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INFLUENCE OF POTASSIUM DICHROMATE-ZN^{2+} SYSTEM ON CORROSION INHIBITION OF REBAR STEEL IN SIMULATED CONCRETE PORE SOLUTION

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ABSTRACT

The inhibition efficiency (IE) of Potassium dichromate - Zn^{2+} system in controlling corrosion of rebar steel in Simulated Concrete Pore Solution (SCPS) prepared in well water in the absence and presence of Zn^{2+} has been investigated by mass loss study. It can be seen from the data obtained that formulation consisting of 250 ppm of $K_2Cr_2O_7$ and 50 ppm of Zn^{2+} provides 98 % of inhibition efficiency. Inhibition was found to increases with an increasing concentration of Zn^{2+}. Polarization study confirms the formation of inhibitor film formed on the rebar steel surface. The nature of the protective film formed on the rebar steel surface was examined by UV-Visible, FTIR, CV, SEM, Edx and AFM spectral studies. The results obtained shows that the $K_2Cr_2O_7$ could serve as an effective inhibitor for the corrosion of rebar steel in simulated concrete pore solution.

Keywords: Concrete corrosion, Simulated concrete pore solution, Rebar steel, Potassium dichromate, Well water.

1.INTRODUCTION

Corrosion is the deterioration of materials by chemical interaction with their environment[1]. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals. The most widely used metal is iron (usually as steel) and the following discussion is mainly focused on rebar steel corrosion behaviour in simulated concrete pore solution. A corrosion inhibitor is a chemical additive, which, when added to a corrosive aqueous environment, decreases the rate of metal wastage existing in actively corrosive environments. It can perform in any one of the means such as anodic inhibitors, cathodic inhibitors, adsorption type corrosion inhibitors, or mixed inhibitors. The rate of corrosion can also be reduced by using corrosion inhibitors. There are corrosion inhibitors known to protect bare steel, and its usage is probably more attractive from the point of view of economics and ease of applications[2]. There is a wide range of inhibitors for steel in reinforced concrete[3-13].

The present work in undertaken

1) To assess the inhibition efficiency of $K_2Cr_2O_7$- Zn^{2+} in controlling corrosion of rebar steel in SCPS in well water in the absence and presence of Zn^{2+} using mass-loss method.
2) To study the mechanistic aspects of corrosion inhibition by polarization technique.
3) To evaluate the protective film formed on the metal surface by UV-Visible, Fluorescence, FTIR, CV, SEM , Edx and AFM spectral studies and
4) To propose the mechanism of corrosion inhibition based on the above results.

2. MATERIALS AND METHOD

2.1 Preparation of Simulated Concrete pore solution (SCPS):

Simulated concrete pore solution is mainly consisted of saturated calcium hydroxide
$Ca(OH)_2$, sodium hydroxide (NaOH) and potassium hydroxide (KOH) with the pH ~ 13.5[14]. A saturated calcium hydroxide solution is used in present study, as SCPS with the pH ~ 12.5.

Table1: Physico-chemical parameters of well water

Parameters	Value
Ph	8
Conductivity	$1770\mu\Omega^{-1}cm^{-1}$
Chloride	665 ppm
Sulphate	214 ppm
Total dissolved solids	1204 ppm
Total hardness	402 ppm
Total Alkalinity	390 ppm
Magnesium	83 ppm
Potassium	55 ppm
Sodium	172 ppm
Calcium	88 ppm

2.2 Preparation of the specimens:

Rebar steel specimens of 415 grades were used in the present study with Composition (wt. %): 0.06 S, 0.06 P, 0.11 P+S, 0.3 C, and the rest iron were used for the study. Rebar specimens of cylindrical structures of cross section 10 mm and height of 150 mm were used for weight loss study, specimens of exposed area 1 × 1 cm^2 with stem were used for electrochemical study. The Physico-chemical parameter of well water is given in **Table 1.**

2.3 Mass Loss Method

Determination of Corrosion Rate:

The weighed specimens in triplicate were suspended by means of glass hooks in 100 ml SCPS prepared in well water containing various concentration of Potassium dichromate in the presence and absence of Zn^{2+} for 24 hours, the specimen were taken out, washed in running water, dried, and weighed. From the change in mass of the specimens, corrosion rates were calculated using the following relationship:

CR = [(Weight loss in mg) / (Area of the specimens in dm^2× Immersion periods in days)] mdd

Corrosion inhibition efficiency (IE %) was then calculated using the formula:

$$I.E = 100[1-(W_2/W_1)]\ \%$$

where, W_1 and W_2 are weight losses of steel in uninhibited and inhibited solutions.

2.4 Surface Examinations study:

The rebar steel specimens were immersed in various test solutions for a period of 24 hours, After 1 day the specimens were taken out and dried. The nature of the film formed on the surface of rebar steel specimen was examined by various surface analysis techniques.

Potentiodynamic Polarization and AC Impedance:

Electrochemical studies were carried out in a CHI–Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was rebar steel. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters were calculated. The scan rate (V/S) was 0.01.Hold time was zero and quit time(s) was two.

UV visible absorbance spectra:

The instrument UV Spetord S-100 Analytic Jena was used for recording UV visible absorbance spectra.

Fourier Transform Infrared Spectra:

These spectra were recorded in a Perkin-Elmer-1600 spectrometer. The spectrum of the protective film was recorded by removing the film, mixing it with KBr and making the pellet.

Cyclic Voltammetry

Cyclic voltammograms were recorded in Versa STAT MC electrochemical system. A three-electrode cell assembly was used. The working electrode was rebar steel. The exposed surface area was 1 cm^2. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. The cyclic voltammetry curves were recorded in the scan range of −1.8 to −1.8 V (SCE) with a scan rate of 20 mV s^{-1}.

Scanning Electron Microscopic Studies (SEM& Edx):

The surface morphology measurements of the rebar steel were examined using Tescon, Vega3, and USA computer controlled scanning electron microscope. The elemental analysis of the rebar steel surface at the same condition was carried out using an energy dispersive X-ray analyzer (EDAX) [Brucker, Nano, GMBH, Germany] unit attached to the SEM machine.

Atomic Force Microscopic Studies (AFM):

Atomic Force microscopic measurements of the rebar steel surface were carried out by Pico SPM 9500-21 with the software version of Pico scan version 5.4.

3. RESULTS AND DISCUSSION

3.1 Mass loss method

Table 2: Corrosion Rate (CR) and Inhibition Efficiency (IE) of PDC- Zn^{2+} System to Rebar Steel immersed in SCPS prepared in well water for Immersion Period 1 day

Inhibitor PDC (ppm)	**Zn^{2+}**			
	0ppm		50ppm	
	CR (mdd)	**IE%**	**CR (mdd)**	**IE %**
0	1.44	-	-	-
50	0.54	63	0.14	90
100	0.38	74	0.084	94
150	0.32	78	0.078	95
200	0.21	85	0.049	97
250	0.16	89	0.035	98

It is observed from Table 2 that Potassium dichromate (PDC) shows some inhibition efficiency. 50 ppm of PDC has

63% IE and 250ppm of PDC shows 89% of IE. As the concentration of PP increases, the IE increases, and corrosion rate decreases. When 50 ppm of Zn^{2+} is added, the IE increases in each case ie., 50 ppm PDC has 90% IE and 250 ppm PDC shows 98 % IE. That is addition of PDC and Zn^{2+} increases the corrosion protection of rebar steel immersed in SCPS prepared in well water. That is, the system passes from active to passive region.

3.2 Analysis of potentiodynamic polarization study

When rebar steel is immersed in SCPS prepared in well water the corrosion potential was -959mV vs SCE (saturated calomel electrode). When $K_2Cr_2O_7$ (250 ppm) and Zn^{2+} (50 ppm) were added to the above system the corrosion potential shifted to the anodic side -754 mV vs SCE; that is noble side. This indicates that the passive film is formed on the metal surface in presence of inhibitor[15-21].

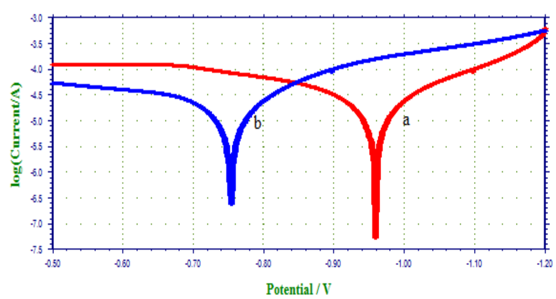


Figure 1 Polarization curve of rebar steel immersed in SCPS prepared in well water a)SCPS b)SCPS + $K_2Cr_2O_7$ 250 ppm+ Zn^{2+} 50 ppm

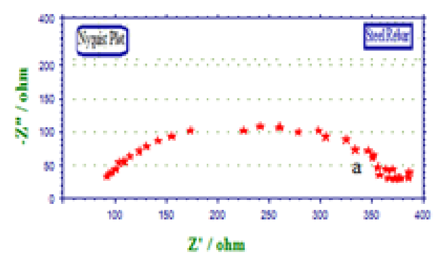
Table 3: Corrosion parameters of rebar steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from Polarization Study

System	SCPS	SCPS + 250 ppm PDC + 50ppm Zn^{2+}
E_{corr} (mV Vs SCE)	-959	-754
Bc (mV/ decade)	5151	5246
Ba (mV/ decade)	4016	2768
LPR (ohmcm^2)	1708.6	2074.5
Icorr (A/cm^2)	2.776 x10^{-5}	2.615 x10^{-5}

Further, the LPR value increases from 1708.6 ohm cm^2 to 2074.5 ohm cm^2; the corrosion current decreases from 2.776 x10^{-6}A/cm^2 to 2.615 x10^{-5} A/cm^2.When a inhibitor film formed on rebar steel surface, in presence of inhibitor system, the electron transfer from the metal surface towards the bulk of the solution is difficult and prevented. So corrosion rate decreases and hence Icorr decreases in presence of inhibitor system.

3.3 Analysis of AC impedance spectra

AC impedance spectra have been used to confirm the formation of protective film on the metal surface[22, 23]. The AC impedance spectra of rebar steel immersed in SCPS prepared in well water in presence and absence of inhibitors are shown in Figs. 2 (a, b) (Nyquist plots) and Figs.3 (a,b) (Bode plots).



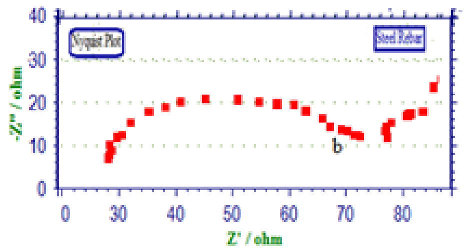


Fig.2: AC Impedance spectra of rebar steel immersed in (a): SCPS prepared in well water (b): SCPS + 250ppm of PDC+50ppm of Zn^{2+} (Nyquist plots)

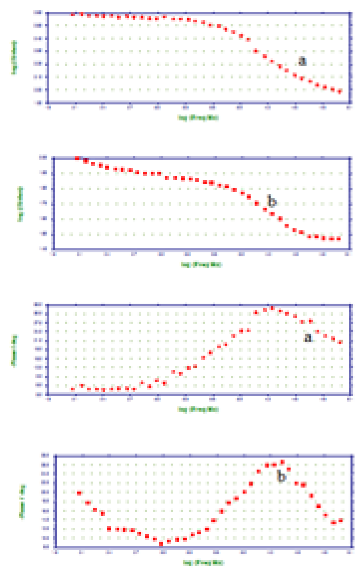


Fig. 3. Bode plots of rebar steel immersed in (a) SCPS prepared in well water (b) SCPS+ 250 ppm PDC+50 ppm Zn^{2+}

Table 4: Impedance parameters of rebar steel immersed in SCPS prepared in well water in the absence and presence of inhibitor system obtained from AC impedance spectra.

System	**Nyquist plot**		**Bode plot**
	R_t ohm cm^2	**C_{dl} F/cm^2**	**Impedance value log (z/ohm)**
SCPS	56.41	0.886 x 10^{-7}	1.914
SCPS+PP 250 ppm + Zn^{2+} 50 ppm	64.64	0.773 x 10^{-7}	1.994

From the Table 4 data, it is observed that when rebar steel is immersed in SCPS prepared in well water, R_t value is 56.41 ohm cm^2 and C_{dl} value is 0.886 x10^{-7} F/cm^2. When the inhibitor (PP 250 ppm and Zn^{2+} 50 ppm) is added to the above system R_t values increases from 56.41 ohm cm^2 to 64.64 ohm cm^2 and the C_{dl} value decreases from 0.886 x10^{-7}F/cm^2 to 0.773 x10^{-7} F/cm^2, The impedance log(z/ohm) value increase from 1.91 to 1,99.This suggests that a protective film is formed on the metal surface.

3.4 Analysis of UV-visible absorption spectra

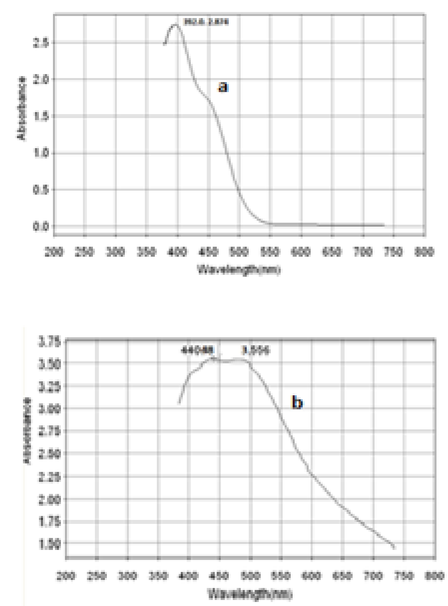


Fig.4:UV-Visible spectrum of solution containing (a) SCPS + pure PDC (b) SCPS+PDC+Fe^{2+}

The UV- visible absorption spectrum is used to confirm the protective film formed on the metal surface. The UV – visible absorption spectrum of an aqueous solution containing SCPS- PDC is shown in Fig.4

(a). A peak appears at 392 nm. When Fe^{2+} (as $FeSO_4$. $7H_2O$) is added a peak appears at 440 nm is shown in Fig 4(b), and there is decrease in intensity. There is shift in λ_{max} value. This indicates that a complex is formed between PDC - Fe^{2+}.

3.5 Analysis of FTIR spectra:

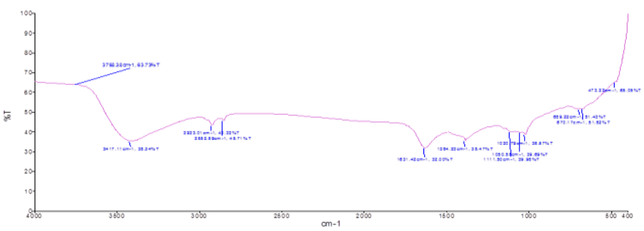


Fig.5 (a): FTIR spectrum of Pure Potassium dichromate

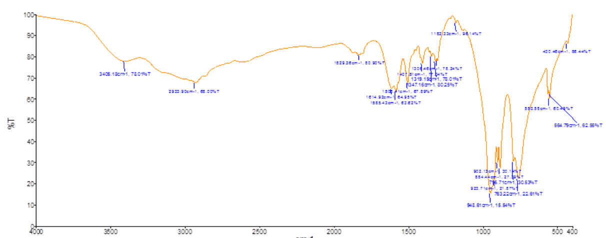


Fig.5(b): FTIR spectrum of film formed on the metal surface after immersion in aqueous solution containing SCPS + 250 ppm PDC + 50 ppm of Zn^{2+}

The FTIR (KBr) spectrum of pure Potassium dichromate is shown in figure 5(a). The Cr_2O_7 $^{2-}$ -stretching frequency appears at 1111.5. The FTIR spectrum of the film formed on the rebar steel surface after immersion in SCPS prepared in well water containing 250 ppm of $K_2Cr_2O_7$ and 50 ppm of Zn^{2+} is shown in figure 5(b). It is seen from the spectrum that the Cr_2O_7 $^{2-}$ stretching frequency of $K_2Cr_2O_7$ shifted from 1111.5 to 1319.15cm $^{-1}$. This confirms that the oxygen atom of the dichromate has coordinated with Fe^{2+} resulting in the formation Fe^{2+}- Cr_2O_7 $^{2-}$ complex on the metal surface. Also, there is possibility of anchoring of dichromate on the layer of consisting $CaCO_3$, CaO and $Ca(OH)_2$.

Peak appears at 763 cm^{-1} is due to Zn–O stretching. The -OH stretching frequency appears at 3406cm^{-1}. These observations indicate the presence of Zn $(OH)_2$ formed on the metal surface. Peak appears at 1347.16, 593.58 and 1506.41 cm^{-1} confirms the presence of calcium carbonate, calcium oxide, and calcium hydroxide on the metal surface.

3.6 Scanning Electron Microscopy (SEM):

SEM analysis was carried out for characterizing the inhibitive film formed on the rebar steel surface. SEM microscope of a polished rebar steel surface (control) in Figure 7(a) shows the smooth surface of the rebar steel and thus the absence of any corrosion products formed on the rebar steel. The SEM micrographs of rebar steel immersed in SCPS prepared in well water for 24 hours in the absence and presence of inhibitor system are shown Figures 7(b), 7(c) respectively.

The SEM micrograph of rebar steel immersed in SCPS prepared in well water shows the roughness of the metal surface which indicates the corrosion of rebar steel in SCPS prepared in well water where in presence of 250 ppm of $K_2Cr_2O_7$ and 50 ppm of Zn^{2+} mixture in SCPS, the surface coverage increases which in turn results in the formation of insoluble complex on the metal surface (Dichromate-Zn^{2+} complex). In the presence $K_2Cr_2O_7$ and Zn^{2+}, the surface is covered by a thin layer of inhibitors which effectively control the dissolution of rebar steel. Such results have been reported earlier[24, 25].

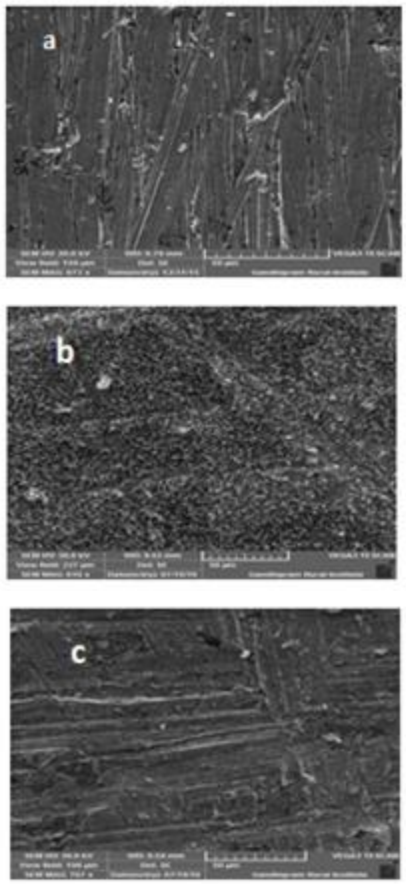


Figure 6. SEM Micrographs of a) Polished rebar steel (control); b) rebar steel immersed in SCPS (blank); c) rebar steel immersed in SCPS+ $K_2Cr_2O_7$,250 ppm and Zn^{2+} 50 ppm

3.7 Surface Examination by EDAX:

EDAX is used to analyze corrosion films Fig.10 a) spectrum shows the EDAX analysis of rebar steel surface immersed in SCPS prepared in well water. The analysis shows the presence of corrosion products elements (Fe, O and C) Fig.10(b) spectrum shows the EDAX analysis of rebar steel immersed in SCPS prepared in well water containing 250 ppm of Potassium dichromate and 50 ppm of Zn^{2+}. The analysis shows the presence of (K, Cr) which could be attributed to the presence of zinc and Potassium dichromate on the rebar steel surface forming inhibitor film .

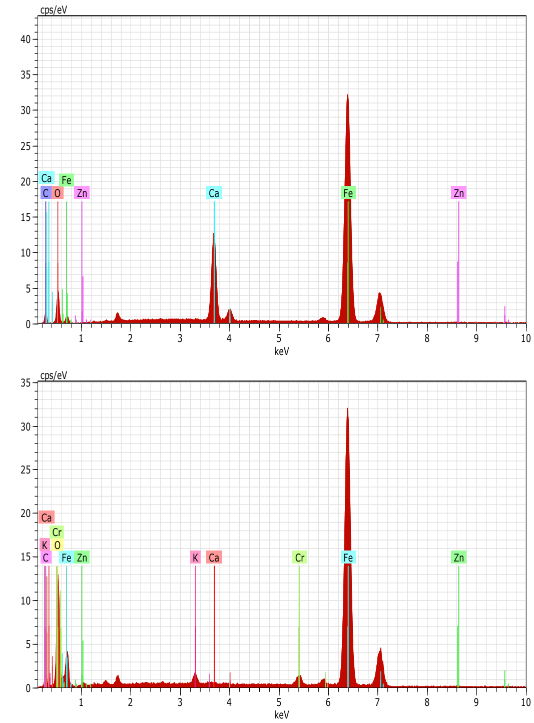


Figure 7. EDAX analysis of rebar steel immersed in (a) SCPS in well water (blank) (b) SCPS in well water+ 250 ppm of Potassium dichromate + 50 ppm of Zn^{2+}

3.8 Cyclic Voltammetry

During corrosion inhibition process, protective film is formed under the metal surface. This must be stable, In order to test the stability of the film the experiment was carried out in the 3.5% NaCl solution. In the present study, cyclic voltammograms were recorded by measuring the working electrode; rebar steel, in 3.5% NaCl solution and the parameters are given in Table 5.

Table 5 Cyclic voltammetry parameters (PDC + Zn^{2+})

Sample	Control (rebar steel)	Blank (SCPS)	Inhibitor system (PDC + Zn^{2+})
Ep (mV)	930	250	623
Peak ip (mA)	-12.29	-2.21	-5.23
Pitting Corrosion Product (mV)	-	-450	-340
Pitting Potential (V)	-1.15	-0.4	-1.11

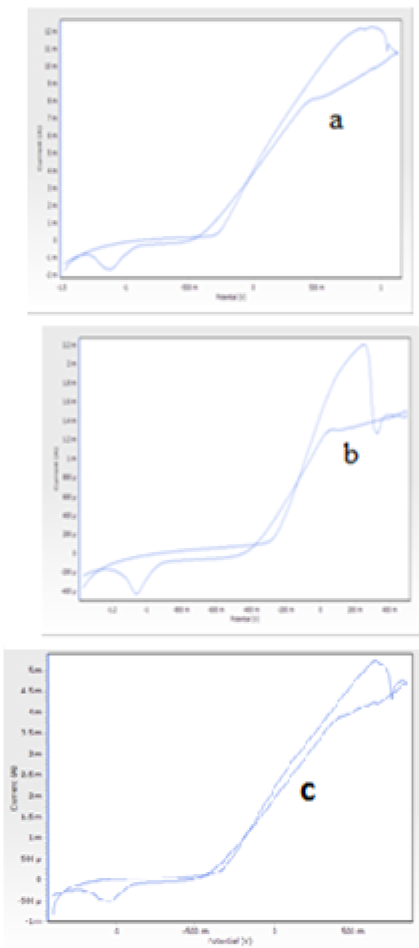


Figure 8: Cyclic voltammogram of electrode submerged in 3.5% NaCl solution (a) polished rebar steel (b) rebar steel in SCPS for one day (c) rebar steel in SCPS containing 250 ppm of PDC and 50 ppm of Zn^{2+} for one day

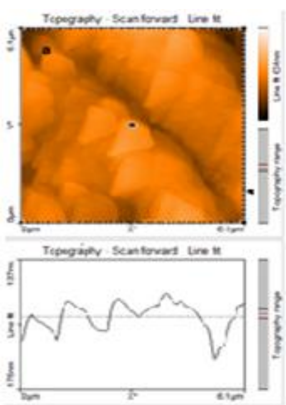
The current density increases from -12.29 m A to -5.23 m A. The increase in current density may be explained as above. It is observed from the Fig.9 (a), 9 (b), 9 (c) that the pitting potentials for the three systems are at -1.15 V, -0.4 V, and -1.11 V respectively. That is when rebar steel electrode is immersed in the SCPS medium; the pitting potential is shifted to more negative side (active side, i.e., -0.4V). It accelerates corrosion because the protective film formed is porous and amorphous. When the electrode is immersed in the inhibitor medium, the pitting potential is shifted to the noble side, i.e., -1.11 mV. This indicates that the passive film found on the metal surface in the presence of inhibitors is compact and stable. It can withstand the attack of chloride ion present in 3.5% NaCl.

3.9 Atomic Force Microscopy Characterization

Atomic force microscopy is a powerful technique for gathering roughness statistics from a variety of surfaces[26]. AFM is attractive and accepted method of roughness investigation[27-30]. The AFM cross – sectional profile and histogram images of surface for polished rebar steel surface, rebar steel surface immersed in SCPS and rebar steel surface immersed in SCPS containing the formulation of 250 ppm of PDC are shown in Fig.6 (a) (b) and (c) respectively. Table – 6 is the summary of the average roughness (R_a), rms roughness (R_q) value for rebar steel surface immersed in different environments. Fig.6 (a) displays the uncorroded metal surface, the value of R_{RMS} and R_a shows a more homogeneous surface, with slight roughness observed is due to atmospheric corrosion. In Fig.6 (c) smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - PDC complex and $Zn(OH)_2$ thereby inhibiting the corrosion and the film is protective in nature.

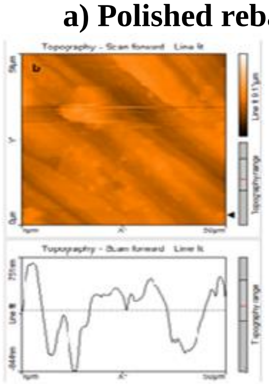
Table 6: AFM data for rebar steel surfaces immersed in inhibited and uninhibited environments

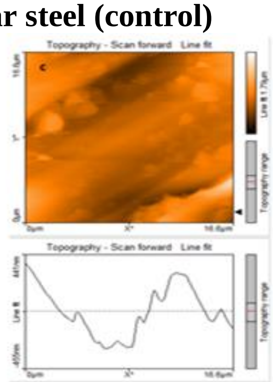
Samples	RMS Roughness R_q(nm)	Average Roughness R_a (nm)
Polished rebar steel (Control)	45.871	34.049
Rebar Steel immersed in SCPS	455.63	390.81
Rebar steel in SCPS + 250 ppm of PDC + 50 ppm Zn^{2+}	48.867	43.474



(a)

Fig.5.1.13: AFM cross sectional images of the surface of
a) Polished rebar steel (control)





(b) (c)

b) Rebar steel immersed in SCPS (blank)
c) Rebar steel immersed in SCPS + 250 ppm of PDC + Zn^{2+} 50 ppm

4. CONCLUSIONS

The high efficiency exhibited by potassium dichromate proves its potential in controlling corrosion. The formulation consisting of 250 ppm of $K_2Cr_2O_7$ and 50 ppm of Zn^{2+} offers 98 % IE to rebar steel immersed in simulated concrete pore solution prepared in well water. Polarization study indicates that $K_2Cr_2O_7$ system controls the anodic reaction. AC impedance, Cyclic voltametry, UV, FTIR, SEM, Edx and AFM spectral studies reveals that a protective film (Fe^{2+}-dichromate complex and $Zn(OH)_2$) is formed on the metal surface.

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