

Microscopic Studies on The Corrosion Resistance of Reinforced Carbon Steel

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The corrosion resistance of reinforced Carbon steel in saturated $\text{Ca}(\text{OH})_2$ solutions has been investigated. The influence of additions of vanadium and titanium micro-alloying elements on the corrosion resistance of carbon steel has been studied using weight loss , open Circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).. The results obtained from the steady state potential (E_{SS}) and the polarization resistance (R_p) measurements indicated the beneficial addition effects of Ti and V as micro-alloying elements for decreasing the corrosion rate. The grain refining due to micro-alloying additions plays an important role in an improvement of the corrosion resistance of the investigated steel.

Keywords: Carbon Steel, Vanadium, Titanium, Polarization and Electrochemical Impedance Spectroscopy.

1. INTRODUCTION

Deterioration of concrete, resulting from corrosion of steel reinforcing, is an important problem. The newly developed micro-alloyed steels seem to be capable of combining excellent balance of high strength with other desirable engineering properties. The unique combination of properties is achieved by modifying the common hot-rolled carbon steel by means of small additions (micro-alloying) of some elements. In recent years, micro-alloying has been attracted great attention

and gained an importance to attain steels with attractive properties. Improvements in the mechanical properties of low carbon steels have been achieved by micro-addition of strong carbide forming elements such as Nb, V or Ti [1-20]. Micro-alloying elements are added intentionally to improve steel properties and influence the microstructure via the precipitation of a second phase [5]. The newly developed micro-alloyed steels seem to be capable of combining excellent balance of high strength with other desirable engineering properties. In recent years, there is a growing awareness of the necessity to reduce the weight of products made of steel. The corrosion resistance of steel is mainly related to its passivation behavior. Various elements are added as alloying elements to modify the structure and /or to increase the corrosion resistance of steel. Chloride ion has acquired a significant reputation as the most aggressive ion among the various anions encountered in corrosion environments [2]. Numerous investigations have been carried out to determine the effect of the chloride concentration on the corrosion behavior of reinforcing steel in alkaline solutions and simulated concrete pore solutions, with the purpose to establish a unique critical chloride concentration for pitting initiation. However, the chloride threshold depends on several variables. Many researchers reported significant scatter values for chloride threshold concentrations [3].

The aim of this study is to determine the influence of additions of vanadium and titanium as micro-alloying elements on the corrosion performance of carbon steel in a simulated concrete environment. The corrosion resistance of carbon steel will be investigated by weight loss, open circuit potential (OCP), potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

2.1 Chemical composition

Table 1. Chemical composition of investigated non-micro-alloyed, V-micro-alloyed and Ti-micro-alloyed steels.

Steel No	Chemical composition, wt%				
	C	Mn	Si	V	Ti
X1	0.094	0.63	0.18		
X2	0.214	0.94	0.26		
X3	0.304	0.79	0.20		
X4	0.395	0.72	0.14		
V1	0.210	1.00	0.28	0.12	
V2	0.195	1.27	0.32	0.22	
V3	0.300	1.03	0.37	0.08	
V4	0.320	0.97	0.35	0.20	
T1	0.230	0.68	0.20		0.037
T2	0.230	1.61	0.14		0.029
T3	0.250	0.87	0.71		0.058
T4	0.220	1.27	0.36		0.062
T5	0.300	1.16	0.31		0.068
T6	0.136	1.08	0.50		0.100
T7	0.214	1.02	0.28		0.120
T8	0.230	0.98	0.37		0.200

Table (1) represents the chemical composition of investigated steels. The three types of carbon steel samples used in this work are non micro-alloying carbon (Steel X), Vanadium micro-alloyed steel (Steel V) and Titanium micro-alloyed steel (Steel T). Vanadium and Titanium as Micro-alloying elements were added as ferrovanadium and ferrotitanium after tapping one half of the heat. The ladle was held for 5 minutes before teeming to achieve homogeneity of the composition and to minimize contamination of the steel samples with non-metallic inclusions [4].

2.2 Materials

The area of the steel sample used in weight loss and electrochemical measurements was 0.15 cm². It was fitted into glass tubing of appropriate internal diameter by an epoxy resin (Araldite type), leaving only the front surface areas to contact the test solutions. Surface of the electrodes was abraded with emery papers of different grades down to 4/0, degreased with acetone then thoroughly rinsed with bi-distilled water and air dried. All the test solutions (Ca(OH)₂ solution at pH = 12, 0.5 M Na₂CO₃ and 0.6 M NaCl) were prepared from bi-distilled water and reagent grade chemicals.

2.3 Polarization and EIS measurements

Polarization measurements were carried out in Ca(OH)₂ solution at pH 12 by scanning the potential at scan rate 0.5mVs⁻¹ using SCE as reference electrode and platinum as counter electrode. All the electrochemical measurements will be carried out using A VOLTA LAB 40 (Model PGZ301) with the aid of software (Volta Master 4 version 7.08). The electrode potential was measured periodically until the corresponding stationary value (E_{SS}) was reached.

2.4. Open circuit potential measurements

Open circuit potential (OCP) of mechanically polished carbon steel electrodes was recorded over a period of 90 min. in naturally aerated [Ca(OH)₂, Ca(OH)₂ + 0.5M Na₂CO₃ and Ca(OH)₂ + 0.6M NaCl] at pH 12.

2.5. Weight loss measurements

The weight losses (mg/cm²) of carbon steel specimens in different aqueous mediums at pH 12 [Ca(OH)₂, Ca(OH)₂ + 0.5M Na₂CO₃ and Ca(OH)₂+0.6M NaCl] will be determined. Triplicate specimens were exposed to each condition and the mean weight loss was reported.

2.6. Metallographic examination

Optical microscopy was carried out on the examined hot rolled steel samples after polishing and etching as shown in figure (1).

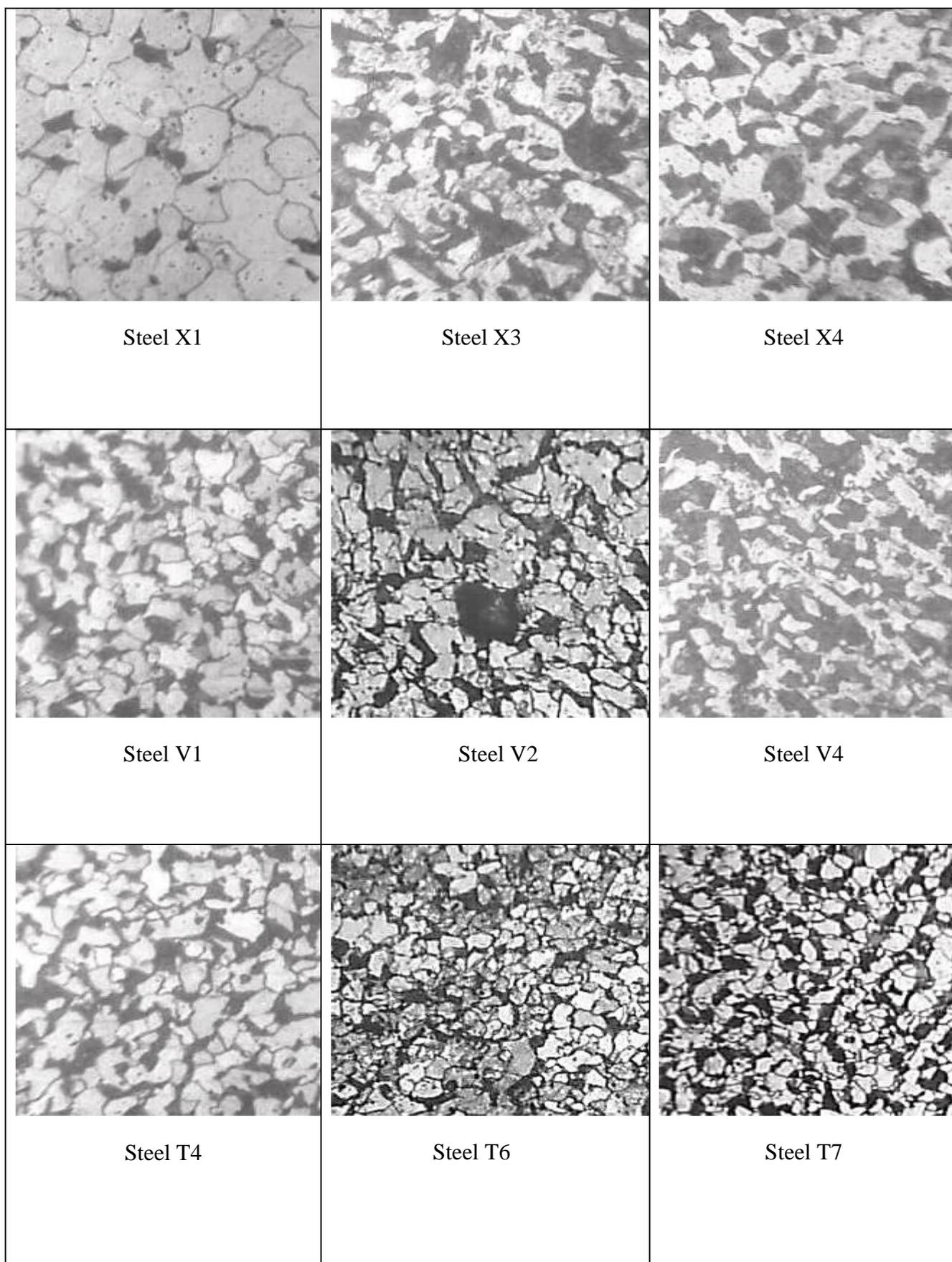


Figure 1. Micrographs represent the microstructure of investigated steels.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

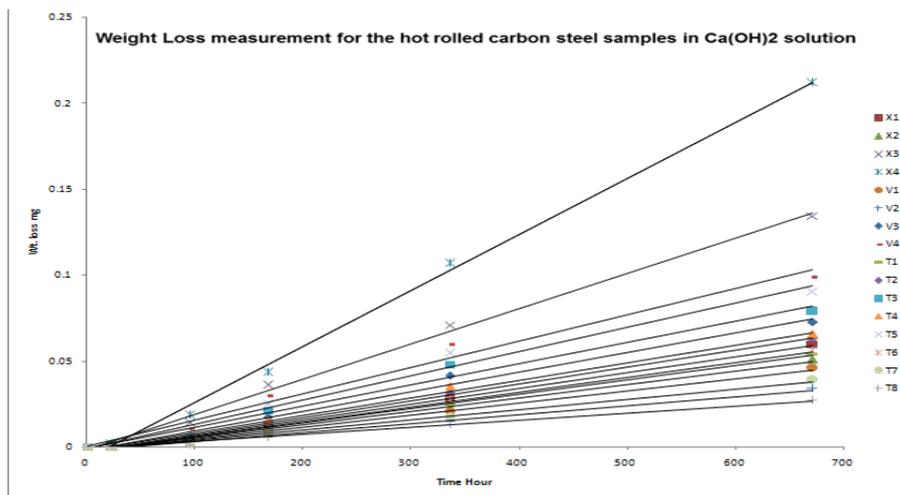


Figure 2. Weight loss measurement for hot rolled carbon steel samples in Ca(OH)_2 solution at pH 12

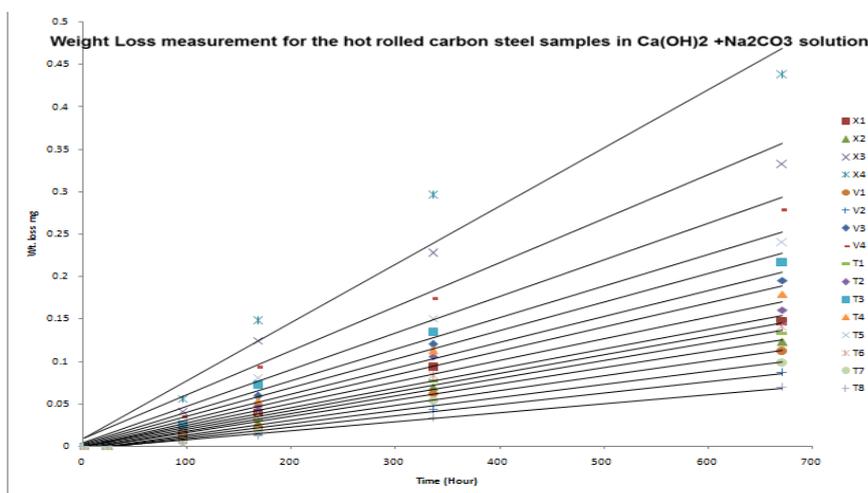


Figure 3. Weight loss measurement for hot rolled carbon steel samples in $\text{Ca(OH)}_2 + 0.5\text{M Na}_2\text{CO}_3$ solution at pH 12

Figs. 2- 4 show the weight loss–time curves of carbon steel in different aqueous mediums at pH 12 [Ca(OH)_2 , $\text{Ca(OH)}_2 + 0.5\text{M Na}_2\text{CO}_3$ and $\text{Ca(OH)}_2+0.6\text{M NaCl}$]. The corrosion rate of the examined carbon steel samples in saturated Ca(OH)_2 solution is lower than the solutions containing anions like chloride and carbonate. The results indicated that the carbon steel containing vanadium and titanium as micro-alloying elements exhibit lower corrosion rate than the free one. It can be concluded that the addition of micro-alloying elements like V and Ti to the reinforced carbon steel is playing an important role in the improvement of the mechanical properties [4] and corrosion resistance of the micro-alloyed carbon steel.

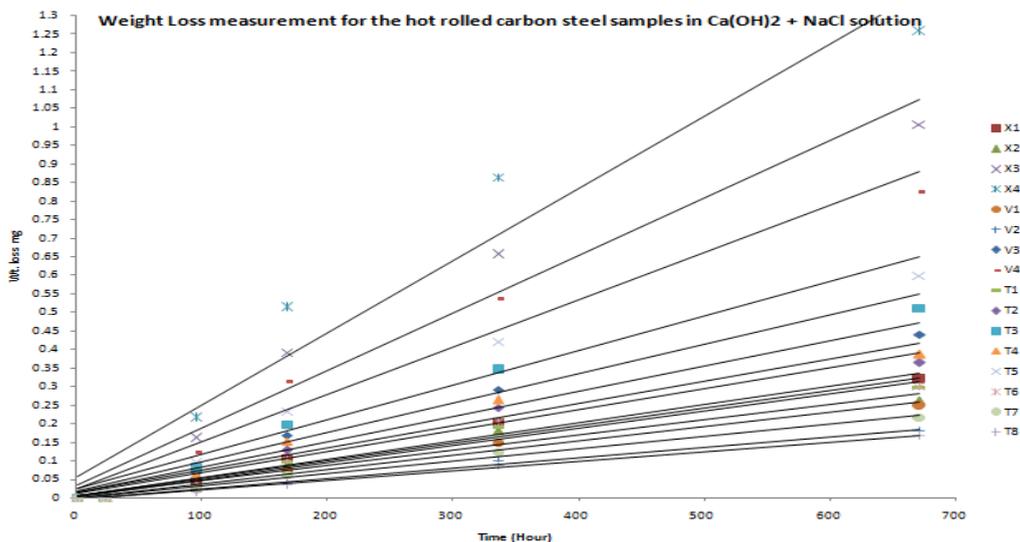


Figure 4. Weight loss measurement for hot rolled carbon steel samples in $\text{Ca(OH)}_2 + 0.6\text{M NaCl}$ solution at pH 12

The results may be attributed to the grain size refinement, which is the main factor of decreasing the corrosion rate of the micro-alloyed carbon steel samples. Vanadium is a good aspect of alloying elements of the steel, as it exists on crystal and grain boundary. It inhibits the growing of grain and causes its refinement. In additions, it dissolves much less in ferrite than in austenite, while the addition of Ti to the carbon steel can form number of compounds that enhances the grain refinement. A small amount of Ti is effective to enhance grain refinement in reheated or continuously cast steels because they retard the grain growth of re-crystallized austenite. The corrosion performance is mainly dependent on grain size as dominant factor. It can be concluded that the smaller the grain size, the lower the corrosion rate. It can be seen that the corrosion rate of the examined samples increases with increasing carbon content. The results can be attributed to the formation of carbides, which lead to a significant deterioration of the resistance to localized corrosion such as intergranular corrosion and stress corrosion cracking, which limited the use of carbon to very low level. The lower corrosion rate observed for the samples containing more content of Mn was attributed to the grain size refinement. It clear that the corrosion resistance of steel is substantially improved by the addition of silicon. The lower corrosion rate experienced for the sample containing Si can be attributed to formation of thin dense and adherent oxide films, which protect the surface of the steel from further attack [15]. This finding confirms that the addition of micro-alloying elements as Ti and V promotes the grain size refinement and thus improving the corrosion resistance of the micro-alloyed carbon steel.

3.3 Open circuit potential measurements

The variation of the open circuit potential (OCP) of carbon steel electrodes as a function of exposure time in naturally aerated Ca(OH)_2 solution at pH 12 is shown in Fig.5.

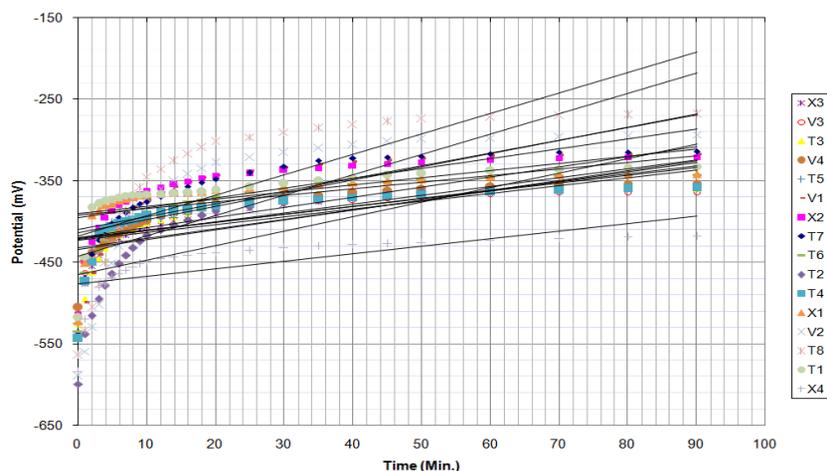


Figure 5. Open circuit potential for carbon steel samples in saturated Ca(OH)_2 solution at pH 12

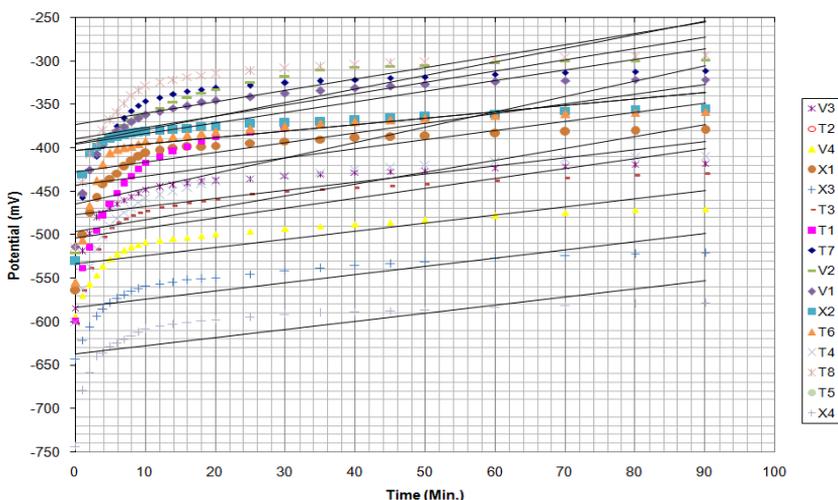


Figure 6. Open circuit potential for carbon steel samples in saturated $\text{Ca(OH)}_2 + 0.5\text{M Na}_2\text{CO}_3$ solution at pH 12

The potential rapidly shifts towards less negative potential during the initial stage of immersion followed by a slow shift in potential during the middle stage of immersion and eventually attain a quasi steady state of potential during the last stage of exposure.. The shift in the steady state potential occurs in the following order: Steel X > Steel V > Steel T. The data of open circuit potential for examined carbon steel samples immersed in saturated Ca(OH)_2 solution at pH 12 containing 0.5M Na_2CO_3 and 0.6M NaCl are displayed in Figs. (6) and (7), respectively. The samples have a tendency to shift towards less negative potential values immersion. The open circuit potentials of samples containing less carbon content and high V or Ti micro-addition have a tendency to shift towards more noble potential values . There are two competing processes during open circuit potential measurement, the first is the oxide film formation and the second one is oxide film dissolution. The latter process is predominant process as the concentration of chloride and carbonate ions increase. The results can be attributed to the high susceptibility of the oxide film to dissolution process in presence of both ions. In

addition, the decrease in the rate of oxide film thickening may be attributed to the partial dissolution of the formed oxide.

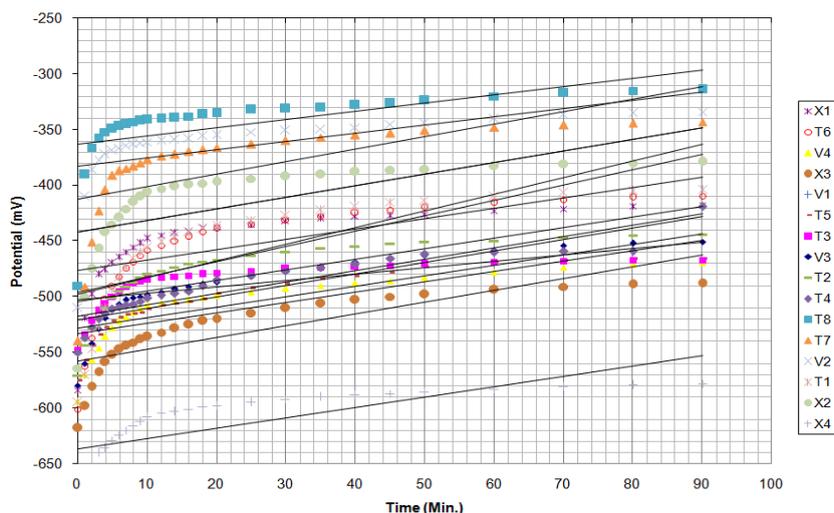


Figure 7. Open circuit potential for carbon steel samples in saturated $\text{Ca(OH)}_2 + 0.6\text{M NaCl}$ solution at pH 12

The results obtained from the monitoring the potential with time are in good agreement with that reported previously for measurement of potential with immersion time [15]. The presence of Cl^- in the solution is accompanied by a slow shift in the open circuit potentials toward negative direction, implying that the formed oxide film is susceptible to anodic dissolution in presence of Cl^- ion [16]. Therefore, the observed trend in OCP values can be explained by considering the competition processes between the oxide film formation and dissolution. The rapid shift in potential during the initial stage of monitoring can be attributed to high formation process of the oxide film, which causes a rapid shift in the OCP toward a noble direction. The slow rate in potential observed during the last stage of monitoring can be explained by increasing the rate of oxide film dissolution.

3.4 Potentiodynamic Polarization measurements

The results of cathodic and anodic potentiodynamic polarization curves for carbon steel electrodes recorded at scan rate 0.5mVs^{-1} in saturated Ca(OH)_2 solution at pH 12 are shown in Figs. 8-11. The samples were immersed in the test solution for 90 minutes until a steady state potential was attained and anodic polarization was subsequently commenced. Generally, all scans exhibit similar performance over the potential domain examined versus SCE. In Ca(OH)_2 solution at pH=12. The cathodic curves are almost similar, indicating that the same cathodic reaction takes place on the surface. When anodic polarization starts, the current in the active region increases due to metal dissolution. At more positive potential the rate merges into a more or less plateau dependent on percentage of the V and Ti additions. The electrochemical dissolution parameters including the corrosion potential (E_{corr}) and the corrosion current density (I_{corr}) were estimated and quoted in table

(2). The results indicated clearly that E_{corr} shifts towards more negative and the rate of corrosion I_{corr} increases with increasing the carbon percentage.

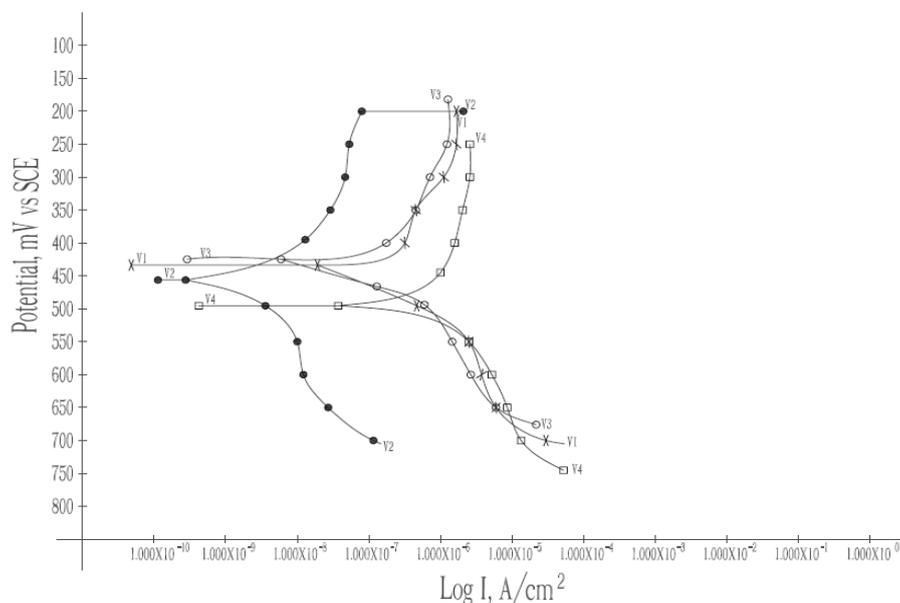


Figure 8. Potentiodynamic polarization curve for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.

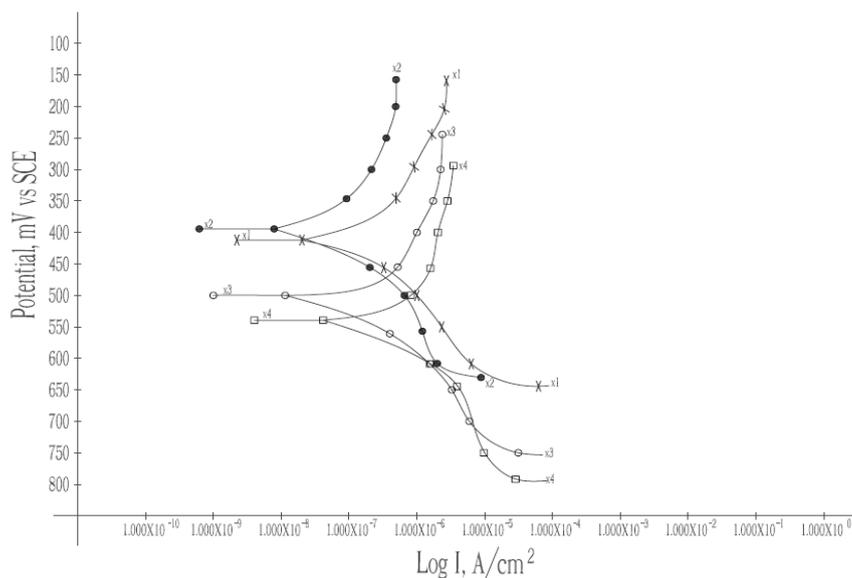


Figure 9. Potentiodynamic polarization curve for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.

The corrosion rate of carbon steel decreases with the addition of V and Ti as micro-alloying elements. It is clear that the influence of Ti addition is more effective than the influence of V addition. In case of Vanadium addition, the results can be attributed to an increase in strength, hardness, creep

resistance, impact resistance due to formation of hard vanadium carbides and reducing the grain size of the steel. The additions of titanium as an alloying element increase the carbide stabilization. It combines with carbon to form titanium carbides, which are quite stable and hard to dissolve in steel. Thus, tends to minimize the occurrence of inter-granular corrosion [17]. The influence of chloride ions on the potentiodynamic polarization behavior of carbon steel in saturated $\text{Ca}(\text{OH})_2$ solution + 0.6M NaCl at pH =12 is shown in figure (12).

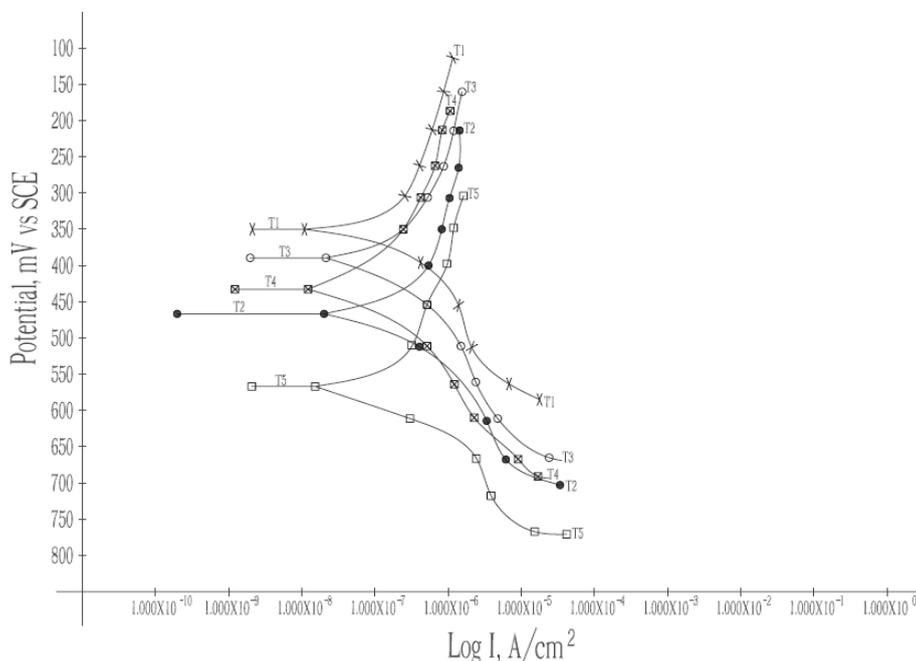


Figure 10. Potentiodynamic polarization curve for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.

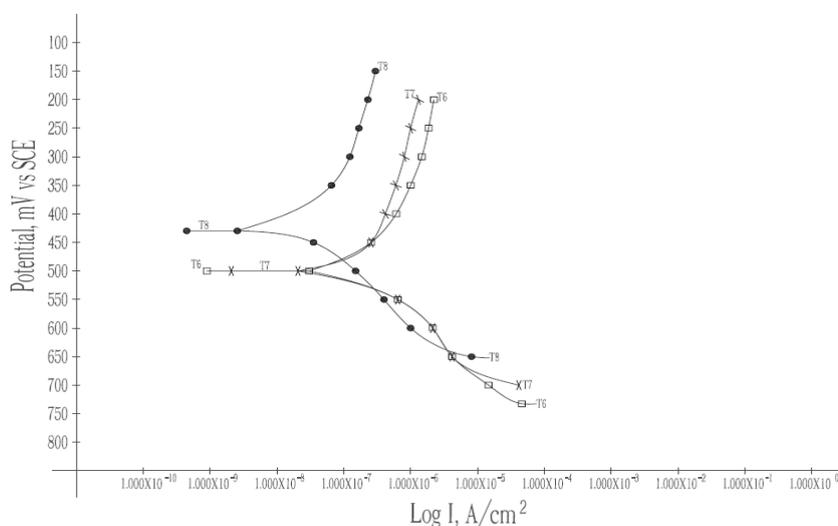


Figure 11. Potentiodynamic polarization curve for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12.

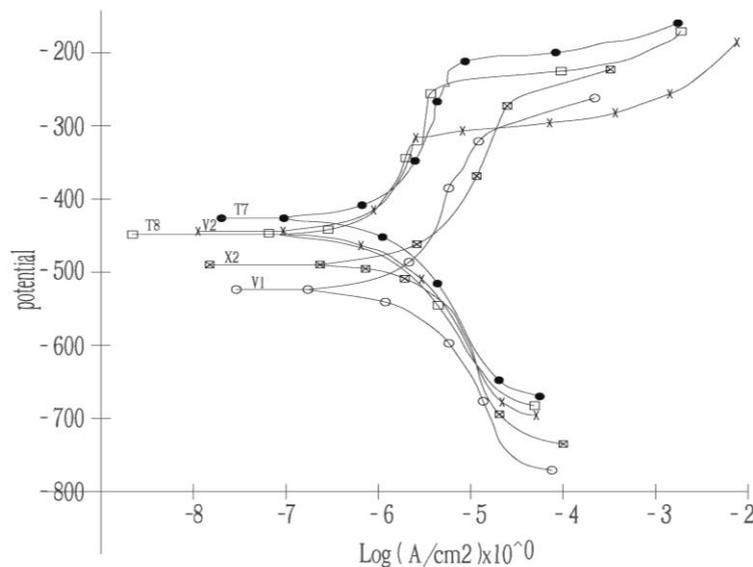


Figure 12. Potentiodynamic polarization curve for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution + 0.6 M NaCl at pH 12.

Table 2. Polarization parameters for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution at pH 12

	Icorr. A	Icorr. A/Cm2	bc V/dec	ba V/dec	Rp Ohm	E-begin V	E-end V	Corr. rate (mm/year)	Corr. Rate ($\mu\text{m}/\text{year}$)	Corr. Resistance
T8	3.05E-07	3.89E-07	0.179	0.106	2.71E+04	-0.464	-0.373	2.91E-03	2.91E+00	2.61E+04
V2	1.35E-07	1.72E-07	0.67	0.098	2.13E+04	-0.483	-0.435	3.29E-03	3.29E+00	1.22E+04
T7	3.59E-07	4.57E-07	0.11	0.065	8.69E+03	-0.524	-0.469	3.42E-03	3.42E+00	9.63E+03
V1	4.02E-07	5.12E-07	0.104	0.065	7.29E+03	-0.461	-0.417	3.54E-03	3.54E+00	1.27E+04
X2	3.73E-07	4.76E-07	0.133	0.083	1.28E+04	-0.42	0.356	3.56E-03	3.56E+00	3.38E+04
T1	4.14E-07	5.27E-07	0.15	0.117	1.84E+04	-0.394	-0.313	3.95E-03	3.95E+00	3.76E+04
T6	4.36E-07	5.56E-07	0.127	0.789	9.82E+03	-0.525	-0.47	4.16E-03	4.16E+00	1.67E+04
X1	4.45E-07	5.67E-07	0.105	0.091	9.35E+03	-0.466	-0.381	4.24E-03	4.24E+00	2.73E+04
T2	4.47E-07	5.69E-07	0.13	0.093	1.17E+04	-0.497	-0.439	4.26E-03	4.26E+00	2.23E+04
T4	4.86E-07	6.19E-07	0.142	0.93	1.18E+04	-0.462	-0.394	4.64E-03	4.64E+00	3.29E+04
T3	5.45E-07	6.95E-07	0.14	0.082	9.15E+03	-0.417	-0.366	5.20E-03	5.20E+00	2.21E+04
V3	5.50E-07	7.00E-07	0.148	0.108	1.26E+04	-0.469	-0.389	5.24E-03	5.24E+00	3.76E+04
T5	6.58E-07	8.38E-07	0.109	0.074	5.30E+03	-0.589	-0.548	6.27E-03	6.27E+00	1.33E+04
V4	6.99E-07	8.91E-07	0.1	0.061	3.76E+03	-0.517	-0.475	6.67E-03	6.67E+00	8.79E+03
X3	9.95E-07	1.27E-06	0.155	0.82	5.57E+03	-0.535	-0.471	9.48E-03	9.48E+00	1.22E+04
X4	1.85E-06	2.35E-06	0.125	0.104	3.06E+03	-0.578	-0.509	1.76E-02	1.76E+01	1.47E+04

Table 3. Polarization parameters for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution + 0.6M NaCl at pH 12.

	Ecorr. mV	i corr. $\mu\text{A}/\text{cm}^2$	Rp kohm.cm ²	β_a mV	β_c mV	Corrosion $\mu\text{m}/\text{Y}$
X2	-500.6	1.0666	8.63	58.3	-57.2	12.46
T 8	-459.6	0.3056	25.95	57.3	-44.7	3.571
V 2	-455.2	0.3565	25.07	62.8	-50.8	4.165
V 1	-533.8	0.5353	12.81	46.0	-41.0	6.255
T7	-436.5	0.4239	21.28	60.3	-53.2	4.953

The curves exhibit a passive region that disappears as the potential increases in the noble direction. In addition, the polarization resistance, which is proportional to the inverse of the instantaneous corrosion rate, decreases with exposure time progresses. Table (3) shows the polarization parameters for carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution + 0.6 M NaCl at pH 12. The results indicate clearly the shifts in E_{corr} towards more negative. The addition of V and Ti decreases the rate of corrosion I_{corr} and the influence of Ti addition is more effective than the influence of V addition. Addition of chloride ions markedly increased the corrosion rate of steel as indicated from the lower value of R_p and the more negative E_{ss} values. In general, the presence of chloride and carbonate ions is the controlling factor, which causes corrosion of reinforcement in concrete to proceed to an unacceptable degree. These ions may either present in the concrete constituents from the beginning or introduced into the concrete through ingress during the service life. The presence of chloride shifts corrosion potential towards less noble direction and decreases the corrosion resistances, positively suggesting that the chloride ions speed up the corrosion rate of carbon steel. It is widely known that chlorides can induce the corrosion of reinforcing steel in concrete by causing breakdown of the passive film on the steel surface [18].

Chloride ions are the major cause for the corrosion of steel reinforcement in concrete. There are several ways by which chlorides can be introduced into concrete. They may exist at small levels within the mix ingredients of concrete (e.g. aggregates), or they may be introduced by the use of a chloride-containing admixture (e.g. calcium chloride as an accelerator) or saline water as mixing water (when fresh water is not available). However, chlorides in concrete most often come from the service environment to which the concrete structure is exposed (e.g., exposure to deicing salt or a marine environment) [19]. Therefore, the difference in corrosion rate is caused by a difference in composition and quantity of corrosion products formed on the steel surface.

3.5 Electrochemical impedance spectroscopy measurements

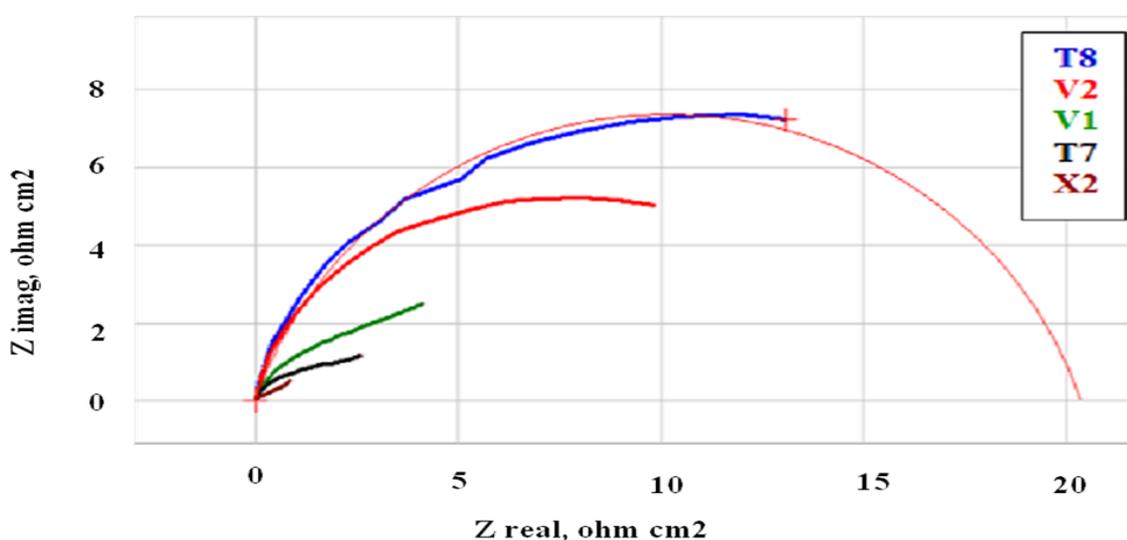


Figure 13. Nyquist plot for the examined Carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution +0.6 M NaCl at pH 12

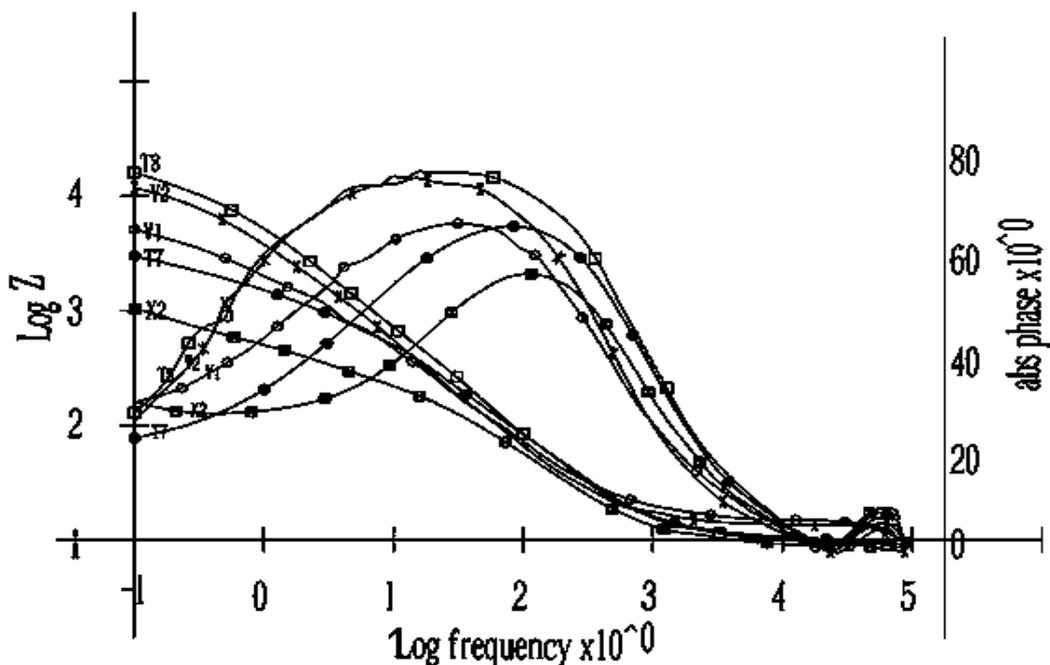


Figure 14. Bode plot for the examined carbon steel samples in saturated Ca(OH)_2 solution + 0.6M NaCl at pH 12

The impedance measurement was performed over the frequency range of 100 kHz to 100 mHz. Figures 13-14 show the impedance data of micro-alloyed carbon steel samples immersed in saturated Ca(OH)_2 solution + 0.6 M NaCl at pH 12, respectively. The impedance data shown in Fig. 13 does not show perfect semicircles. This behavior can be attributed to the frequency dispersion as a result of roughness and non-homogeneities of the electrode surface. Thus, the capacitive semicircle is correlated with the dielectric properties and the thickness of barrier adsorbed film. The presence of micro-alloyed elements changes the impedance plots in both shape and size.

Table 4. Data obtained from EIS measurements for carbon steel in saturated Ca(OH)_2 solution at pH 12.

	R_s ohm.cm ²	R_p kohm.cm ²	C_{dl} μF/cm ²
X2	29.74	1.144	439.6
V1	17.3	12.12	131.2
V2	8.96	14.31	55.57
T7	9.31	4.189	189.9
T8	26.1	20.42	49.24

The plots exhibited impedance spectra consisted of one capacitive loop at the higher frequencies, which was attributed to a Faradaic process involving a charge transfer resistance in parallel with double-layer capacitance element. Impedance parameters, such as, charge transfer resistance R_{ct} , which is equivalent to R_p in Dc measurement, and the double layer capacitance C_{dl} are given in Table (4) for the examined carbon steel samples in saturated $\text{Ca}(\text{OH})_2$ solution + 0.6M NaCl at pH 12. It is obvious that the values of R_{ct} increase with increasing the concentration of micro-alloyed elements (Ti and V) and this in turn leads to a decrease in corrosion rate of micro-alloyed carbon steel. The charge transfer resistance increases as the concentration of the micro-alloying elements addition increases. Also, the values of double layer capacitance, C_{dl} , decrease with increasing the concentration of the micro-alloying elements addition. These values are obtained by fitting with $R_1 R_2 C_{dl}$ circuit. R_1 is resistance solution, R_2 is charge transfer resistance (R_{ct}), and C_{dl} is double layer capacitance. The data obtained from EIS measurements EIS gives a support and an evidence for the data obtained from the DC polarization for the tendency of steel to corrosion in saturated $\text{Ca}(\text{OH})_2$ solution decreases with micro-addition of Ti and V as alloying elements.

4. CONCLUSIONS

1- The addition of micro-alloying elements like V and Ti to the reinforced carbon steel is playing an important role in the improvement of corrosion resistance.

2-The data obtained from AC techniques gives a support and an evidence for the data obtained from DC technique for increasing of steel corrosion in saturated $\text{Ca}(\text{OH})_2$ solution containing chloride ion. .

3-The corrosion process of the steel samples corroded in saturated $\text{Ca}(\text{OH})_2$ solutions is mainly controlled by charge transfer reaction.

4-The grain size refinement is highly dependent on the amount of C, V and Ti content.

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