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Rare earth metals asecofriendly corrosion inhibitors for mild steel in produced water A. S. Fouda^{1*}, S. M. Abd El-Wahab², M. S. Attia², A. O. Youssef² and H. O. Elmoher^{2,3}

¹Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt ²Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt ³Quality Control Section Head, South Dabaa Petroleum Company (Dapetco)

ABSTRACT

Rare earth metals have been investigated as anti-corrosion of mild steel in produced water which results during petroleum activity. The techniques utilized in this approach namely "massloss (WL), DC Tafel polarization, AC electrochemical frequency modulation (EFM), AC impedance spectroscopy (EIS) at25°C.Iron content (dissolved iron) is measured by spectroscopy and pH values of solutions arerecorded.Data declared that IE% rose with addition of rare earth metals and decreased with raising temperature. Langmuir's adsorption isotherm was the best fit with the revealing data. The thermodynamic activation parameters are demonstrated. SEM & EDXtechniques were employed for surface examination of uninhibited and inhibited mild steel. The % inhibition demonstrated from different methodologieswas in a goodtrend.

Keywords: Rare earth metals; mildsteel; produced water; SEM; EDX.

INTRODUCTION

Most of world energy demand is covered by oil and gas industry. Produced water is the by-product accomplished with petroleum activities. Ahmadun et al. [1] stated that "Global produced water production is 250 MMbbls /day compared with 80 MMbbls / day of oil". This means that the water cut is 70% approximately and still increase as the consumption increase. Produced water becomes an environmental issue and a proper disposal or reuse method is a must. It contains beside hydrocarbons, inorganic compounds. TDS of produced water varies from<2000 ppm to >150,000 ppm although average TDS content in seawater is approximately 35,000 ppm[2]. Naturally occurring radioactive materials (NORM) may be found according to the reservoir rock [3].

Mild steel has been used widely in oil and gas industries [4]. The resistance of mild steel towards the attack of produced water with high salinity is very low so inhibitor can enhance this resistance and decrease the pitting attack. Rare earth metals become an environmental competitive for chromates base inhibitors. As the species of Cr(VI) is found to be cancerogenic, toxic and the precaution must be taken for use and disposal. In the other side, rare earth metals have low toxicity [5] and their inhalation not harmful to health; also their oxides are similar to sodium chloride in the toxicity [6].

Goldie and McCarroll [7] found that the concentrations of 0.001 M Ce[NO₃]₃or La[NO₃]₃demonstrated corrosion inhibition efficiencies of 91% and 82%, respectively, with steel in neutral solutions. Hinton et al. [8-10] studied the inhibiting action of the cerium salts on corrosion of some materials in aqueous solutions and considered them as cathodic inhibitors. Issacs et al. [11] claimed that Ce³⁺ ions were acting as an anodic inhibitor beside their cathodic properties. This claim was supported by the results of anodic current density and open-circuit potential. After then, Hinton and coworker [12] have demonstrated that CeCl₃ behaved as both an anodic and cathodic inhibitor for the dissolution of mild steel. Several papers investigated the use of lanthanides as inhibitors in aqueous media [13-24].

This paper aimed to investigate the inhibition action of some rare earth compounds (Sm³⁺ &La³⁺) for the attack of mild steel in produced water environment as a practical application. The film formed is characteristic by SEM and EDX techniques. In this approach, several electrochemical and chemical methods are utilized.

MATERIALS AND METHODS

2.1. Chemical additives and solutions

2.1.1. Chemical additives

a)Hydrochloric acid (37 %) and propanone were purchased from Al-Gomhoria Company, Egypt. b)Rare earth compounds (BDH grade).

Rare earth chloride are purchased from Sigma-Aldrich Co.with the following data; Lanthanum chloride (LaCl₃.7H₂O; Mw= 371.4) and Samarium chloride (SmCl₃.6H₂O; Mw= 364.81).

2.2.2. Solutions

a)Inhibitors solution

Stock solutions of 1000 ppm of Sm^{3+} and La^{3+} were freshly prepared. The required concentrations were prepared by dilution with bidistilled water from stock solutions.

b)Produced water

Water sample collected from drainage system without any chemical treatment. Produced water is from upper and lower Bahariya formation in south Dabaa petroleum (Dapetco) fields, Western Desert, Egypt. Table (1) demonstrated the analysis of this sample

Test	Result	Unit
pH@25 °C	6.90	-
Specific gravity@60/60°F	1.03	-
Conductivity	43	ms/cm
TDS	26400	ppm
TSS (total suspended solids)	3	ppm
Chloride's	16848	ppm
Salinity as NaCl	27800	ppm
Iron (Total)	0.30	ppm
Carbonates	Nil	ppm
Hydroxide	Nil	ppm
Bicarbonates	546	ppm
Sulfates	200	ppm
Sodium	11224	ppm
Calcium	366	ppm
Magnesium	176	ppm
Strontium	39	ppm
Potassium	230	ppm
Barium	7	ppm
Cupper	Nil	ppm
Oil in water	35	ppm

Table (1)Analysis of produced water sample.

2.3. Materials

The composition of mild steel (weight %) is given in Table (2) :-

Table (2) Chemical composition of mild steel (weight %):-

Chemical Constituent	Р	S	С	Mn	Fe
Composition (wt %)	0.04	0.05	0.13	0.6	Rest

2.4. Methodology

2.4.1. Weight loss measurements

Coupons "with dimensions 1 x 1 x 2 cm" were polished with various grades of emery paper sizes up to 2000, afterward degreased with propanone, washed with bidistilled water and dried carefully. Coupons were immediately immersed in produced water with or without 400 ppm of Sm^{3+} and La^{3+} . After then, coupons were removed and cleaned in acid solution [25]. Weight losses were calculated after correcting for any attack of the cleaning solution on the steel, and determination of CR, % IE and (θ) from the weight-loss data was calculated [26].

2.4.2.The pH measurement

The pH values of the produced water with different concentration of rare earth metals are tested by Hach sensION378 Laboratory Multi-parameter Meter.

2.4.3. Spectroscopic analysis

Hach DR 3800 spectrometer (10 cm stoppered silica cells, normal scan speed ,bandwidth of 2.0 nm, in the spectral range 320-900 nm at $25 \pm 1^{\circ}$ C) is used for determination of total dissolved iron as the following :

Mild steel coupons were immersed in produced water solutions with and without 400 ppm of Sm³⁺ and La³⁺at 25 \pm 1°C for 6 days. The amount of iron dissolved in the solution for both uninhibited and inhibited samples was determined by spectrophotometry at λ_{max} =510 nm using 1, 10 Phenanthroline[27] or FerroVer Iron Reagent [28].

2.4.4. SEM&EDX measurement

Coupons were polished using different emery papersupto2000gritsize and washed with propanone and bidistled water and immersed for 6 days inproduced water solution with and without 400 ppm of Sm³⁺ and La³⁺. After the time coursehas been passed, coupons were washedgently withbidistilled water. The surface morphology measurements were carried out using SEM and EDX model JEOL (JXA-840A) electron probe microanalyzer.

2.4.5. Electrochemical measurements

Electrochemical methods, namely "Tafel polarization, EIS, and EFM" were used to investigate the attack of mild steel in produced water environment. All tests were performed using anordinary three-compartment glass cell that composed of mild steel coupon as testing electrode, SCE as a reference electrode and a platinum wire (1.0 cm²) as a counter electrode. The reference electrode was joined to a Luggin capillary. Before each test, the testing electrode was polished, washed with bidistilled water and then degreased with propanone. All tests were conducted under unstirred conditions without deaeration at 25 °C. The testing electrode was immersed in the solutions and open circuit potential was recorded when it became virtually constant before starting the measurements. Gamry Instrument Series G 750TM Potentiostat/Galvanostat/ZRA,"Gamry applications include software DC105 for potentiodynamic measurements, software EIS300 for EIS measurements, EFM140 for EFM measurements" is used in this approach. A personal computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and data fitting.

a- Potentiodynamic polarization

Tafel plots were sulted by changing the electrode potential automatically from -800 to +800 mV with respect to open circuit potential at a scan rate of 5 mV s⁻¹. Stern-Geary method [29]used for the determination of corrosion current is performed by extrapolation of anodic and cathodic Tafel lines of charge transfer controlled corrosion reactions to a point which gives log I_{corr} and the corresponding corrosion potential (E_{corr}) for inhibitor free acid and for each concentration of inhibitor. Then I_{corr} was used for calculation of inhibition efficiency (% IE) and surface coverage (θ) as below:

% IE =
$$\theta \ge 100 = [1 - (I_{\text{corr (inh)}} / I_{\text{corr (free)}})] \ge 100$$
 (1)

Where, I_{corr (free) and} I_{corr (inh) are} the corrosion current densities in the uninhibited and inhibited samples.

b- Electrochemical impedance spectroscopy (EIS)

EIS tests were performed in a frequency range of 100 kHz to 100 mHz with amplitude of 5 mV peak-to-peak using Ac signals at respective corrosion potential. %IEof rare earth compounds has been found out from the charge transfer resistance values using the following equation [30]:

(2)

(3)

% IE_{EIS} =
$$\theta$$
 x 100 = [1 - (R_{ct} / R^o_{ct})] x 100

Where, R^o_{ct} and R_{ct} are the charge transfer resistance with and without rare earth metals, respectively.

The interfacial double layer capacitance (C_{dl}) values were obtained [31] by determining the frequencies at which the imaginary component of the impedance is maximumf (- Z''_{max}), using the following equation:

$$C_{dl} = Y_o (\omega_{max})^{n-1}$$

Where, $Y_0 = CPE$ coefficient, (ω_{max}) = frequency at which ($-Z_i$) has a maximum and (n) = (phase shift).

(4)

c- Electrochemical frequency modulation (EFM)

EFM wasperformed using two frequencies 2 and 5 Hz. The base frequency was 0.1 Hz, so the waveform repeats after 1 s. The resulted spectrum is known asintermodulation spectra contain current responses assigned for harmonical and intermodulation current peaks. The tallest peaks were used to calculate (I_{corr}), (β_c and β_a) Tafel slopes and (CF2& CF3) causality factors [32, 33].Equilibrium time leading to steady state of the specimens was 30 min. % IE_{EFM} calculated as follow:

%
$$IE_{EFM} = [1 - (I_{corr (inh)} / I_{corr (free)})] \times 100$$

Where, $I_{corr (inh)}$ and $I_{corr (free)}$ as before.

RESULTS AND DISCUSSION

3.1. Weightloss measurements

Weight loss of the samples was plotted against immersion time for 400ppmof rare earth metals are demonstrated in Figure (1) at 25°C. The resulted curves in the existence of 400 ppmof rare earth metalsfall significantly below that of blank solution. Additionally, it is clear that the mass loss of mild steel in the presence of rare earth metals varies linearly with time. This can be outlined as theprecipitation of insoluble surface filmwhich isolated the coupon surface from the corrosive media [34] (i.e. these compounds behave as inhibitors). However, for all the concentrations tested, it is appeared to devote metal dissolution and displayed a corrosion rate worse than that of the control sample. It was also noted that the coupon initially took on a reddish appearanceconsistent with the formation of a complex oxide film of iron and rare earth metals.

Table (3) Data of mass loss calculation for mild steel in produced water with and without 400 ppm of rare earth metals at 25 °C

Inhibitor	Conc., ppm	CR (mg cm ⁻² min ⁻¹) $x10^{-4}$	θ	% IE
Blank(produced water)	0	3.12	-	-
Sm ³⁺	400	0.67	0.786	78.6
La ³⁺	400	1.18	0.622	62.2
$Sm^{3+} + La^{3+}$	200 + 200	0.94	0.698	69.8



Figure (1) Mass loss-time plot of mild steel in produced water with and without 400 ppm of rare earth metals at 25°C

3.2. The pH measurement

The pH values of various concentrations of rare earth metals in 100 ml produced water were measured and recorded in Table (4).

Conc.	рН				
ppm	Sm ³⁺	La ³⁺	$Sm^{3+} + La^{3+}$		
100	6.0	5.5	-		
200	6.1	5.6	-		
300	6.2	5.7	-		
400	6.3	5.8	6.2		

Table (4) The pH values of various concentrations of rare earth metals at 25 $^\circ\mathrm{C}$

3.3 Spectroscopic analysis

Spectrophotometric determination of the amounts of dissolved ironin produced water without and in the existence of 400 ppm of rare earth metals after exposing coupons for 6 days at 25°C are summarized in Table (5). Iron content in the produced water before immersion of coupons is 0.30 ppm represented in Table (1). After data correction and rounded, the amount of dissolved iron is low in the case of rare earth metals with respect to blank. The dissolution of metal in the existence of rare earth metals is low with respect to the blank. From the amount of dissolved iron, the surface coverage (Θ) and %IE were calculated as follows [35]:

$\Theta = 1 - A/B(5)$ %IE= (1-A/B) x 100

(6)

Where, A is iron content in the existence of inhibitor and B is iron content in blank solution. Figure (2) shows the electronic spectra of interaction of 1, 10 phenanthroline with the species in the corrosive media (Fe²⁺, Sm³⁺ and La³⁺)at $\lambda_{max} = 510$ nm. It is cleared that the interaction between Fe²⁺ and 1, 10 phenanthroline is achieved without interference of the species of Sm³⁺ and La³⁺in produced water. The values of %IE was found to have the following trend Sm³⁺> (Sm³⁺ and La³⁺) > La³⁺, similar to previously demonstrated results of the studied techniques.



Figure (2) The electronic spectra of interaction of 1, 10 phenanthroline with (Fe²⁺, Sm³⁺ and La³⁺)

Table (5) Iron content,(ppm) for mild steel in produced water with and without 400 ppm of rare earth metals after 6 days of exposure at 25° C

Compound	Iron content, (ppm)	(θ)	%IE
Blank (produced water)	40	-	-
Sm ³⁺	9	0.775	77.5
La ³⁺	14	0.650	65.0
Sm ³⁺ and La ³⁺	12	0.700	70.0

3.4. Results of SEM&EDX techniques:

3.4.1. SEMstudies

The SEM micrographs of coupons surface after 6 days of immersion in produced water with and without400 ppm of rare earth metals are shown in Figure (3). In produced water micrograph, flakes and pits are cleared and can be observed [36]. In case of the rare earth metals the flakes disappeared and nodule formation clearly appeared. Thus, the coupon surface covered with a thin film.

3.4.2. EDX studies

EDX analysis was used to carry out the elementary surface analysis for the pure mild steel coupon and coupons after 6 days of immersion in the uninhibited and inhibited produced water. Figure(4)portrays the EDX spectrum of milds teel in produced water only and in the presence of 400 ppm of rare earth metals. The elemental distribution of species on the coupon surface is shown in Table (6). EDX analysis of the surface reveals the existence of Sm and La in addition to oxygen and iron, suggesting therefore the presence of oxide / hydroxide film.





Sm³⁺ and La³⁺



Figure (3) SEM micrograph for mild steel after immersion for 6 days in the existence of 400 ppm rare earth metals

Table (6) Surface composition (wt %) of mild steel in produced water with and without 400 ppm of rare earth metals after 6 days of immersion

(Mass %)	Fe	Mn	С	0	Na	Cl	Sm	La
Pure	96.88	0.69	2.43					
Blank (produced water)	58.40	0.63	2.35	37.08	0.19	1.35		
Sm ³⁺	20.02	0.21	5.62	52.39	0.65	2.02	19.09	
La ³⁺	30.5	0.34	4.93	46.43	0.58	1.75		15.47
Sm ³⁺ and La ³⁺	26.3	0.24	5.30	50.65	0.62	1.89	6.78	8.13



Figure (4) EDX spectra for mild steel after immersion for 6 days in the existence of 400 ppm rare earth metals in produced water

3.5. Electrochemical measurements

3.5.1. Potentiodynamicpolarization measurements

a. Effect of inhibitor concentration

Tafel polarization plots for the corrosion of mild steel immersed in produced water in the absence and with different concentrations of rare earth metals 25° C are introduced in Figures (5-6). It can be seen from these figures that, in the presence of rare earth metals, the curves are shifted to lower current regions, demonstrating the inhibition action of the rare earth metals. There was no definite course demonstrated in E_{corr} values in the presence of all the

lanthanides. In this approch, shift in E_{corr} values is in the range of 68 mV suggesting that they all behave as a mixed type inhibitors [37, 38]. The estimations of different electrochemical parameters determined by Tafel polarization of all inhibitors are given in Table (7). The results revealed that the values of β_a change slightly in the presence of all lanthanides, whereas more pronounced change occurs in the values of β_c , indicating that both anodic and cathodic reactions are affected but the effect on the cathodic reactions is more prominent [39]. As concentration of all rare earth metals increase, the inhibition efficiency increased. This is reveals that the inhibition action are due to adsorption of oxide/hydroxides on mild steel surface and the adsorption is known to depend on the pit of the medium.



Figure (5) Potentiodynamic polarization curves for the corrosion of mild steel in produced water in the absence and presence of various concentrations of $\mathrm{Sm^{+3}at}$ 25°C



Figure (6) Potentiodynamic polarization curves of mild steel in produced water in the absence and presence of 400 ppm of concentrations of rare earth metalsat 25°C

Inhibitor	Conc., ppm	- E corr., mV vs. SCE	i _{corr.,} μAcm ⁻²	$-\beta_c$ mVdec ⁻¹	$\beta_a \ mVdec^{-1}$	CR, µmyr ⁻¹	θ	% IE
Blank (produced water)	-	572	48.30	382	182	565	-	-
	100	590	23.56	323	128	276	0.512	51.2
S-m+3	200	599	16.50	278	81	194	0.658	65.8
Sm	300	611	12.80	244	80	150	0.735	73.5
	400	640	9.42	125	75	110	0.805	80.5
	100	584	31.85	319	161	373	0.341	34.1
La ⁺³	200	596	24.28	328	119	284	0.497	49.7
	300	608	18.57	312	104	217	0.616	61.6
	400	617	14.63	205	100	171	0.697	69.7
$Sm^{+3} + La^{+3}$	200 + 200	630	11.89	120	85	138	0.754	75.40

Table (7) Data from Tafel polarization of mild steel in produced water containing various concentrations of rare earth metalsat 25°C

b. Adsorption isotherm

Attempts were made to fit Θ values to various isotherms. The results were best fitted with Langmuir adsorption isotherm [40,41]. Figure (7) represets the straight line of C/ Θ vs. C (concentration) at 25 °C. The linear correlation coefficients (0.9969) (0.9947), at 25 °C are almost equal to 1 and the slopes (1.0094), (0.9258) at 25 °C are close to 1, which confirms the assumption that the adsorption of rare earth metalson the mild steel surface obeys Langmuir adsorption isotherm. The values of ΔG°_{ads} and K_{ads} calculated by Langmuir adsorption isotherm are given in Table (8). Datareveals that the large values of ΔG°_{ads} and its negative sign indicate that the adsorption of rare earth metalson mild steel surface is proceeding spontaneously and is accompanied by a highly efficient adsorption. Values of ΔG°_{ads} illustrated that the adsorption of rare earth metalson surface of the mild steel is not a pure one (i.e. physisorption and chemisorption). Values of K_{ads} confirmed that rare earth metalsare adsorbed on surface of mild steel in a strong way and hence imply better inhibition.

Table (8) Some parameters from Lang	muir isotherm model for mild steel in	n produced water for Rare earth metals at 25%
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Inhibitor	K X10 ⁻⁴ , M ⁻¹	Slope	\mathbf{R}^2	$-\Delta G^{\circ}_{ads}$ kJ mol ⁻¹
Sm ³⁺	1.01	1.0094	0.9969	32.8
La ³⁺	0.48	0.9258	0.9948	31.0



Figure (7) A plot of (C/O) vs. C of rare earth metals for the corrosion of mild steel inproduced water at 25°C

c.Activation parameters for corrosion process

 E_a^* activation energy for the corrosion of mild steel in produced waterwith and without various concentrations of rare earth metals at temperature range (25-55°C) were calculated from Arrhenius equation[42].Figures (8) represent plots of the log rate (k) vs. 1/T with and without Sm³⁺. E_a^* values determined from the slopes of these linear plots are shown in Table (9) which represents the value of E_a^* for solutions with rare earth metals is higher than that for produced water only (blank), suggesting that dissolution of mild steel is slow in the presence of inhibitor and can be attributed as due to physical adsorption [43]. (ΔS^*) Activation entropy and (ΔH^*) Enthalpy of the corrosion process were calculated from the transition state theory equation and represented inTable (9).A plot of log (k/ T) vs. 1/T for mild steel in produced water at different concentrations of Sm³⁺, gives a straight lines as shown in Figures (10).The data of Table (9) declared that the existance of rare earth metals render higher values of ΔH^* than produced water alone, demonstrated a higher inhibition efficiency observed for the system. Such behavior, could be assigned to the presence of an energy barrier for the corrosion process).

Inhibitor	Conc., ppm	E _a * kJ mol ⁻¹	$\Delta \mathbf{H}^*$ kJ mol ⁻¹	-Δ S* J mol ⁻¹ K ⁻¹
Blank (produced water)	0.0	13.42	6.96	236.8
	100	26.00	12.42	200.8
C3+	200	30.76	14.49	187.7
Sm	300	32.86	15.40	182.9
	400	37.82	17.55	168.8
	100	20.37	9.97	217.0
La ³⁺	200	24.00	11.55	206.9
	300	27.21	12.94	198.2
	400	29.73	14.04	191.6

 Table (9) Thermodynamic activation parameters for the dissolution of mild steel in produced water with and without different concentrations of rare earth metals



Figure (8) A plot of log k vs. 1/T for corrosion of mild steel in produced waterwith and without various concentrations of $\rm Sm^{3+}$



Figure (10) A plot of (logk / T) vs. 1/ T for corrosion of mild steel in produced water with and without various concentrations of Sm³⁺

3.5.2. Electrochemical impedance spectroscopy

Ac impedance spectra on Nyquist and Bode formats is given for the mild steel electrode at definite corrosion potential after 30 min exposure in inhibited and uninhibited solutions of Sm^{3+} is shown in Figure (11). To varying

EIS data, the electrical equivalent circuit (Randles model) given in Figure (12) is used. The circuit comprises of the charge transfer resistance (R_{ct}), capacitance of the double layer (C_{dl}) and the solution resistance (R_s) which fit well with experimental data. Figure (11-A) demonstrated a single semi-loop represented the single charge transfer process during dissolution with regardless the existence of inhibitor molecules. Deviation from ideal circular shape is related to frequency disorder of interfacial impedance which regarded to impurities, grain boundaries and inhomogeneity of the electrode surface [44, 45]. Review of impedance spectra on the Bode format in Figure (11-B) illustrated that each spectra comprises of a large capacitive loop with one capacitive time constant.



Figure (11) The Nyquist (A) and Bode (B) plots for corrosion of mildsteelin produced waterin the absence and with different concentrations of $\mathrm{Sm}^{3^{+}}$ at 25°C

Parameters of EIS studies are given in Table (10). As the inhibitor concentration increased, R_{ct} values raised and the values of C_{dl} are contrariwise. This can be related to the progressive substitution of water molecules on the metal surface by the inhibitor molecules, reduced the extent of dissolution reaction. As the values of R_{ct} get higher, the metal dissolution get slower [46, 47]. The decrease in C_{dl} is attributed to the lower of the local dielectric constant and/or the increase of the electrical double layer thickness proposed that the inhibitor molecules act by adsorption at the mild steel /solution interface.

Inhibitor	Conc.	R _{ct} ,	C _{dl} ,	$\begin{bmatrix} C_{dl}, \\ D_{dl} \end{bmatrix} = \theta$	
	ppm	Ωcm	µFcm⁻¹	•	
Blank (produced water)		920	238.61	-	-
	100	1.61E+03	193.22	0.428	42.8
\mathbf{Sm}^{3+}	200	2.29E+03	181.91	0.598	59.8
	300	3.39E+03	169.34	0.729	72.9
	400	7.60E+03	152.78	0.879	87.9
	100	1.42E+03	210.11	0.352	35.2
La ³⁺	200	1.89E+03	191.87	0.514	51.4
	300	2.39E+03	179.02	0.615	61.5
	400	3.10E+03	166.41	0.703	70.3

Table(10)EIS	data of mildsteel	with and without	t various concentration	so frare earth	metals at 25°C
1 abic(10)1213	uata of influsteer	with and withou	i various concenti ation	so mare cartin	metals at 25 C



Figure (12) Randles circuit model

3.5.3. Electrochemical frequency modulation

Figure (13) depicted the intermodulation spectrum of EFM which consists of the current response as a function of frequency. Parameters of the electrochemical kinetic are estimated at different concentrations of the investigated lanthanides in produced water at 25°C, were listed in Table (11). % IE_{EFM} increases by increasing rare earth metals concentrations and in a good agreement with other techniques. According to EFM theory, the values of CF-2 and CF-3 (causality factors) are close to 2 and 3 respectively [48, 49] which assure the quality of the measured parameters.

Table (11) Data demonstrated by EFM technique for mild steel in produced water with and without various concentrations of rare earth metals at 25 °C

Inhibitor	Conc. ppm	$i_{corr} \mu Acm^{-2}$	β_a mVdec ⁻¹	$\frac{\beta_c}{mVdec^{-1}}$	CF-2	CF-3	C.R. mpy	θ	% IE
Blank(produced water)		57.5	235	284	2.01	3.02	29.1	-	-
Sm ³⁺	100	26.9	91	96	1.80	2.55	12.3	0.532	53.2
	200	18.6	84	92	1.79	2.87	7.6	0.677	67.7
	300	12.1	69	74	1.53	2.72	5.5	0.790	79.0
	400	6.8	47	53	1.76	2.68	2.2	0.881	88.1
La ³⁺	100	36.1	148	173	1.58	2.43	18.3	0.372	37.2
	200	26.2	105	112	1.92	2.04	12.0	0.544	54.4
	300	19.9	98	104	1.61	2.63	7.9	0.654	65.4
	400	15.5	74	80	1.99	2.57	6.2	0.725	72.5



Figure (13) EFM spectra for mild steel in produced water with and without various concentrations of Sm^{3+} at 25°C

4. Mechanism of rare earth metals inhibition

The inhibition action can be discussed on the basis of formation of lanthanide oxides and/or hydroxides over cathodic sites which decrease the available cathodic current and, therefore, reduce the pitting attack [50, 51]. The main reaction at cathode site in produced water is the oxygen reduction which raises the local pH and therefore causes severe localized attack of mild steel.

$O_2 + 2H_2O + 4e \xrightarrow{-} 4OH \xrightarrow{-}$

The existence of the trivalent ions of rare earth metals in produced water medium suffer from progressive hydrolysis, which may form complex hydroxylated ions [52].

$Ln^{3+} + 3 H_2O \rightarrow Ln (OH)_3 + 3H^+$

Such a complex precipitates to form a hydroxide as the pH of the solution increases. Although rare earth hydroxides are stable in alkali solutions but they dissolve in acids. Pourbaix [53] described the relation between pH and the solubility product of $Ln(OH)_n$ as follow:

$Log [Ln^{3+}]_{sat} = x - 3pH$

Where x is 21.10 and 23.02 for Sm^{3+} and La^{3+} respectively.

The pH values represented in Table (2) at which Ln(OH)3 precipitation take place are lower than theoretical pH that was calculated. Therefore, the precipitation of Ln(OH)n is thermodynamically favorable, whether it occurs with an exchange of two or four electrons. Ln₂O₃can be formed as a product of further oxidation of Ln(OH)n at cathodic gradient.Finally we can conclusion that, at the same pH the rate of formation of Ln(OH)₃ is decreased in the following order: $Sm^{3+} > La^{3+}$, which is parallel to their inhibition efficiency.

CONCLUSION

Rare earth compounds especially chloride can be used as effective, ecofriendly and alternative to other toxic inorganic. This conclusion supported by the former results of the chemical and electrochemical methodology utilized.

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