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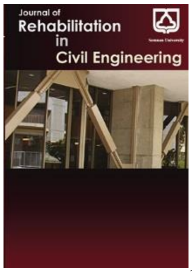

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Influence of Nano-Silica and Silica Fume in the Steel Corrosion Embedded in Concrete

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ABSTRACT

Corrosion of steel is one of the essential potential dangers and threats in concrete structures. Corrosion of steel embedded in reinforced concrete plays a key role in reducing the strength and durability of reinforced concrete. Several studies have proposed that alternative approaches to enhancing the performance of reinforced concrete and its resistance to corrosion. In this article, the results of steel corrosion embedded in reinforced concrete with silica fume and Nano-silica particles are presented. In the testing phase, samples with a mixture of these particles ranging from 0 to 133 grams were generated, and their performance was compared applying Corrosion Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Linear Polarization (LPR), and TOEFL polarization tests. The results demonstrate that silica fume is effective in reducing the permeability of the concrete against malicious (adverse) ions, but nano-silica had far satisfying performance in reducing the corrosion rate of steel embedded in concrete.

1. Introduction

The concrete component has an important role in the steel corrosion embedded in concrete. The attack of chloride to concrete is the major factor in corrosion of steel rebars. A number of steel corrosion in the concrete have been observed in sea environments or in the topside of a bridge that is disposable to antifreeze salt which these environments are full of chloride ion. Consequently, the type of concrete and its combinations in many situations can prevent the disintegration of the reinforced concrete constructions [1-5]. Moreover, the density of invasive ion is remarkable in the study of corrosion. Chloride ion (cl^{-}) is an invasive anion which has many effects on corrosion qualities. Since chlor has a smaller ray than other invasive ions, its ability to circulate is great.
Also, chlor is available in many environments around us [6, 7]. The particles

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of silica fume are small; thus, it quickens reaction with calcium hydroxide, which is produced from the hydration of Portland cement. The particles of silica fume, which are tiny, can settle in space between cement particles and ameliorate compactness [8, 9]. Furthermore, smut of silica can have an essential role in permeability [10]. Corrosion of rebars can damage reinforced concrete in two ways. First, it diminishes cross-section facet of rebars. Next, productions of corrosion generate larger bulk than steel itself. This growth of bulk makes tonic tension in concrete, which causes crackup and finally break down of construction [11]. Concrete which is compacted well and also produced accurately and has little water in proportion to cement has little permeability that minimizes contaminants which are the starter to corrosion such as chloride, carbon dioxide, humidity and etc. Moreover, the high especial electric resistance of concrete restricts the process of corrosion with diminishing electric currency from anode site to cathodes [12]. Influence of silica fume on concrete permeability is much more than its influence on pressure resistance. The more resistance against chloride ions is the consequence of reducing the permeability. Correlated to resistance against freezing and thawing. In some studies [13], a weak resistance of concrete with bubble bearing silica fume versus concrete without silica smut has been reported. Then again , other researchers [14], have reported a good resistance of concrete bearing silica fume against freezing and melting and also in desquamating with freezing factors. When silica fume exists in admixture, super lubricates will be valuable, because silica fume increases the need for construction water.

When discord of electric potential develops along the length of steel rebar, an electrochemical cell is created, and also anode and cathode parts are developed, which connect with electrolyte (into porous water in the pulp of hardened cement). Since electrochemical can provide the need for connection between anode and cathode through porous water and also steel rebars itself, the collection of apertures in the pulp of hardened cement is the basic effective factor on corrosion. If silica fume is applied in concrete admixture with an appropriate proportion, it effectively decreases the capacity of concrete permeability and increases electric resistance, so it diminishes the corrosion rate [8, 9, 15, 16]. Many researchers have examined the influence of silica fume on rebars corrosion tenacity with concrete lining. But the simultaneous influence of silica fume and nano-silica has not been investigated yet. In this study, the influence of silica fume and nano-silica on the chloride ion permeability in concrete and corrosion rate of the armature(rebar) in reinforced concrete will be discussed The steel which is eroded in concrete which damages concrete through expansion, crackup and finally by a burst of concrete lining on the rebars. The bulky expansion which causes iron to oxidize in according to the oxidizing condition may be the bulk of initial metal to 600 percent which researchers believe the main reason for expansion and concrete crackup, destruction of concrete by steel corrosion is an increase of bulk. Iron is covered through a thin layer of stone which is impervious, and this layer inactivates steel against corrosion. This layer in an acidic environment and also in the presence of chloride ions ($\boldsymbol{cl^-}$) is destroyed and become permeable. As a result, steel oxidized through chemical reactions that will be expressed in follows [17, 18].

The reaction of iron corrosion in chloride acid:

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

Because chloride ion doesn′t interface in reaction, so this equation can be written as:

$Fe + 2H+ \rightarrow Fe^{+2} + H_2$

This equation is easily divided into two anode and cathode reactions as follows:

(Anode reaction) $Fe \rightarrow Fe^{+2} + 2e^{-}$

According to the presence of oxygen, which is solvated because of the relation between environment and atmosphere, and also since water is approximately neutral, cathode reaction will be:

(Cathode reaction) $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH$

2. Experimental Procedures

In this study, type 2 Portland cement, made by tap water with a ratio of 0.44, is applied. Furthermore; samples are manufactured based on certain proportions of silica fume as powder and nano-silica as liquid mixed with super-plasticizer. Table 1 depicted the mixed pattern of each sample. table 2 presents the characteristics of silica fume and nano-silica as well. Rears are 37st with diameters of 16 mm.

Samples are in the form of a cylinder with 10 cm in diameter and 15 cm in height. There is one rebar placed in the middle of each sample. Figure 1 schematically indicates the sample shapes and placement of rebar [19]. To facilitate a clearer comparison between the silica fume and nano-silica, a non-nano-silica sample and a non- silica fume sample are created.

Table 1. Mix pattern of samples.

Sample Number	**Fine Aggregate (gr)**	**Cement (gr)**	**Water (gr)**	**Nano-Silica (gr)**	**Nano-silica (%)**	**silica fume (gr)**	**Silica fume (%)**	**Super plasticizer (gr)**
1	3800	1197	532	0	0	133	2.34	**19**
2	3800	1197	532	38	0.68	95	1.67	**19**
3	3800	1197	532	66.5	1.17	66.5	1.17	**19**
4	3800	1197	532	95	1.67	38	0.68	**19**
5	3800	1197	532	133	2.34	0	0	**19**

Table 2. Characteristics of silica fume and nano-silica.

Characteristic	**Silica fume**	**Nano-silica**
Specific gravity	2.2 **gr** cm^{-3}	1.2 **gr** cm^{-3}
PH	7	-9
Color	Gray	Opalescent
State	Solid	Liquid

3. Experimental Tests

Since the corrosion of steel embedded in concrete is an electrochemical process [16], so in this study, a set of electrochemical tests such as the Open Circuit Potential (OCP), Linear Polarization Resistance (LPR), electrochemical impedance spectroscopy (EIS), and TOEFL polarization were applied. The tests carried out under the three-electrode method that the counter electrode was a 2-square-centimeter-area Platinum sheet counter electrode, the reference electrode was saturated calomel electrode (SCE), and the working electrode was steel rebar in the concrete. The potential corrosion test was conducted for 300 seconds. The LPR test was achieved as much as 10 mV (10000 volts) above and below the corrosion potential with a Corrosion rate of 10 mV/min. The electrochemical impedance test with range 10 mV from a frequency 100,000 to 0.1 Hz was applied. The TOEFL Polarization test was implemented with a scan rate of 60 mV/min from a range of 250 mV cathodic to 250 mV anodic. Figure 2 schematically portrayed the electrochemical cell applied in this study [11]. After 28 days, all samples were maintained in a NaCL 3.5% solution for 24 hours and then were inspected.

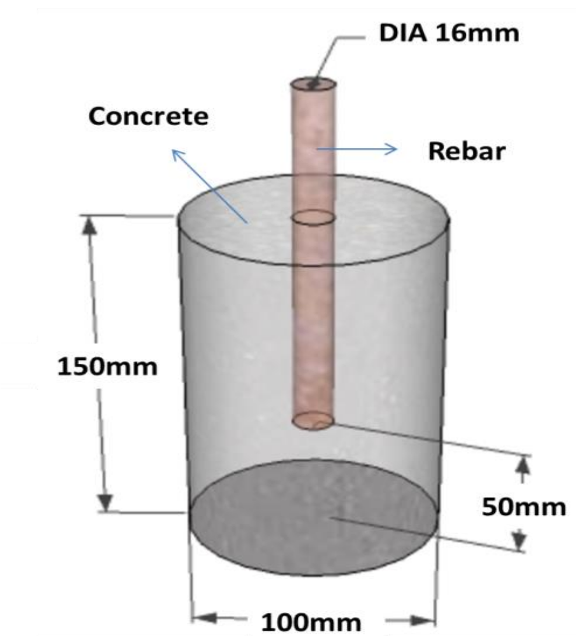

Fig. 1. Dimensions of the specimens.

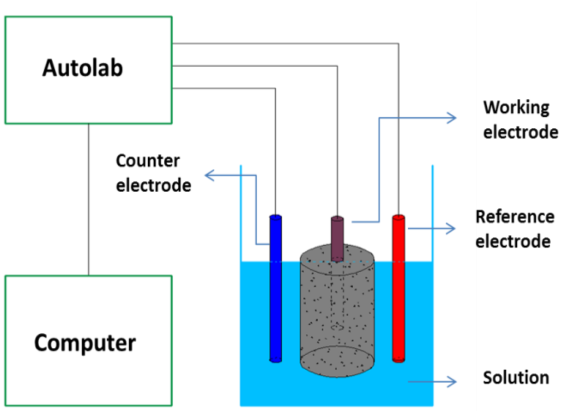

Fig. 2. Schematic of electrochemical cell use.

4. Results and Discussions

4.1. Corrosion Potential Test (OCP)

Figure 3 presents the corrosion potential of the samples. In general, it is possible to theorize that the corrosion potential decreases when the likelihood of further corrosion rises [20]. As observed in Figure 3, Sample 3, which possesses equal shares of silica fume and nano-silica, has the maximum amount of potential corrosion. Because silica fume prevents from malicious ions permeability into concrete and nano-silica averts the water permeability into concrete and with decreasing in amounts of each factor and increasing the other one the amount of potential corrosion been reduced. As for other instances, the test results confirm that the samples containing more nano-silica have greater corrosion potential. It should be noted that the OCP test is an indirect test for corrosion and cannot establish an accurate amount of the corrosion. Consequently, the corrosion potential is not a proper measure to get the amount of corrosion in concrete samples. Since Linear Polarization test and TOEFL Polarization test are based on the measurement of corrosion, more accurate and reliable data can be obtained on the corrosion process.

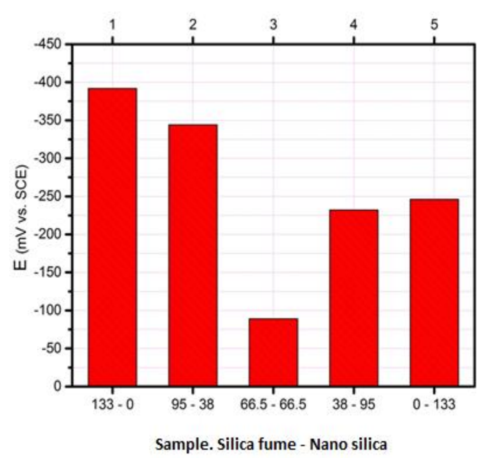

Fig. 3. The OCP test results for samples.

4.2. Linear Polarization Test (LPR)

LPR test is one of the tests that direct Circuit (DC) is applied. The LPR test acquires the steel polarization resistance against corrosion in concrete. Then based on the Stern-Geary equation, corrosion current density (i_{corr}) is calculated [21, 22].

Stern-Geary equation:

$$i = \frac{B}{R_p} \tag{1}$$

In the above formula, Rp is the polarization resistance, i_{corr} is corrosion current density, and the value of B is assumed 26[21]. Figure 4 illustrates the polarization resistance values and the corrosion current density of the samples.

As seen in Figure 4-a, samples which contain more nano-silica are more resistant to corrosion. Samples 1, 2 with more silica fume demonstrate less resistance than the other samples do. Samples 3 and 4 are similar in performance but compared to Sample **5,** which lacks silica fume is very resistant.This graph clearly reveals that the nano-silica betters silica fume reducing the corrosion rate.

Figure 3-b depicted the corrosion current density. Sample **5** has the least corrosion current density. Samples 3, 4, and 5 are nearly similar in performance; however, the samples containing more silica fume have higher corrosion current density. This graph clearly illustrates that the nano-silica is better than silica fume in reducing the corrosion rate.

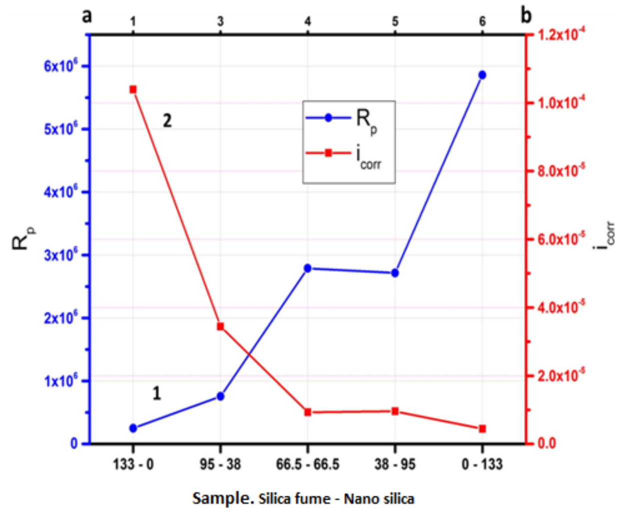

Fig. 4. The LPR test results, (a) The polarization resistance of samples, (b) Corrosion current density.

4.3. Electrochemical Impedance Spectroscopy Test (EIS)

The EIS test measures alternating Circuit (ac) impedance in a range of frequencies and determines the corrosion rate. The main significance of this test is to compute the polarization resistance (Rp), solution resistance (Rs), and double-layer capacity (C), which gives spacious information on the corrosion process. Interpreting the given information provides the corrosion rate and its controlling mechanism [21]. Thus, it can be claimed that The EIS test is very efficient in reinforced concrete (RC) samples.

Figure 5 displays an equivalent circuit for the EIS test also the circuit's relation with the circles in the Nyquist diagram. The first circle, appeared at high frequencies, shows the concrete behavior as the coating on steel.

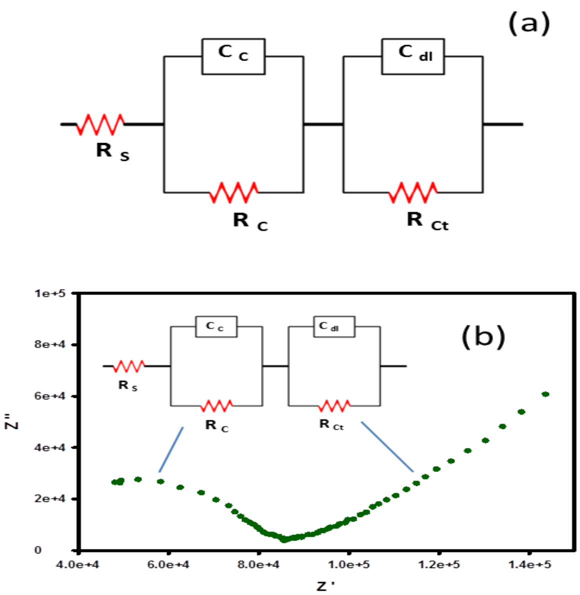

Fig. 5. (5-a) The equivalent circuit for the EIS test results (5-b) the circuit's relation with the circles in the Nyquist diagram.

Figure 6 presents a sample's Nyquist diagrams. As can be observed, Sample 5 has the maximum amount of nano-silica and, consequently, surpass the others at resisting against the corrosion. Sample 3 is more resistant than Samples 1 and 2. Similar to previous experiments, comparing Diagrams clearly indicates that nano-silica is better than silica fume in reducing the corrosion rate.

Figure 7 indicates the Bode diagrams obtained from the EIS test. The advantage of Bode diagrams is that they illustrate the impedance and phase angle as explicit functions of the frequency. In Bode diagrams, the absolute value of the impedance (│Z│) affected to Rs at very high frequencies and tends to (Rs + Rp) at very low frequencies [20]. Hence, this paper acknowledges the value of │Z│ at low frequencies.

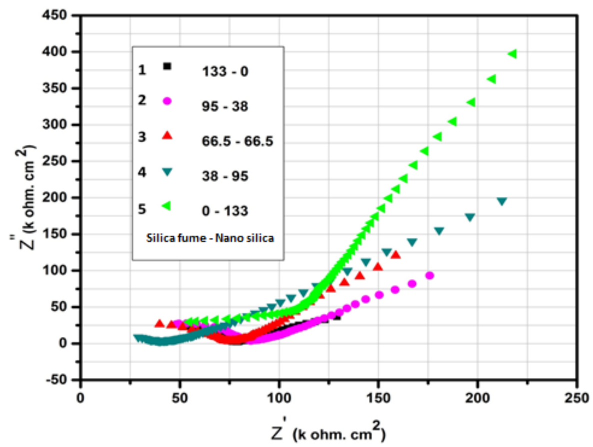

Fig. 6. Nyquist curves obtained from the EIS test.

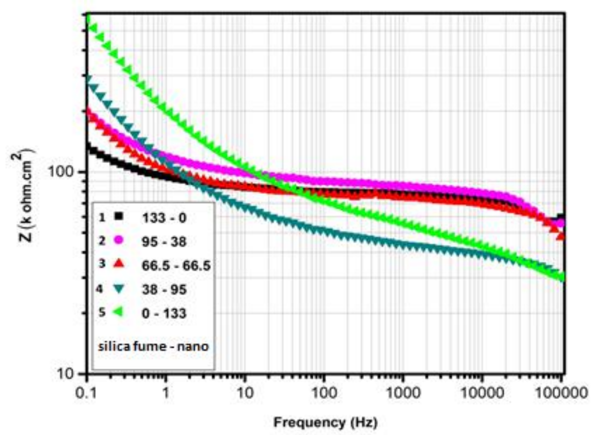

Fig. 7. Bode curves obtained from the EIS test.

Figure 7 highlights that Sample **5**, and then Sample 4, has the best performance against the corrosion.

Figure 8 displays the resistance of concrete samples against ion's malicious permeability (RC) with graph1-a, Capacitance of the concrete (CPEC) with graph 2-b, and Constant Phase Element on steel (RCT) with graph 3-c. Figure 8-a exhibits that Sample 4 has a minimum amount of RC and Has been weaker than other samples. The figure also illustrates that Samples 1, 2, and 3 containing more silica fume have lower permeability. It can be concluded that micro-silica has been able to reduce the ion's malicious permeability in concrete better than nano-silica.

In consonance with graph 2-b, it can be seen that sample 4 has the lowest amount of CPEC, and this indicates that water permeability into the concrete of this sample is less than other samples, and then sample 5 surpasses the other samples. So we can say nano-silica is stronger than silica fume in reducing water permeability into the concrete. Axis 3 persuade the amount of load transfer on the rebar, and as can be seen, sample 5 has been much stronger in comparison with another sample.

Figure 8 illustrates the importance of water and malicious ions permeability within the concrete clearly. Means in samples with much malicious ions permeability or much water permeability, rebar has been weaker against corrosion. Sample 5 that its permeability is lower has more resistance against corrosion. Samples 3 and 4, which are close in their resistance, have been better than Samples 1 and 2. This issue indicates nano-silica has better performance than silica fume.

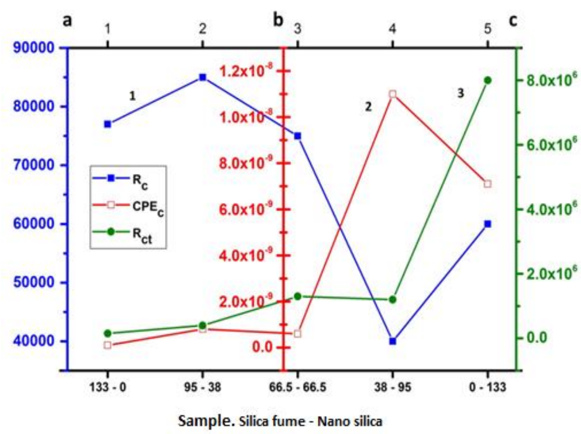

Fig. 8. RC is a-1, CPEc is b-2, and Rct is c-3

4.4. TOEFL Polarization Test:

Figure 9 displays how to compute the corrosion process from TOEFL polarization curves it can be explained the potential to start drawing curves is called Potential corrosion. If the potential applied at sample change to positive, the polarization curve is anodic; and if it changes to negative, it is cathodic. If the slope of these two curves extend to the corrosion potential, from their confluence place the corrosion current achieved, which can after that by using Faraday's law, calculate the density of current corrosion. Conducting extra-polarization on cathodic area yields more accurate results than the anodic part [21, 23]. Faraday's law as follows:

$$i_{corr} = \frac{I_{corr}}{A_a} \quad (2)$$

In Equation 2, A_a is the area of the anodic part In this paper A_a is the area of rebar's certain part embedded in concrete.

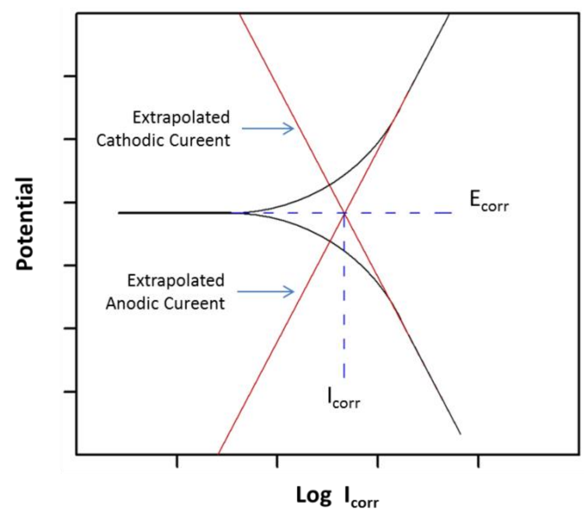

Fig. 9. Process of determining $\mathbf{i_{corr}}$ from the polarization curves.

Figure 10 indicates the results of TOEFL polarization test of samples. Confirming to Figure 10, samples that their silica fume amount is 133 and 95 g, have more silica fume, and their performances are weaker in comparison with another samples and corrosion process occurs more in them and the samples that have more nano-silica, have shown more strong performance against corrosion. This reveals that nano-silica appears stronger than silica fume. The corrosion potential difference observed in this test, by the OCP test, is the cause of the cathodic reaction in this test.

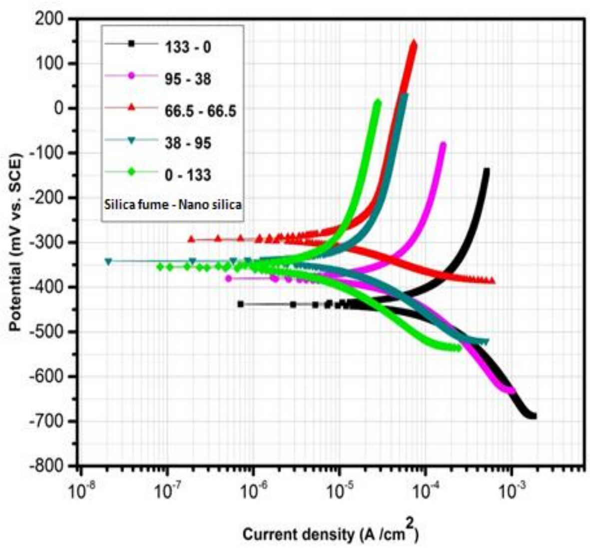

Fig. 10. TOEFL polarization curves.

5. Conclusion

The purpose of this study is the evaluation of the influence of silica fume and nano-silica particles on the corrosion rate of steel embedded in concrete. To this end, samples were generated in the presence of the different values of silica fume and nano-silica particles. Next, samples were compared with each other through OCP, LPR, EIS, and TOEFL polarization tests. The results can be summarized as follows:

- EIS test results indicate that silica fume effectively bettered than nano-silica in decreasing the concrete permeability against malicious chloride ions, but nano-silica has better performance than silica fume in reducing the concrete permeability against water.
- The results of OCP and TOEFL polarization test reveals that if we apply an equal amount of both silica fume and nano-silica particles, acquire a higher corrosion potential for concrete.
- Overall it can be concluded that silica fume has better performance than nano-silica in decreasing the concrete permeability against malicious chloride ions and nano-silica acts better than silica fume in decreasing the concrete permeability against water. According to the results of the tests, it can be said that however, both factors have an important effect in decreasing the corrosion rate, but the influence of nano-silica is more than silica fume.

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