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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_2NPs. 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_2NPs

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).

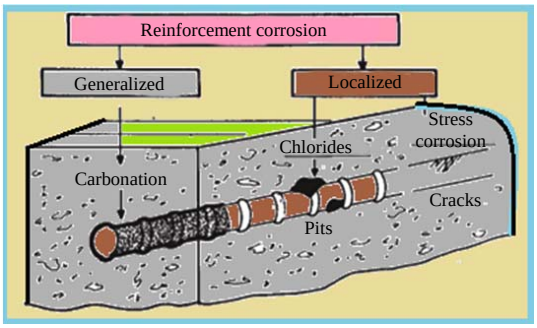

Fig. 1: Scheme represents factors responsible for corrosion of steel bar in concrete

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

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left to dry, the steel sample serve as working electrode was warped with adhesive tape except for a known distance which was (16.55 cm^2), 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 SiO_2 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	0.730
Ni	0.130
Cr	0.120

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 SiO_2 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 ($g.m^{-2}d^{-1}$), penetration loss in (mmper year (mmpy)) were measured and calculated from above Tafel plots while polarization resistance Rp in ($\Omega.cm^2$) and corrosion protection efficiency (%) were calculated using the Eq. 1 and 2 (Kaesche, 2003) are listed in Table 1:

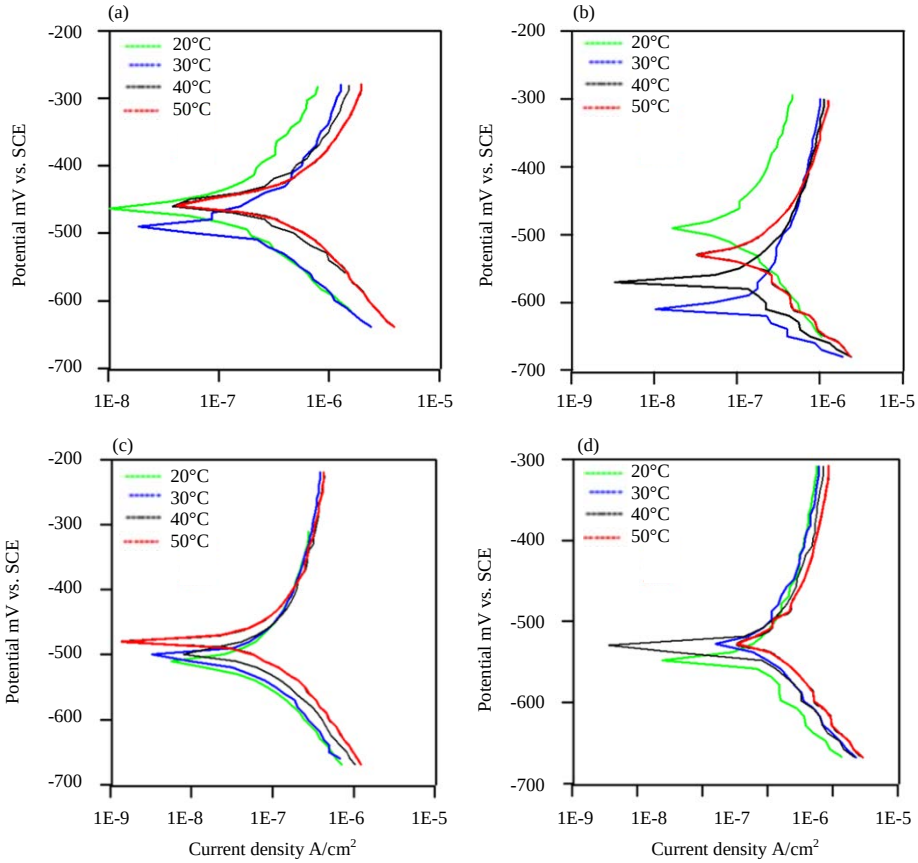

Fig. 2(a-d): Tafel plots of steel rebarpolarized in simulated concrete solution containing TiO_2 NPs (a) Without, (b) -1, (c) -3.0 and (d) -5.0%) with 3.5% NaCl and different temperatures

Table 2: Corrosion rate parameters of steel rebar polarized in simulated concrete solution containing SiO_2 NPs (12 nm) and 3.5% NaCl at 20, 30, 40, 50°C

SiO_2 (%)	T (K)	E_{corr} (mV)	i_{corr} ($A*10^{-6}cm^{-2}$)	βc (mV/Dec)	βa (mV/Dec)	R_p $\Omega.cm^2$	CR (WL) $g.m^{-2}d^{-1}$	CR (PL) mmpy	PE (%)
0	293	-458.7	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	145.6	1766.12	14.10	0.653	41.33
	303	-468.3	77.07	-118.4	137.3	2127.56	19.30	08.950	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	-149.0	224.7	2448.49	15.70	0.731	37.53
	313	-477.7	68.29	-134.3	194.2	2354.25	17.10	0.793	68.35
	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
6	323	-475.4	46.46	-145.4	216.7	1755.41	11.60	0.539	81.96

$$Rp = \frac{\beta a \beta c}{2.303(i_{corr})(\beta a+\beta c)} \quad (1)$$

Where, βa and βc are Tafel slopes:

$$IE\% = \frac{i_{corr}(wo)^{-1}\,Corr(W)}{i_{corr}(Wo)} \times 100 \quad (2)$$

Where, i_{corr} (wo) and i_{corr} (w) are the corrosion current without and with using SiO_2NPs, respectively (Table 2).

The Rp values were decreased with adding SiO_2 NPs which may attributed to the metallic property of the steel rebar which remain unaffected by corrosion in comparison with SiO_2 free concrete as the corrosion product (Iron oxides) have less electrical conductivity (Hashim and Kassim, 2014).

The corrosion Protection Efficiency(PE%) increased with increasing the added amount of SiO_2 NPs, this result may explained by the effect of SiO_2 to stabilized the protective layer on the steel rebar (Razaqpur and Isgor, 2009). A maximum PE was achieved on using 5% SiO_2 while using 1% SiO_2 exhibited the lowest PE (23%). The thermodynamic properties (Ea, G*, H* and S*) were calculated using the following relationships (Abeng *et al*., 2017):

$$Log\ CR = log\ A - \frac{Ea}{2.303RT} \quad (3)$$

$$Log\frac{CR}{T} = log\left(\frac{R}{Nh}\right) + \frac{\Delta Sa}{2.303R} - \frac{\Delta Ha}{2.303RT} \quad (4)$$

Where:

R : The universal gas constant (8.314 J mol^{-1} K^{-1})
T : The temperature (K)
h : The Plank's constant (6.626176×10^{-34} Js)
N : The Avogadro's number (6.022×1023 mol^{-1})
ΔSa : The entropy of activation
ΔHa : The enthalpy of activation

Table 3: Thermodynamic function (Ea, ΔH*, ΔS* and ΔG*) of steel rebar in/concrete electrolyte solution containing 3.5 NaCl and SiO_2 NPs

SiO_2 (%)	T (K)	Ea (kJ/mole)	ΔH* (kJ/mol)	ΔS* (kJ/mol.K)	ΔG* (kJ/mol)
0	293	16.090	18.569	-0.144	60.761
	303				62.201
	313				63.641
	323				65.081
1					
	293	12.485	6.467	-0.188	61.551
	303				63.431
	313				65.311
	323				67.191
3					
	293	13.296	7.218	-0.187	62.009
	303				63.879
	313				65.749
	323				67.619
5					
	293	13.861	8.371	-0.188	63.455
	303				65.335
	313				67.217
	323				69.095

Then, G can calculated using Eq. 4:

$$\Delta Ga = \Delta Ha - T\Delta Sa \quad (5)$$

All thermodynamic functions are tabulated in Table 3. The values of energy of activation (Ea) do not indicates a reduction of the corrosion rates with adding SiO_2 content buit changing the properties the steel surface lead to decreasing the corrosion rate in the concrete solution (Novoa, 2016).

The enthalpy of activation of the corrosion process (ΔH*) took positive value which reflected endothermic process and also decreased with increasing SiO_2 contents (Fig. 3 and 4).

Values of the calculated ΔG***** 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

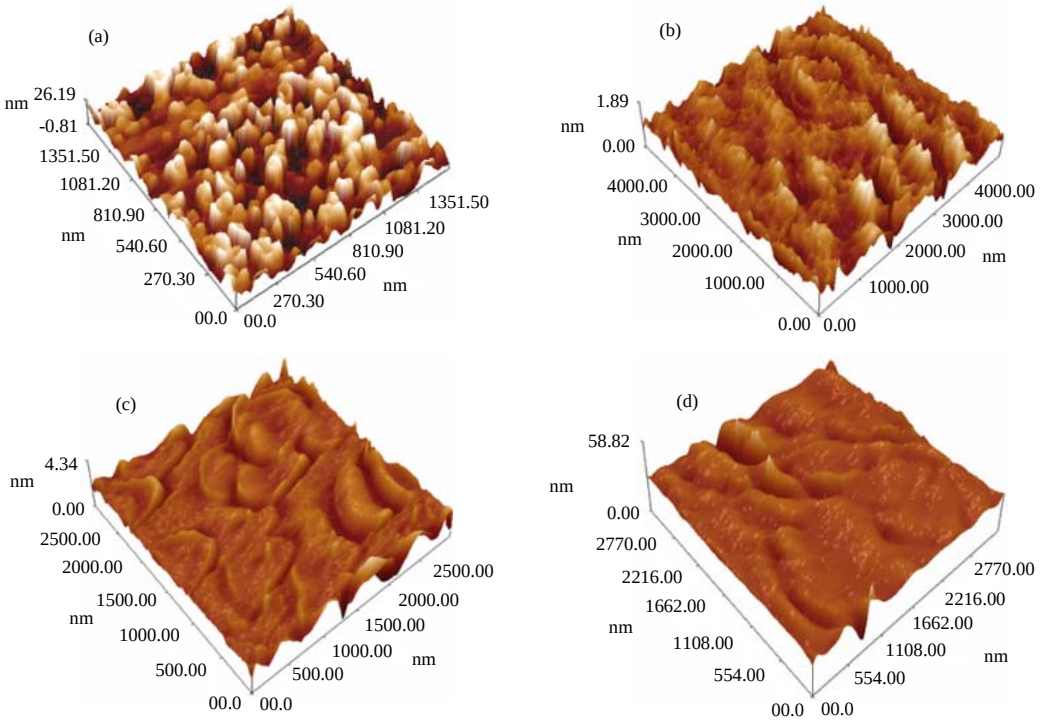

Fig. 3(a-d): AFM 3D views of steel rebar polarized in artificial concrete solution containing 3.5% NaCl, (a) Without SiO_2 NPs and with adding SiO_2 NPs (12 nm) (b) -1, (c) -3 and (d) -5%

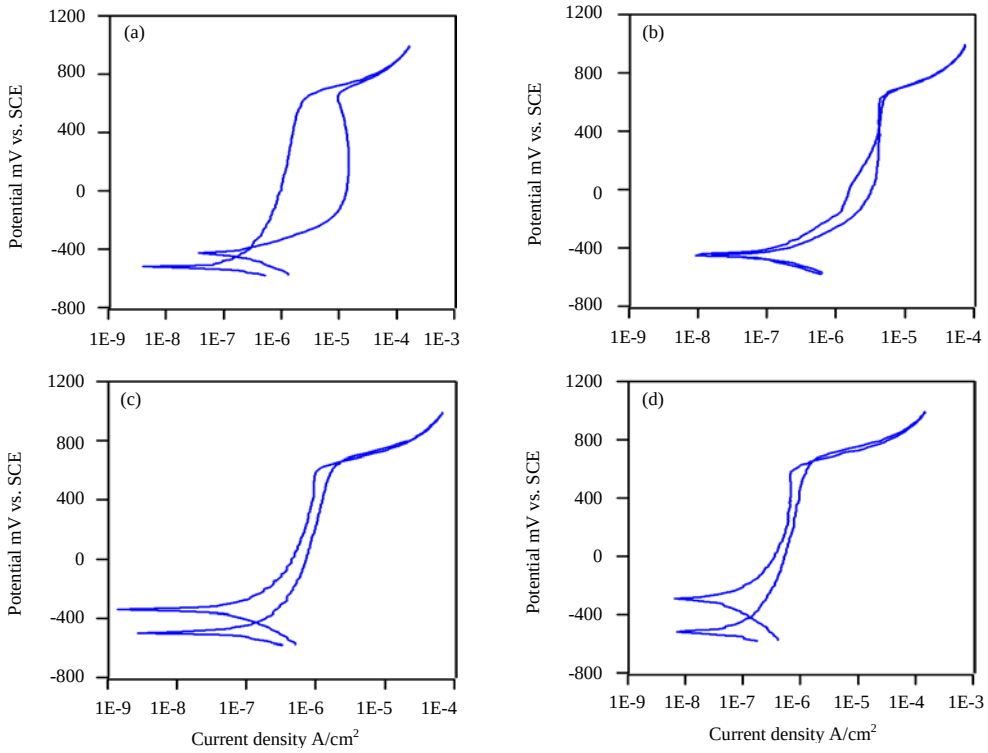

Fig. 4(a-d): Cyclic polarization voltagram of steel rebar polarized in artificial concrete solution containing 3.5% NaCl, (a) Without SiO_2 NPs and with adding SiO_2 NPs (12 nm) (b) -1%, (c) -3% and (d) -5% at 20°C

freedom and it reduced by increasing the SiO_2 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 SiO_2 is very rough containing deep valley (Fig. 3a) while the surface roughness on using SiO_2 NPs reduced SiO_2 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 SiO_2 as additive and 3.5% NaCl (Fig. 4a-d).

These polarizations voltagram show that remarkable pitting area produced when cyclic polarization conducted for steel rebar in simulate concrete solution with 3.5% NaCl without adding SiO_2 NPs. In another hand the SiO_2 NPs at all concentrations reduces the pitting area and fully diminished the pitting problem.

CONCLUSION

The following conclusions have drowned from this research; all SiO_2 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 SiO_2 NPs.

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