The corrosion inhibition effect of Cerium (III) ions for X70 steel in 3% NaCl medium

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Abstract:

The inhibition of the corrosion of X70 steel in aerated 3% NaCl solutions by cerium (III) nitrate hexahydrate has been studied using polarization method, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The results indicated that the protection efficiency (%IE) rises with an increase in the concentration of Ce (III) and reached an optimal value of 72%. The results of EIS show that when the concentration of the inhibitor increases, both charge transfer resistance and inhibition efficiency tend to increase while the value of constant phase element, CPE, tends to decrease. SEM analysis was performed to study the persistence of the Ce(III) hydroxide layer.

KEYWORDS: X70 steel, corrosion, inhibition, Ce(III) ions.

1.Introduction:

Corrosion scientists and engineers are still very concerned about how corrosion and its products continue to emerge on steel structures [1-2]. Iron alloy failure in aqueous chloride solutions is commonly caused by the oxidation of passive oxide coatings by aggressive anions like Cl-, O2 et H2O [3-4].

One of the most recognizable applications for inhibitors is in oil and gas facilities. Inhibitors can be organic or inorganic compounds and they are usually dissolved in aqueous environments. The way these Inhibitors worked was either by oxidizing the metal to create an impervious layer (in the case of inorganic inhibitors) or by adhering to the metal surface through their heteroatoms and/or double bonds (in the case of organic inhibitors) to create a hydrophobic layer that prevented the aggressive environmental agents from penetrating the metal surface [5]. The two types of organic and inorganic corrosion inhibitors are film-forming and absorptive inhibitors. According to how they affect the kinetics of the anodic and cathodic electrodes, corrosion inhibitors can also be classified as anodic, cathodic, or mixed inhibitors [6].

some of the studies focus on inorganic inhibitors such as vanadate [7,8], molybdate and cerium nitrate [9,10,11].

Chromates (Cr(VI)) are the most common compounds due to their effectiveness in harsh atmospheres and their low cost. But chromium compounds are extremely toxic additives. Currently the use of chromates is strictly prohibited in the majority of industrial fields [12], zinc salts also have very high inhibitory efficiencies but the displacement of the corrosion potential becomes in the negative direction [13]. K. F. Khaled [14] studied the effect of inhibiting the corrosion of steel by cerium sulfate. in general, few studies have focused on the study of transitional metals and rare earths ions as corrosion inhibitors, and

through this study we hope to pave the way for new studies in this field, in particular the in-depth study of the use of rare earth ions in the study of synergistic action with other compounds[15-18].

This work represents a systematic study of corrosion inhibition effect of eco-friend cerium (III) nitrate on mild steel corrosion in aerated 3% NaCl using polarization method, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

2.Experimental:

The material tested in this study is the low alloy X70 mild steel. The chemical composition of the material is given in table1. The chemical composition of the steel is shown in Table 1 determined by spectrometry type SPECTROMAXx LMX05.The test media were 100 ml, 3 wt% NaCl prepared from reagent grade chemicals and bi-distilled water. When needed, HCl or NaOH, were added to adjust the pH which is monitored with a pH/temperature (°C) meter. All experiments were conducted at pH 6. $Ce(NO3)3.6H2O$ were furnished from Sigma-Aldrich Chemie GmbH.

Table 1: Chemical components of the X70 steel used in the tests.

Element	Cr	Ni	Mn	Si	Nb	Co	Mo
(Wt %)	0.005	0.062	1.664	0.021	0.032	0.0159	0.0123
Cu	S	P	Ti	Al	C	V	Fe
0.3152	0.001	0.009	0.003	0.034	0.172	0.0665	rest

2.1. Potentiodynamic polarization measurements:

For polarization studies, the X70 steel specimen was embedded in PVC holder using epoxy resin with an exposed area of 1.0 cm2 as a working electrode. A platinum foil was used as an auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE) coupled to a Luggin capillary whose tip was located between the working electrode and the auxiliary electrode. Before measurement, the electrode was immersed in a test solution at open circuit potential for 30 min until a steady state was reached. All polarization measurements were performed using TACUSSEL model PGP201 galvanostat / potentiostat corrosion measurement system at room temperature under aerated conditions, the scanning rate was 0.5mVs−1 and a sweep range from an initial potential of -1000 mV/SCE to a final potential of 0 mV/SCE.

(%IE) were determined from (jcorr) in Equations (1).

$$IE(\%) = 100 \times \frac{j_{corr} - j'_{corr}}{j_{corr}} \qquad (1)$$

2.2. EIS measurements:

The electrochemical impedance spectroscopy measurements EIS were carried out using AC signals of amplitude 10 mV peak to peak at open circuit potential in the frequency range from 10 kHz to 10 mHz, using TACUSSEL model PGZ401 at room temperature in an aerated solution. The working electrode has been prepared from a cylindrical rod of X70 steel to get an area exposed to solution of 1 cm2, and immersed in the test solution for 120 min, to establish a steady state open circuit potential. EIS is recorded at open circuit potentials. The charge transfer resistance values were obtained from the diameter of the semi circles of the Nyquist plots, and (%IE)

and (θ) were measured by utilizing the charge transfer resistance (Rct) as a function of the performance of protection Equations (2).

$$IE(\%) = 100 \times \frac{R_{ct} - R°_{ct}}{R_{ct}} \qquad (2)$$

where Rct and R°ct are the charge-transfer resistance values without and with an inhibitor, respectively.

2.3. Scanning electron microscopy (SEM).

For surface morphological study of the uninhibited and inhibited X70 steel samples, scanning electron microscopy (SEM) images were recorded using the instrument VEGA3 TESCAN.

3.Results and discussion:

3.1. Potentiodynamic polarization measurements:

The polarization curves of X70 steel in 3% NaCl in the presence of various concentrations of Ce(NO3)3.6H2O are shown in Figure 1.
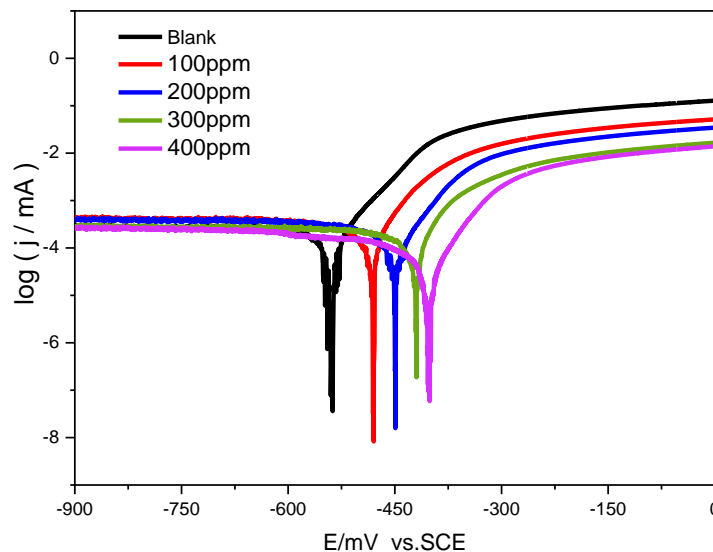

Figure 1. Tafel curves for X70 steel substrate immersed in 3% NaCl in the absence and presence of different concentrations of $Ce(NO_3)_3.6H_2O$ at room temperature.

The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (j_{corr}) and anodic (Ba)Tafel slope associated with the polarization measurements for the X70 steel in the presence of different concentrations of $Ce(NO_3)_3.6H_2O$ are summarized in Table 2. The linear portion of the cathodic region is not well defined; the corrosion current densities in all the above cases were determined by the extrapolation of anodic Tafel slopes to the respective corrosion potentials [19].

The results showed that the corrosion current density decreased with increasing the $Ce(NO_3)_3.6H_2O$ concentration, which indicates that this compound acts as an inhibitor. The values of inhibition efficiency increase with $Ce(NO_3)_3.6H_2O$ concentration, reaching a maximum of 72.08 % at 400ppm concentration. The corrosion potential values (E_{corr}) shifted slightly toward the positive direction, which means that the $Ce(NO_3)_3.6H_2O$ adsorption enhance the hydrogen reduction in the cathodic region [20-21] , and owing to the formation of uniform passive film, such type of inhibitor works as anodic inhibitor [22,23,24].the cerium nitrate hexahydrate suppresses the anodic processes and thus it acts as anodic-type inhibitor.

3.2. Electrochemical impedance spectroscopy measurement:

EIS measurements were collected to investigate the inhibition behavior of $Ce(NO_3)_3.6H_2O$ on X70 steel in a 3% NaCl at room temperature. The Nyquist and bode plots are shown in Figure 2.

In figure 2 the Nyquist diagrams show a large capacitive loop at high frequencies (HF) and a small inductive loop at low frequencies (LF) for all concentrations of inhibitors. The inductive loop is connected to an adsorption process, whereas the semi-circle system for the 3% NaCl without inhibitor corresponds to the dissolution of the steel and the subsequent production of the complex. Migration causes precipitation and ion adsorption, most likely in the presence of an electric field.

When inhibitors were added, a semicircle developed at high frequencies, but at lower frequencies, a second, smaller inductive resistive semicircle arose. The result suggests a passive state associated with the formation of a film inhibitor (semicircle at high frequency) while the low frequency semicircle charges transfer processes that are the salt of the film at local sites [25-26].

Table 2. Polarisation parameters and the corresponding inhibition efficiency of X70 steel corrosion in 3% NaCl containing different concentrations of $Ce(NO_3)_3.6H_2O$ at room temperature.

Concentration	$-E_{corr}$ (mV/ESC)	j_{corr} (mA/cm^2)	B_a (mV/Dec)	%IE
Blank	540,12	0,1357	66,66	/
100ppm	482,66	0,092	43,47	32,13
200ppm	445,55	0,0835	47,61	38,37
300ppm	420,58	0,0608	35,71	55,13
400ppm	403,47	0,0378	62,5	72,08

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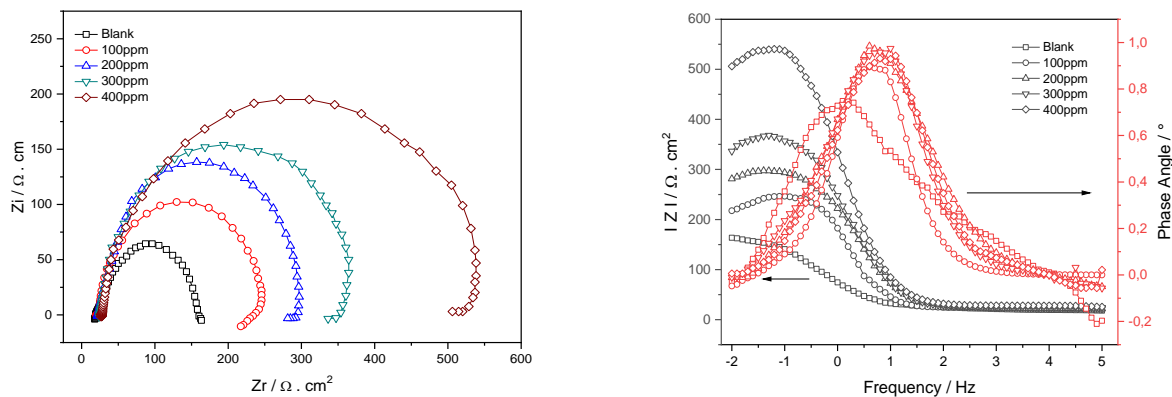

Figure 2: Impedance diagrams of X70 steel electrode in a 3%NaCl at E_{corr} in presence and absence of $Ce(NO_3)_3.6H_2O$ at room temperature.

Table 3: Inhibition efficiency and parameters related to electrochemical impedance measurements of X70 steel in 3% NaCl solutions without and with various concentrations of $Ce(NO_3)_3.6H_2O$ at room temperature.

Concentration	Rs	Rct	CPE	n	E%
Blank	22,371	157,23	7,41E-05	0,879	/
100ppm	22,35	225,1	6,91E-04	0,941	30,151
200ppm	18,726	281	4,48E-06	0,986	44,046
300ppm	19,74	356,76	7,76E-07	0,916	55,928
400ppm	21,457	507,05	5,34E-07	0,846	68,991

The calculated inhibition efficiencies are listed in Table 2, where Rs represents the solution resistance, Rct is the resistance of the electrochemical reaction and can be defined also as the charge-transfer resistance and (CPE, $ZCPE = [Q(j\omega)^n]^{-1}$) is a constant phase element represent double layer capacitors with their n values $1 > n > 0$ with some pores [27]. Addition of

$Ce(NO_3)_3.6H_2O$ increases the values of Rp and lowers the values of CPE and this effect is seen to be increased as the concentrations of $Ce(NO_3)_3.6H_2O$ increase. The presence of the inductive loop RL - L can be attributed to the relaxation process obtained by adsorption species as Cl^-_{ads} , H^+_{ads} and NO_3^-ads on the electrode surface [28, 29-31]. Nitrate ions adsorbed by the anodic site to form a barrier between the metal surface and the corrosive solution. The cerium ions are precipitate on the cathode site as cerium hydroxide (III).

3.3. Scanning electron microscopy:

(SEM). Figure 3 presents the SEM micrographs of the X70 steel substrates after immersion in 3% NaCl for 48 h in the blank solution (a) and presence of 400 ppm $Ce(NO_3)_3.6H_2O$ the corrosive solution (b).

It is evident that the X70 steel surface was severely corroded, with sections where the metal was attacked more or less uniformly across the entire surface (Figure 3(a)). When compared to untreated X70 steel, treated X70 steel with 400 ppm $Ce(NO_3)_3.6H_2O$ has smoother surfaces (Figure 3(b)), indicating that the metal surface is in better condition.
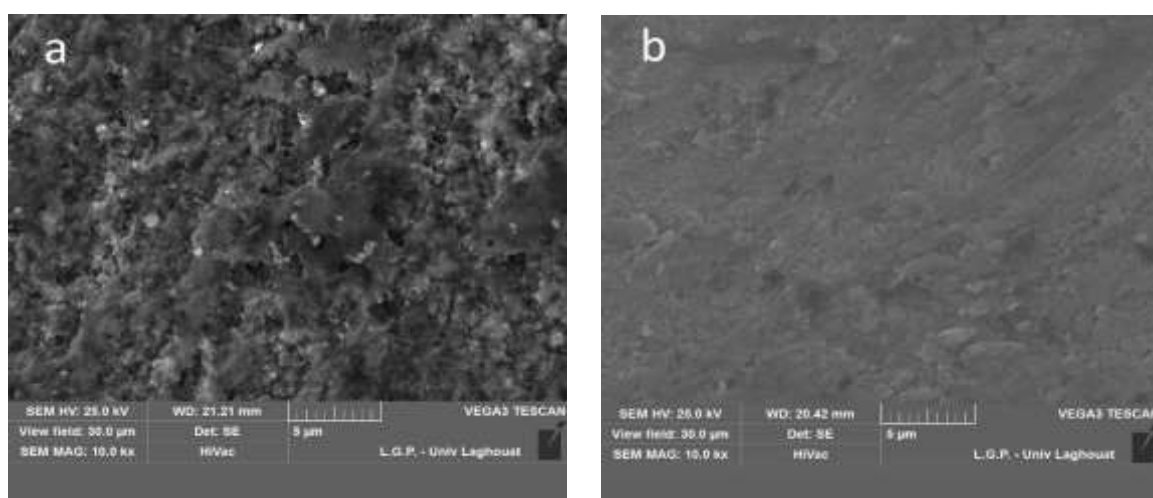

Figure 3. SEM micrographs of the X70 steel substrates after immersion in 3% NaCl for 48 h in the blank solution (a) and presence of 400 ppm $Ce(NO_3)_3.6H_2O$ at room temperature.

4.Conclusion:

The corrosion inhibition performance of Ce(NO3)3.6H2O on X70 steel in 3% NaCl solution have been studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The following conclusions are drawn based on the findings:

The inhibition efficiency of $Ce(NO_3)_3.6H_2O$ increased with increase in its concentration reaching a maximum of 72% with potentiodynamic polarization measurement at optimum inhibitor concentration.

Polarization studies indicated that $Ce(NO_3)_3.6H_2O$ acted as anodic inhibitor.

According to the data obtained from EIS measurements it can be observed that Rcorr increases with the concentration of $Ce(NO_3)_3.6H_2O$, suggesting that the value of inhibition efficiency increases with concentration.

The obtained surface morphology SEM technique ensure the high efficiency of $Ce(NO_3)_3.6H_2O$ as corrosion inhibitor.

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