for the increase in electrical impedance was investigated. Figure 7 shows the equivalent circuit of rebar in cement with the presence of Fe_2O_3 nanoparticles. It is clear from the figure that this equivalent circuit has two capacitors, one of which is seen at high frequencies and the other at lower frequencies. The first capacitor is due to the presence of concrete between the two conductors and the second capacitor is due to the imperfection of the concrete and the penetration of the solution into it. Figure 8 shows the experimental and simulation bad-phase diagrams. The results of the quantities obtained from fitting the experimental and simulation results are given in Table 7. It is clear from the results that the addition of Fe_2O_3 nanoparticles increases the electrical resistance and reduces the capacitance of the mortar. Decreasing the capacitance along with increasing the electrical resistance and ion diffusion at lower frequencies has increased the electrical impedance of the mortar in the presence of Fe_2O_3 nanoparticles.

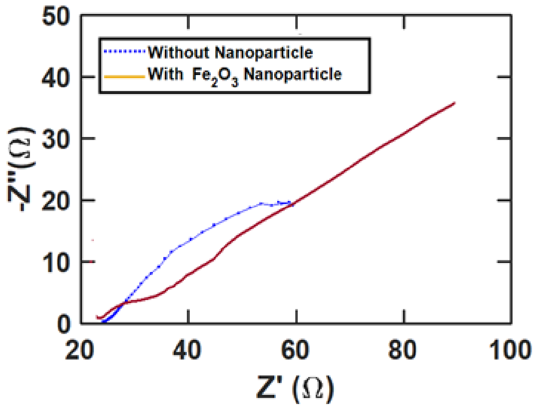

Figure 6. EIS test results with and without Fe_2O_3nanoparticles in cement mortar.

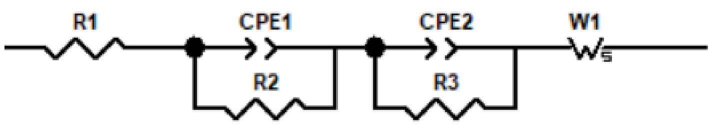

Figure 7. Equivalent circuit of rebar in mortar with and without the presence of Fe_2O_3 nanoparticles.

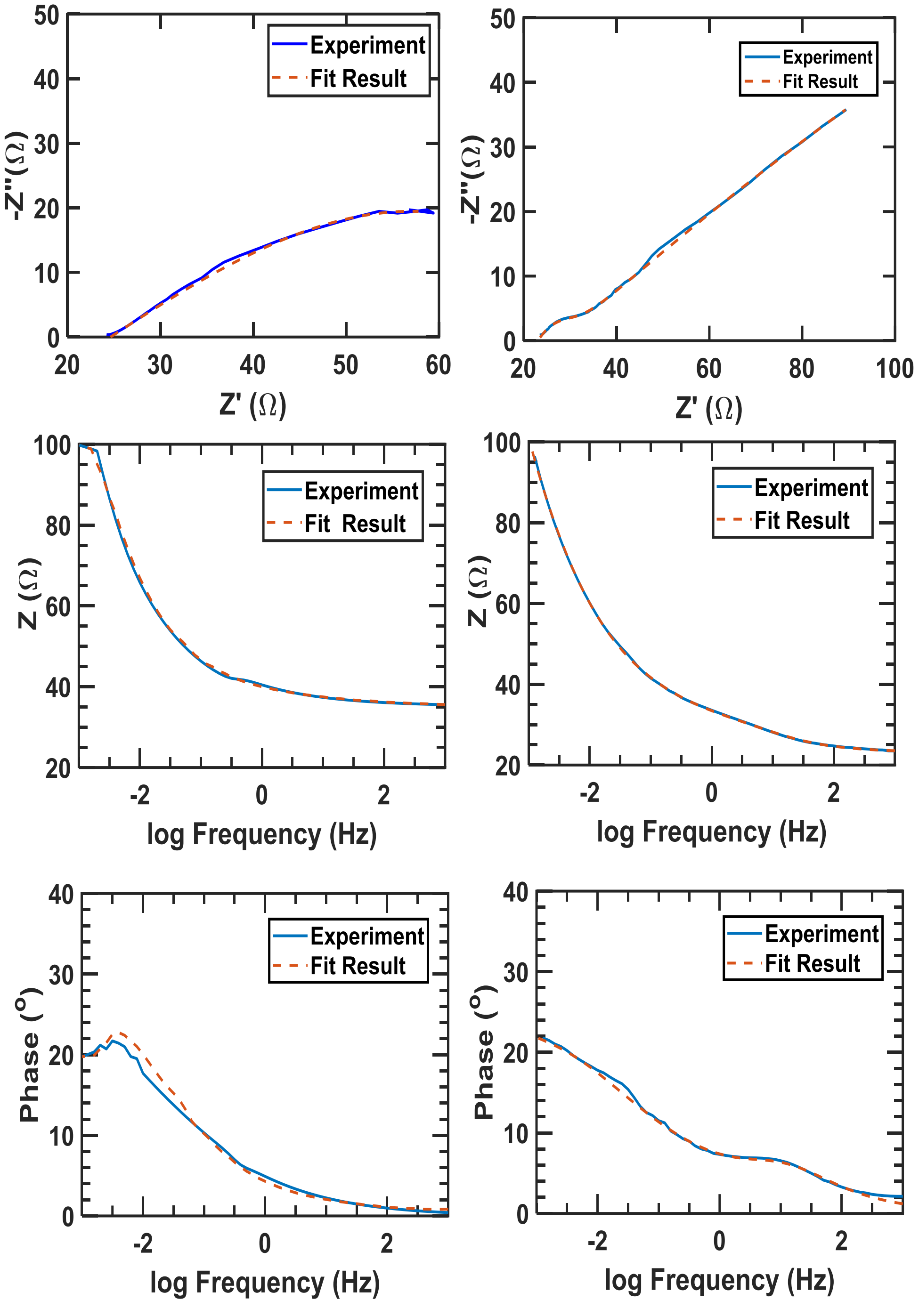

Figure 8. Experimental and simulation results of : first row: Nyquist curve, second row of bod diagram, third row: phase diagram. The first column without the nanoparticles and the second column with the nanoparticles in mortar

Table 5. Equivalent circuit quantities.

	Without Nanoparticle	With Nanoparticle
$R_1(\Omega)$	25	23
$W1-R$	121	-
$W1-T$	324	-
$W1-P$	0.43	-
$CPE_1(F)$	1071×10^{-4}	792×10^{-4}
α	0.9	0.9
$R_2(\Omega)$	54	717
$CPE_2(F)$	-	113×10^{-4}
α	-	0.91
$R_3(\Omega)$	-	6
$W2-R$	-	18
$W2-T$	-	394
$W2-P$	-	0.5

Conclusions

In this work, Fe_2O_3 nanorods were added to the mortar with one percent by weight of cement. 7-day and 28-day bending and compressive strengths showed that the presence of this Fe_2O_3 nanoparticle in cement mortar increases the strength of cement. To evaluate the effect of this nanoparticle on the corrosion protection of rebar inside the mortar, corrosion tests were performed and compared with the results of the control sample. The results showed that these nanoparticles increase the electrical impedance of the mortar. While electrical impedance increases, the tendency for electron loss and corrosion decreases. By simulating the equivalent circuit, the cause of the increase in electrical impedance was attributed to the increase in electrical resistance and the decrease in capacitance.

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