Study the Effect of SiO$_2$ Nanoparticles as Additive on Corrosion Protection of Steel Rebar in Artificial Concrete Solution

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Abstract: It well known the advantages of using SiO$_2$ nanoparticles as additive for improving the mechanical properties of concrete structure and reducing the liberation of CO$_2$ gas to the atmosphere. This research investigate the effect of adding SiO$_2$ nanoparticles (12 nm; 1, 3 and 5% by weight) to artificial concrete solution (2gCa(OH)$_2$, 0.0225 g KOH and 0.008 g NaOH in one litter of distilled water) on the corrosion of steel rebar against seawater environment (3.5% NaCl) at four temperatures; 20, 30, 40 and 50°C. The corrosion parameters and pitting probability of the carbon steel rebar were measured in separate experiments using Tafel plot and cyclic polarization procedures, respectively. The corrosion protection efficiency was increased with increasing SiO$_2$ content and values of 37-80% were recorded in comparison with the concrete solution free of SiO$_2$NPs. The cyclic polarization voltagrams show that the SiO$_2$ NPs reduces the pitting area in all SiO$_2$ concentrations and fully stopped the pitting problem because of the chloride ions. The surface morphology of the steel rebar was examined before and after polarization using Atomic Force Microscope (AFM).

Key words: Corrosion inhibition, nanomaterials, steel rebar, SiO$_2$NPs

INTRODUCTION

The study of the conditions leading to steel rebar corrosion is of high importance because corrosion may significantly affect the load-bearing capacity of reinforced concrete (Wei et al., 2013) and causes widespread damage to critical such as highway bridges sewage pipelines and other critical assets made of concrete (Angst et al., 2009; Ann and Song, 2007). Figure 1 shows the main factors responsible for reinforcement corrosion, carbonation induces a generalized corrosion while the presence of chloride ions in the surroundings of the steel leads to localized corrosion (Figueira et al., 2017).

The main sources of chlorides for concrete structures are marine environments and the use of deicing salts in roads in cold climates (Alonso et al., 2000). While carbonation implies a gas that needs the pore network partially empty (Pacheco, 2015).

Many strategies were used to decreases the risk of concrete corrosion (Paul and Van Zijl, 2017; Zhao et al., 2017) such as using additives to the concrete mix (Goyal et al., 2018; Bamforth, 2004), coating the steel rebar and others (Bamforth, 2004; Broomfield, 2006; Berrocal et al., 2016; Osial and Wilinski, 2016).

Nanomaterials has become one of the best choice for enhancing corrosion resistance, several materials have been used for this goal such as ceramic materials and others (Raki et al., 2010; Lin et al., 2008; Sato and Beaudoin, 2007; Anaee, 2015; Shen et al., 2005; Xiong et al., 2006).

The present work designed to study the influence adding SiO$_2$ NPs on the corrosion rates and of pitting probability of the steel rebar imbedded in concrete containing 3.5% NaCl.

MATERIALS AND METHODS

The steel rebar which used in this study was (Ukraine origin) with diameter of 16 mm and its chemical composition is given by the manufacturer and listed in Table 1.

Prior to do the polarization experiments the steel rebar was deoxidized by immersion in concentrated HCl (37%, Fluka/Switzerland), followed by rinsing with running tab water and then dewatered with ethanol and

Fig. 1: Scheme represents factors responsible for corrosion of steel bar in concrete
left to dry, the steel sample serve as working electrode was warped with adhesive tape except for a known distance which was (16.55 cm²), Pt-electrode serve as counter electrode and Ag/AgCl as references electrode.

Then, the steel rebar polarized in the concrete simulation solution (Ca (OH)₂ (2 g), KOH (0.02244 g), NaOH (0.008 g) in 1L of distilled containing 3.5% NaCl and SiO₂ NPs (12 nm, Degussa, Germany) in different concentration (1, 3 and 5%) as additive. After that, Tafel plots were recorded for corrosion rate measurement by scanning the potentials ±200 mV around the OCP with a rate of 2 mV sec⁻¹. The same procedure repeated at four temperatures 20, 30, 40 and 50°C.

Table 1: Chemical composition of the steel rebar used in this study

| Elements | Percentage |
|----------|------------|
| C        | 0.260      |
| S        | 0.031      |
| Si       | 0.280      |
| N        | 0.010      |
| Cu       | 0.280      |
| Mn       | 0.280      |
| Ni       | 0.730      |
| Cr       | 0.130      |

For pitting corrosion investigation the steel rebar subjected to a cyclic polarization at 20°C starting from few millivolt lower than OCP going up to about 1000 mV. Atomic force microscope (SPM AA3000, Angstrom Advanced Inc., USA) was used to study the change in the morphology of the steel rebar surface before and after polarization.

RESULTS AND DISCUSSION

Figure 2 show the recorded Tafel plots for the steel rebar in simulated concrete solution containing 3.5% NaCl, without and with adding SiO₂ NPs (1, 3 and 5%), at temperatures of 20, 30, 40 and 50°C.

All corrosion parameters including \( E_{corr} \) in (millivolt), \( I_{corr} \) in (ampere), weight loss in (g.m⁻²d⁻¹), penetration loss in (mmpy) were measured and calculated from above Tafel plots while polarization resistance \( R_p \) in (Ω.cm²) and corrosion protection efficiency (%) were calculated using the Eq. 1 and 2 (Kaesche, 2003) are listed in Table 1:

![Fig. 2(a-d): Tafel plots of steel rebar polarized in simulated concrete solution containing TiO₂ NPs (a) Without, (b) -1, (c) -3.0 and (d) -5.0% with 3.5% NaCl and different temperatures](image-url)
Table 2: Corrosion rate parameters of steel rebar polarized in simulated concrete solution containing SiO2 NPs (12 nm) and 3.5% NaCl at 20, 30, 40, 50°C

| SiO2 (%) | T (K) | \( E_{corr} \) (mV) | \( i_{corr} \) (A*10^{-6}cm^{-2}) | \( \beta_a \) (mV/Dec) | \( \beta_c \) (mV/Dec) | \( R_p \) (Ω.cm²) | \( CR \) (WL g.m⁻²d⁻¹) | \( CR \) (PL μmpy) | PE (%) |
|----------|-------|---------------------|-------------------------------|----------------------|----------------------|----------------|----------------|----------------|--------|
| 0        | 293   | -548.7              | 95.86                         | -125.1               | 145.5                | 2799.85       | 24.00          | 1.110          | -      |
|          | 303   | -478.1              | 100.76                        | -91.6                | 102.1                | 2112.44       | 25.20          | 1.170          | -      |
|          | 313   | -467.8              | 215.79                        | 97.6                 | 176.3                | 5886.36       | 53.90          | 2.500          | -      |
|          | 323   | -457.1              | 257.57                        | -123.6               | 142.3                | 7397.86       | 64.40          | 2.990          | -      |
| 1        | 293   | -431.2              | 56.24                         | -143.7               | 145.5                | 1766.12       | 14.10          | 0.653          | 41.33  |
|          | 303   | -468.3              | 77.07                         | -118.4               | 137.3                | 2127.56       | 19.30          | 0.850          | 23.51  |
|          | 313   | -458.8              | 81.29                         | -104.6               | 120.9                | 1979.49       | 20.30          | 0.944          | 62.32  |
|          | 323   | -448.4              | 90.52                         | -106.2               | 132.6                | 2317.84       | 22.60          | 1.050          | 64.85  |
| 3        | 293   | -509.7              | 46.45                         | -122.8               | 169.3                | 1435.54       | 11.60          | 0.539          | 51.54  |
|          | 303   | -503.9              | 62.94                         | -131.8               | 181.9                | 2448.49       | 15.70          | 0.731          | 37.53  |
|          | 313   | -477.7              | 68.29                         | -136.7               | 192.4                | 2354.25       | 17.10          | 0.793          | 68.32  |
|          | 323   | -477.6              | 77.11                         | -148.4               | 217.8                | 2955.22       | 19.30          | 0.895          | 70.06  |
| 5        | 293   | -524.9              | 27.39                         | -124.4               | 183.5                | 881.74        | 6.85           | 0.318          | 71.42  |
|          | 303   | -509.0              | 35.12                         | -131.8               | 181.9                | 1165.45       | 8.78           | 0.408          | 65.14  |
|          | 313   | -491.6              | 41.95                         | -136.7               | 192.4                | 1455.74       | 10.50          | 0.487          | 80.55  |
|          | 323   | -475.4              | 46.46                         | -145.4               | 216.7                | 1755.41       | 11.60          | 0.539          | 81.96  |

\[
Rp = \frac{\beta_a \beta_c}{2.303(i_{corr} (\text{wo})/i_{corr} (\text{w}))} \tag{1}
\]
Where, \( \beta_a \) and \( \beta_c \) are Tafel slopes:

\[
iE\% = \frac{i_{corr} (\text{wo}) - i_{corr} (\text{w})}{i_{corr} (\text{wo})} \times 100 \tag{2}
\]

Table 3: Thermodynamic function (\(E_a\), \(\Delta H^*\), \(\Delta S^*\) and \(\Delta G^*\)) of steel rebar in/concrete electrolyte solution containing 3.5 NaCl and SiO2 NPs

| SiO2 (%) | T (K) | \( E_a \) (kJ/mole) | \( \Delta H^* \) (kJ/mol) | \( \Delta S^* \) (kJ/mol.K) | \( \Delta G^* \) (kJ/mol) |
|----------|-------|---------------------|--------------------------|--------------------------|--------------------------|
| 0        | 293   | 16.090              | 18.569                   | -0.144                   | 60.761                   |
|          | 303   | 62.201              | -0.188                   | 61.551                   |
|          | 313   | 63.641              | -0.187                   | 62.009                   |
|          | 323   | 65.081              | -0.188                   | 63.455                   |
| 1        | 293   | 12.485              | 6.467                    | -0.188                   | 61.551                   |
|          | 303   | 63.431              | -0.188                   | 63.431                   |
|          | 313   | 65.311              | -0.188                   | 65.311                   |
|          | 323   | 67.191              | -0.188                   | 67.191                   |
| 3        | 293   | 13.296              | 7.218                    | -0.187                   | 62.009                   |
|          | 303   | 63.879              | -0.187                   | 63.879                   |
|          | 313   | 65.749              | -0.187                   | 65.749                   |
|          | 323   | 67.619              | -0.187                   | 67.619                   |
| 5        | 293   | 13.861              | 8.371                    | -0.188                   | 63.455                   |
|          | 303   | 65.335              | -0.188                   | 65.335                   |
|          | 313   | 67.217              | -0.188                   | 67.217                   |
|          | 323   | 69.095              | -0.188                   | 69.095                   |

Then, \(G\) can calculated using Eq. 4:

\[
\Delta G^* = \Delta H^* - T\Delta S^* \tag{5}
\]

All thermodynamic functions are tabulated in Table 3. The values of energy of activation (\(E_a\)) do not indicate a reduction of the corrosion rates with adding SiO2 content but changing the properties of the steel surface lead to decreasing the corrosion rate in the concrete solution (Novoa, 2016).

The enthalpy of activation of the corrosion process (\(\Delta H^*\)) took positive value which reflected an endothermic process and also decreased with increasing SiO2 contents (Fig. 3 and 4).

Values of the calculated \(\Delta G^*\) were nearly constant and have positive value at all temperature which describe the process as non-spontaneous. The negative values of the entropy means that the reactant had some degree of...
Fig. 3(a-d): AFM 3D views of steel rebar polarized in artificial concrete solution containing 3.5% NaCl, (a) Without SiO$_2$ NPs and with adding SiO$_2$ NPs (12 nm) (b) -1, (c) -3 and (d) -5%

Fig. 4(a-d): Cyclic polarization voltagram of steel rebar polarized in artificial concrete solution containing 3.5% NaCl, (a) Without SiO$_2$ NPs and with adding SiO$_2$ NPs (12 nm) (b) -1%, (c) -3% and (d) -5% at 20°C
freedom and it reduced by increasing the SiO2 content and remain constant at all concentrations. The surface morphology changing was examined by Atomic force microscope as shown in (Fig. 3).

These images clearly supported the investigations deduced from the electrochemical polarization procedure, since, the surface morphology in 3.5% NaCl without using SiO2 is very rough containing deep valley (Fig. 3a) while the surface roughness on using SiO2 NPs reduced SiO, Fig. 3b-d.

The probability of pitting corrosion occurrences was investigated by cyclic polarization procedure (Ebell et al., 2016; Chauhan and Sharma, 2019; Gu et al., 2018) as mentioned in the experimental part. Fig. 3 shows the cyclic Volta grams and the histories loops which have formed during the polarization in each solution. A pitting at high positive pitting potentials with very small histories loop area for the steel rebar in simulate concrete electrolyte with different concentrations of SiO2 as additive and 3.5% NaCl (Fig. 4a-d).

These polarizations voltogram show that remarkable pitting area produced when cyclic polarization conducted for steel rebar in simulate concrete solution with 3.5% NaCl without adding SiO2 NPs. In another hand the SiO2 NPs at all concentrations reduces the pitting area and fully diminished the pitting problem.

CONCLUSION

The following conclusions have drowned from this research; all SiO2 concentration lead to enhancing the corrosion protection efficiency of steel rebar in concrete at seawater environment. The pitting corrosion of the steel rebar is totally overcome on using SiO2 NPs.

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