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Simultaneous effect of nano and micro silica on corrosion behaviour of reinforcement in concrete containing cement strength grade of C-525

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Abstract

The present study investigated the changes in the effect of additive nano-silica replacing micro-silica to reduce corrosion rate of steel in the concrete made of C-525 cement in a corrosive environment, and also the optimum combination of these additives in reinforced concrete for the production of reinforced concrete with high resistance to corrosion of the reinforcement. To this end, 7 series of cylindrical corrosion samples were prepared, which comprised a base design and 6 designs of various combinations of micro and nano silica, weighing a constant 11% in total of the weight of cement used in each sample. Samples were placed in a 3.5% salt-water solution and underwent various electrochemical tests, including corrosion potential (OCP), linear polarization (LPR), impedance spectroscopy (EIS), and Tafel polarization test. The results obtained suggested combined use of 1.6% nano and 9.4% micro-silica for achieving the most appropriate cost considering the increased useful life of concrete structures and the optimum reduction in rate of corrosion of concrete.

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Keywords: Concrete, Corrosion, Electrochemical methods.

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1. Introduction

According to The need for manufacturers in different parts of the world to produce concrete with higher corrosion resistance to build structures in exposed to corrosive ions at optimal cost, minimum damage to the environment, requires materials that are usually available everywhere. Caused by exposure to chloride ions is considered the main destructive factor in reinforced concrete structures [1-5]. The ability of a substance to resist displacement of ions usually depends on electrical resistivity, and inversely proportional to concrete resistivity [6]. Researchers have demonstrated that concentration of corrosive materials and environmental conditions [7], percentage of micro-silica [8] and nano-silica [9] additives can reduce corrosion in concrete [10]. The interest in these additives is because of their advantages over other corrosion protection methods including diversity in type and amount and lower costs [11, 12]. Although the effects of micro and nano silica in increasing corrosion resistance of ordinary concretes is well-known [13], their combined effects and optimum amounts have not yet been studied. Moreover, since these tests are non-destructive, performing several different electrochemical corrosion tests plus one destructive test in a chloride medium, instead of a single test, will produce better and more acceptable results and different parameters for identifying potential and rate of corrosion [14, 15].

It should be noted that in the research conducted on the combination of micro and nano silica binary at different doses in the manufacture of concrete with cement 525 with the aim of reducing the corrosion rate from chlorine ion and reaching their optimal consumption together they are not used. For this purpose, 3 non-destructive tests (corrosion potential OCP; linear polarization LPR; and impedance spectroscopy EIS) and Tafel polarization destructive test were carried out on 7 series of test samples, so that different dimensions of the effects of these additives can be accurately studied and compared.

2. Experimental

2.1. Materials properties and mixture proportions

To perform the corrosion test, seven 100 × 150 mm cylindrical concrete samples reinforced with 18Ø ribbed polished steel bars were exposed to salt ion attack, such that 70 mm of the steel bar length was placed in the middle of cylindrical samples (epoxy-free) and was tested after the standard 90 days curing age. Portland cement II-525 kg/cm^2 of standard specification [16], and river-type aggregate of 9 mm maximum diameter, with standard poly-carboxylic superplasticizer [17] were used. Nano-silica (NSF) of $20gr/cm^3$ density was used as an emulsion suspended-in-water, with 29.6-31% silica, pH of 9.6-10.2, maximum viscosity of 7, and specific area of 200-240 m^2/gr. Micro-silica powder (MSF) of specific area 20-25 m^2/gr, was used as spherical particles of 229 nm diameter and amorphous structure according to standards [18].

Samples were made from cement grade 350 kg/m^3, W/C = 0.44 and superplasticizer weight 0.36% of cement weight. Total percentage weight of MSF and NSF mixture in each sample was 0.11 of weight of cement used, which was within the range recommended by some researchers as the appropriate amount of micro-silica for enhancing certain endurance properties of concrete [19]. Mix 1 (control mixture) was prepared without nano or micro silica. The difference in mixture designs was in the proportion of additives used, such that in mix2 to mix7 designs, the following percentages of NSF and MSF were respectively used: (0.111, 0.0), (0.095, 0.016), (0.079, 0.032), (0.055, 0.055), (0.032, 0.079), and (0.0, 0.111).

3. Methods

First, to find natural corrosion potential of samples according to standards [20], OCP test was performed at temperature of 25 °C, using a potentiostat (model ACM Instrument-Gill AC) and platinum counter electrode of 2 cm2 area in 3-electrode method.

Then, samples were subjected to Linear Polarization Resistance (LPR) test with DC current and potential sweep range on from -10 mV cathode surface to +10 mV anode [21] compared to corrosion potential found in OCP test. Next, current was found from resistance using Stern-Geary equation [21-23]. The corroded mass and ultimately corrosion rate were found according to ASTM G102-89 standard and Faraday's current law [10, 23].

To find corrosion rate, EIS test was performed with AC current using equivalent circuit used by A Batysta [24] at 10 mV [15]. This test was carried out over a broad frequency range from 0.0001 to 100 KHz [15, 25], ignoring the negligible value of Rs (about 3-10 Ωcm^2).

Lastly, the destructive Tafel polarization test was performed at sweep speed of 60 Mv/sec. In the Tafel plots, the potential values imposed on a sample were based on standards, ranging from -250 mV cathode to +250 mV anode, compared to values obtained in OCP test for that sample [10].

4. Results and discussion

The results of OCP and LPR tests are presented in Fig. 1. It can be seen that from control mix to mix2, replacement of micro-silica in the cement by 11% leads to reduced corrosion rate in LPR test by 3.9 times. Also, from mix2 to mix3, by replacing micro-silica with 1.6% nano-silica, corrosion rate and potential will reduce by 5 and 12.5 times respectively. Comparison of mix7 and mix2 shows that complete replacement of MSF with NSF will result in improved electrochemical properties of concrete in 90-day curing age. This improvement may have been due to the filling ability and reduced ion penetration due to greater pozzolanic reactions of nano-silica compared to micro-silica [26]. Some researchers have argued that smaller particles create a relatively denser structure and greater discrete cavities in the concrete [8]. According to the above argument, design 3 will be the best overall choice.

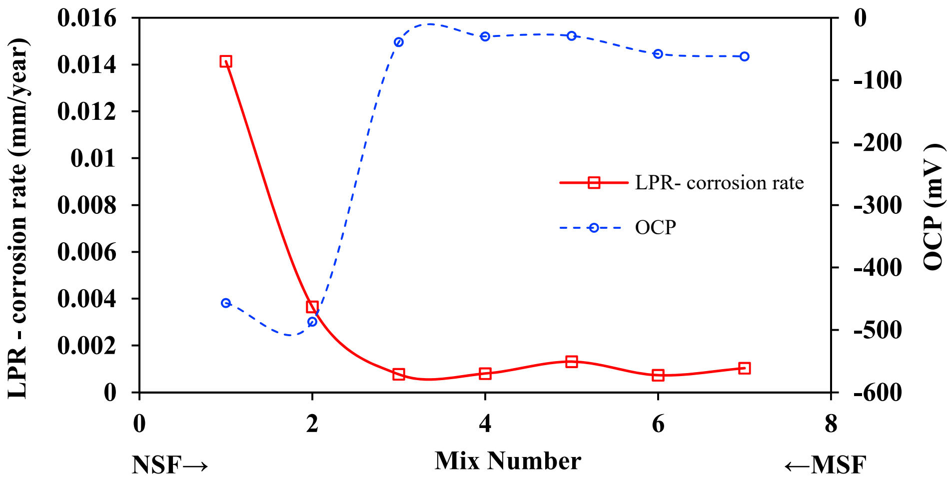

Fig. 1. Matching values of OCP test and corrosion rate compared to LPR test in terms of micro-nano proportions used.

The results from EIS, LPR, and Tafel tests for all designs are presented in Fig. 2. Comparing control mix and mix2 shows improvement in corrosion resistance by 5.85 and 2.5 times due to increased I_{corr} and total resistance (Z). Moreover, corrosion current and total resistance (Z) obtained in Tafel and EIS tests improved by 2 and 8.8 times respectively, to reduce corrosion rate. Recent studies have shown that addition of different doses of MSF and FGP to concrete was able to reduce I_{corr} by a maximum of 34% [8], and also showed that design 3 produces the best results.

As a general trend, increasing Rs (Rp, Rc, and Rct) is clearly seen in Fig. 3. The increase in electrical resistance and decrease in corrosion rate are due to MSF replacement with cement, which has been cited and explained by researchers [8, 27-29]. OCP test does not show an ascending trend in corrosion potential in mix2 compared to control mix, which may be due to the error in this method in some cases. An increase in values of R is observed in mix3 compared to mix2, and this figure also confirms superiority of design 3, which means replacement of equivalent weight of cement with 1.6% nano and 9.5% micro silica can produce better corrosion results.

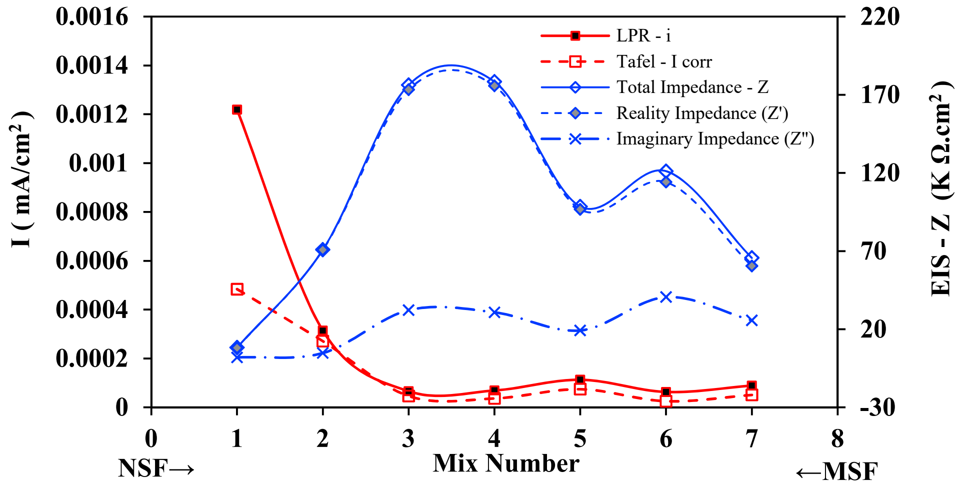

Fig. 2. Comparing the results of impedance from total EIS test with I found in Tafel polarization and LPR tests in terms of proportions of micro-nano used.

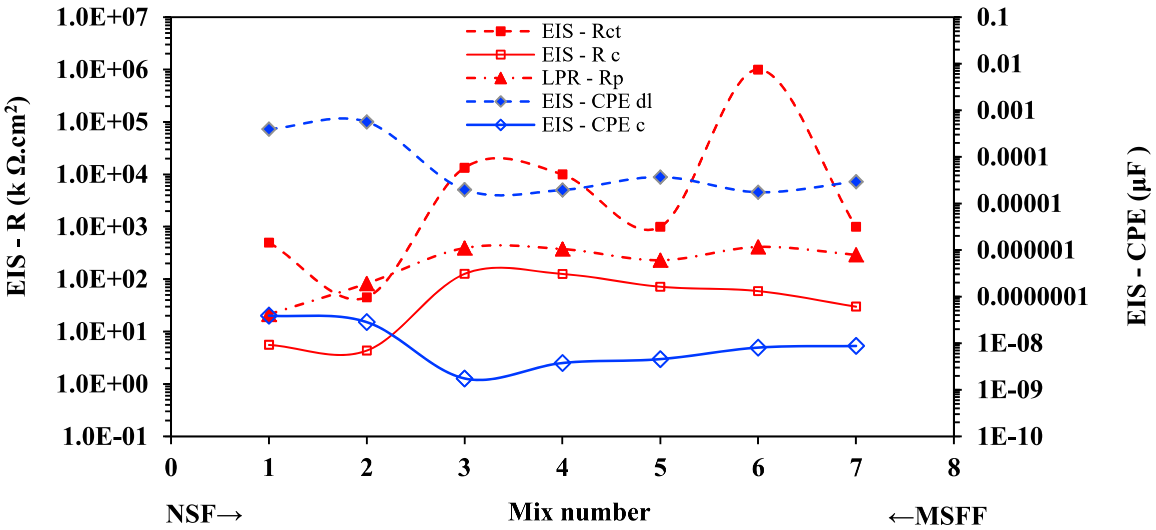

Fig. 3. The trend of changes in resistance (Rp) obtained in LPR test and values found for resistance and capacitors in EIS test in relation to micro-nano proportions (Rct=Rcharge transfer; Rc= Rcoute; Rp=Rpolarization; CPEdl= CPE double layer; CPEc=CPEconcrete (coute)).

Comparison of tests performed on all samples shows that replacement of nano-silica of more than 1.6% with micro-silica powder does not produce a positive effect in reducing corrosion rate, and that because of the optimum balance in the binary combination of NSF and MSF, mix3 produces the best results. The reasons for limited use of nano-silica include reduced density, relatively greater absorption of water, and clear porosity due to use of nano-silica in exceeding certain dosage [30, 31]. It has been argued that concurrent use of these two provides greater corrosion resistance than using them individually; however, increasing use of nano and micro (even in combination) will not necessarily improve endurance property of concrete [26, 32], which confirms the above results. Also, by using relatively high doses of nano alone, electrical resistance can be observed [33]. Previous studies have shown that in combination of nano and micro, even tiny amounts of nano-silica produce substantial effects in increasing charge transfer resistance and resistance against corrosion. As a result, given the higher cost of nano silica, we found its optimal use which will be economically optimal in terms of reducing both the cost of production and increase lifespan of concrete structures constructed with this consumable dose.

The electrical properties of double-layer can have a significant role in chloride-induced corrosion in the reinforced concrete steel bars [34]. This trend is due to an electro-capillary process and the interaction between pore walls and pore solution, which creates an electrical absorptivity that slows down chloride ion penetration [35, 36]. A highly important parameter of electrical double layer is the pore size, such that any changes in pore size cause a substantial change in concentration of chloride inside the pores [35]. Hence, reduced diameter of pores, and thus penetration of chloride ions, can be considered a reason for increasing R and relatively high level of resistance against corrosion, and provides another explanation for increased corrosion resistance in mix3 compared to other mixture designs (Fig. 3). Given the above discussion, due to their matching hydration rate on the one hand, and creating better bond between cement micro-grains due to their optimal mixing including cement powder, NSF, and MSF on the other hand, combination of NSF and MSF reduces diameter of pores and closes the connections between them, resulting in increased density of concrete, and ultimately reduced penetration of chloride ions into concrete, and ions reaching surface of steel bars to cause corrosion.

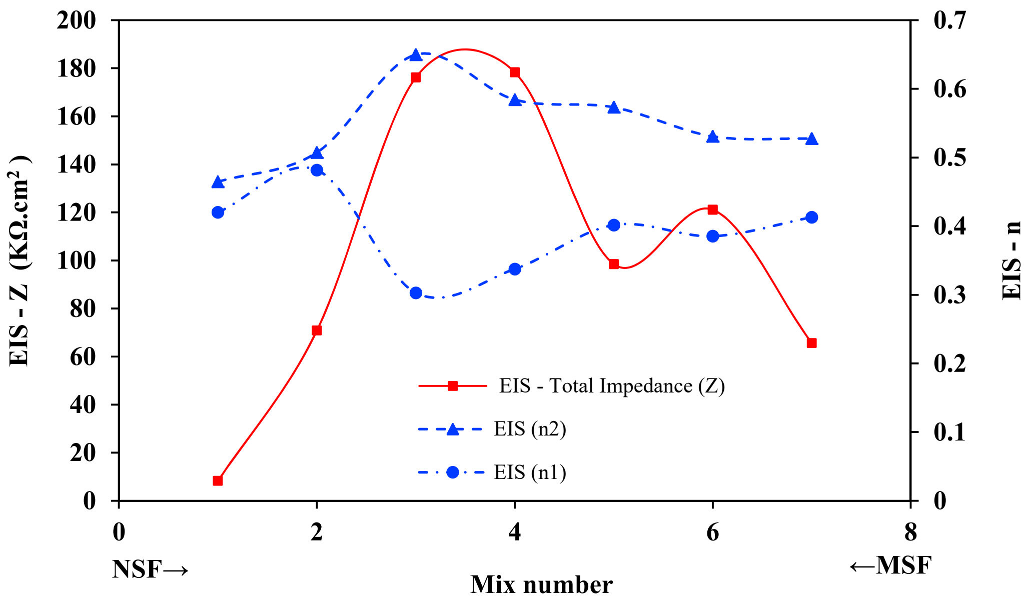

Fig. 4. Changes in parameter n and total impedance Corrosion rate found in LPR test, and potential corrosion in OCP test, in relation to proportions of nano-micro used.

The value of parameter n associated with CPE (usually less 1 [37], and generally ignored [38]) has a particular trend here. Previous studies have shown that value of n can be considered as a criterion for surface toughness, and test results indicate that value of n increases with increasing surface toughness [39]. Interestingly, Fig. 4 shows that corrosion resistance is the highest, and values of n1 (steel surface) and n2 (concrete surface) are the lowest and the highest, respectively, in mix3. Perhaps, n can be an effective parameter in reducing corrosion rate, and n1 compared to n2 is more effective in increasing corrosion resistance in mix3 compared to other designs.

5. Conclusion

1- As a general trend, for cement 525, replacement of micro-silica with values of nano-silica greater than 1.6% adversely affects reduction in corrosion rate. This amount varies according to type of cement and other conditions.
2- Among the 4 tests used, OCP test lacks sufficient accuracy and cannot be used alone.

3- By increasing specific surface or reducing diameter of nano particles, the optimum range of silica particles against reduction in concrete corrosion rate can be reduced
4- Compared to other additives, micro and nano silica compensate weaknesses of each other, and perform better, which may be due to compatibility of their specific surface and hydration rate.
5- Although using nano alone produces better chlorine ion corrosion resistance results compared to using micro alone, their binary combination produces better results still compared to their use separately.

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