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SYNERGISTIC INFLUENCE OF NITRITE ON INHIBITION OF MILD STEEL CORROSION IN CHLORIDE CONTAMINATED ALKALINE SOLUTION

M. Vishnudevan

* *visdevan@karunya.edu*

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Karunya University, Coimbatore, Department of Chemistry, 641114, India

Abstract:*Corrosion behavior of mild steel in chloride contaminated alkaline solution has been studied for the period up to 100days. Saturated Calcium hydroxide solution was used as alkaline solution and 0.5M NaCl solution was used to accelerate mild steel corrosion. The Charge transfer resistance Rct, Current density Icorr and inhibition efficiency values were obtained from tafel polarization and electrochemical impedance spectroscopic technique for sodium nitrite, sodium citrate and sodium benzoate mixed inhibitors. The results were compared with nitrite inhibitive system. The combination of nitrite inhibitor along with benzoate and citrate inhibitors enhanced the durability of mild steel through formation of nanosized -Fe_2O_3 film on steel suface even in presence of high chloride contamination. The results obtained from gravimetric method proved that the 100 days exposure of mild steel in nitrite with citrate, nitrite with citrate and benzoate mixed inhibitors showed the maximum inhibition efficiency of 98% in comparison with nitrite inhibitive system alone (41.5%). The maximum corrosion resistance performance of these mixed inhibitors system was due to the formation of thick layer of nano γ Fe_2O_3 fibrous film on steel surface.*

Keywords: *Corrosion, Chloride, Calcium Hydroxide, Tafel Polarization Technique.*

1. INTRODUCTION

The corrosion behavior of mild steel in chloride contaminated alkaline solution [1-3, 5, 6, 8, 11-13] has received considerable attention in the recent years due to its rebar corrosion problem facing by the construction industries, especially in industrial and in marine environmental conditions [10,14]. Mild steel protection in these chloride contaminated alkaline environment is due to the formation of protective iron oxide (magnetite) layer [1,9] on steel surface. There are many corrosion protective system which are available to mitigate rebar corrosion in concrete structure such as Cathodic protection, Fiber reinforced concrete, using chemical admixtures and corrosion inhibitors. Among these the use of corrosion inhibitor [1, 5, 8] is one of the effective maintenance free protective systems for minimizing steel rebar corrosion in chloride contaminated alkaline environment.

Ameer et al [2] have investigated inhibition of steel in chloride contaminated alkaline solution using two carbonitrile type of organic inhibitor and the results of the potentiodynamic polarization tests revealed that the current density of these inhibitors decreases while increasing the concentration of inhibitors. In one investigation ascorbic acid [5] was used as corrosion inhibitor for steel in alkaline media containing chloride ions, ascorbic acid suppress the pitting corrosion through cathodic mechanism. Simulated concrete pore solution study [6] was also carried out for carbon steel corrosion by impedance and polarization tests using benzotriazole inhibitor. In this study 3.5% NaCl contamination was used to accelerate corrosion. Sodium nitrite inhibitor is identified as an effective corrosion inhibitor for rebar corrosion [1, 6, 8] in chloride contaminated alkalinemedium. An extensive electrochemical studies were reported using this nitrite inhibitor. Recently the synergistic action of nitrite inhibitor along with other inhibitors were also studied and reported. Girciene et al [1] evaluated inhibition of nitrite inhibitor along with silicate inhibitor in chloride contaminated alkaline solution by voltametric and electrochemical impedance study and found that the additional introduction of sodium silicate increased the oxide layer thickness by 8 nm.

The present investigation deals with finding

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out the corrosion resistance performance of mild steel in chloride contaminated saturated $Ca(OH)_2$ solution containing novel mixed inhibitive system of sodium nitrite, sodium citrate and sodium benzoate.

2. EXPERIMENTAL

The corrosion resistance performance of mild steel in chloride contaminated saturated calcium hydroxide solution containing various concentration of sodium nitrite, sodium benzoate and sodium citrate inhibitors were evaluated by 1. Gravimetric method, 2. Tafel polarization method and 3. Electrochemical impedance spectroscopic method. 0.5M NaCl solution was used to accelerate corrosion of mild steel. The maximum exposure period for this investigation was 100 days.

Polished, degreased mild steel specimens (exposed area of 10 cm^2) were immersed in saturated Ca $(OH)_2$ + 0.5M NaCl solution (as control) and various inhibitors added systems were:

a. 0.4M sodium nitrite,
b. 0.05M sodium citrate and
c. 0.2M sodium benzoate respectively.

The mixed inhibitor systems used in this present investigation were;

a. 0.05M sodium citrate + 0.05M sodium benzoate,
b. 0.05M sodium citrate + 0.4M sodium nitrite,
c. 0.05M sodium benzoate + 0.2M sodium nitrite and
d. 0.2M sodium nitrite+0.1M sodium citrate +0.05M sodium benzoate respectively.

2. 1. Gravimetric Method

The initial weight of the mild steel specimens were noted for each set of inhibitive and mixed inhibitive system. The weight loss measurements were made after 40 and 100 days exposure. After 40th and 100 days of exposure periods, the mild steel specimens were taken out, cleaned in clarke's solution (Concentrated HCl (sp.gr.1.19)1 litre + Antimony trioxide (Sb_2O_3)20g + Stannous chloride$(SnCl_2)$50g) and finally rinsed with distilled water, air dried and then weighed. From the weight loss, the corrosion rate was calculated by applying the following formula and reported in Table 1.

$$\text{Corrosion rate (mmpy)} = 87.6 \; \frac{W}{DAT}$$

W = Weight loss, mg
D = density of specimens, g/cm^3
A = area of specimens in cm^2
T = exposure time, hr

From the corrosion rate (mmpy) measured, the inhibition efficiency is calculated by using the following formula

$$I.E = \frac{\text{Corrosion rate of control system} - \text{corrosion rate of inhibitor added system}}{\text{Corrosion rate of control}} \times 100$$

Where I.E is Inhibition Efficiency

2. 2. Tafel Polarization Technique

Polished, degreased mild steel specimens (1 cm^2 area exposed) were subjected to potentiodynamic polarisation (scan rate 1mV/sec, ±200mV from OCP values) for various inhibitor and mixed inhibitors system. A platinum foil (2 cm^2) area was used as counter electrode and Ag/AgCl electrode was used as reference electrode in a three electrode cell system. The experiments were carried out after 0 hour of immersion as (Initial) and after 4hrs, 20 days and 100 days of immersion to verify the stability of the passive film even in the presence of aggressive chloride ions. From the polarisation curve, E_{corr}, I_{corr}, ba and bc values were recorded from the tafel plots shown in Fig. 2-5 and corrosion rate (mmpy) the inhibition efficiency (%) values were calculated and reported in Table 2.

$$Corrosion\ rate(mmpy) = 3.2 * I_{corr}(mA/cm^2) * \frac{Eq.wt}{Density}$$

Note:

For measurement of corrosion rate in Millimeter per year;

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Equivalent weight of iron 55.8 g/mol
Density of iron 7.86 g/cm³ were taken

2. 3. Electrochemical Impedance Spectroscopic technique

Polished, degreased mild steel specimens (1 cm² area exposed) were subjected to impedance analysis (AC voltage 15mV; Frequency range 10mHz – 100 KHz) for saturated $Ca(OH)_2$ +0.5M NaCl as control and various inhibitors added systems. A platinum foil (2 cm²) area was used as counter electrode and Ag/AgCl electrode was used as reference electrode in a three electrode cell system. The impedance behaviour for various inhibitor systems were obtained in terms of Bode Z plot (from Fig. 6-10). From the plots, charge transfer resistance(R_t), corrosion rate (mmpy) and inhibition efficiency (%) values were calculated and reported in Table 3. Corrosion current I_{corr} can be evaluated from R_t using Stern Geary equation.

$$I_{corr} = \frac{b_a b_c}{2.303(b_a + b_c)} * \frac{I}{R_t} = \frac{K}{R_t}$$

b_a = anodic tafel slope
b_c = cathodic tafel slope

$$Corrosion\ rate(mmpy) = 3.2 * I_{corr}(mA/cm^2) * \frac{Eq.wt}{Density}$$

3. RESULTS AND DISCUSSIONS

3. 1. Inhibition Efficiency by Gravimetric Method

The inhibition efficiency calculated for control, various inhibitors added systems were reported in Table 1 and in Fig. 1. From the table, it was inferred that in the case of control, the passivity is heavily destroyed by the aggressive chloride ions as indicated by the corrosion rate data and it was noted that all the inhibitors initially (after 40 days) showed more than 80% inhibition efficiency but after 100 days of exposure, only the mixed inhibitors containing nitrite as one of the inhibitor maintained the passivity even in presence of high chloride concentration. In the case of citrate-nitrite-benzoate system, significant improvement in passivity of mild steel was observed.

Table 1.Weight loss study

System studied	Period of immersion	Weight loss (mg)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Control	40	567	0.6577	--
	100	465	0.0948	--
Nitrite	40	103	0.1195	81.8
	100	107	0.0550	41.5
Citrate	40	48	0.0556	91.5
	100	206	0.0560	40.9
Benzoate	40	105	0.1218	81.5
	100	179	0.0823	13.2
Citrate-benzoate	40	133	0.1543	76.5
	100	109	0.0710	25.1
Citrate-nitrite	40	9	0.0104	98.4
	100	41	0.0048	94.9
Nitrite-benzoate	40	39	0.0452	93.1
	100	40	0.0208	78.1
Citrate-Nitrite-benzoate	40	70	0.0812	87.6
	100	83	0.0014	98.5

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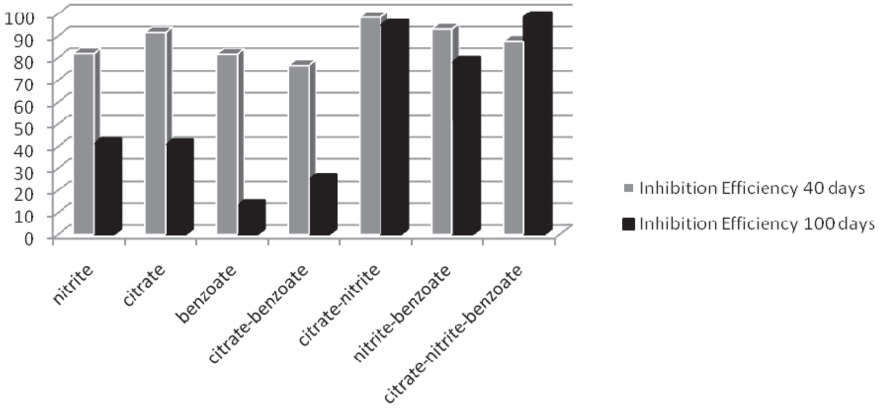

Fig. 1. Inhibition efficiency of various inhibitors and mixed inhibitors by gravimetric method

3. 2. Potentiodynamic Polarization (Tafel)

I_{corr}, corrosion rate (mmpy) and inhibition efficiency (%) calculated for various inhibitive system were reported in Table 2 and shown in Fig. 2-5. From the table, I_{corr} values measured initially and after 4 hrs, 20 days and 100 days of exposures showed that the individual inhibitive systems, nitrite, citrate and benzoate maintained stable passivity (0.0012, 0.0022 and 0.0018) even after 100 days of exposure in aggressive chloride solutions and in the case of 20th days of exposure it was found that the sudden decrease in Icorrwas observed for citrate and benzoate systems and again repassivation occurs during 100th days of exposure. In the case of mixed inhibitive systems, the I_{corr} values showed that all the systems maintained perfect passivity even after 100 days of exposure and an excellent passivation was observed in the case of citrate-nitrite-benzoate inhibitive systems. This may be due to the synergistic effect of nitrite-citrate-benzoate in which the innermost nano layer consists of γFe_3O_4 and the outermost layer consists of iron-citrate and iron-benzoate nanofibrous coating and this has been confirmed in the SEM Fig.14.

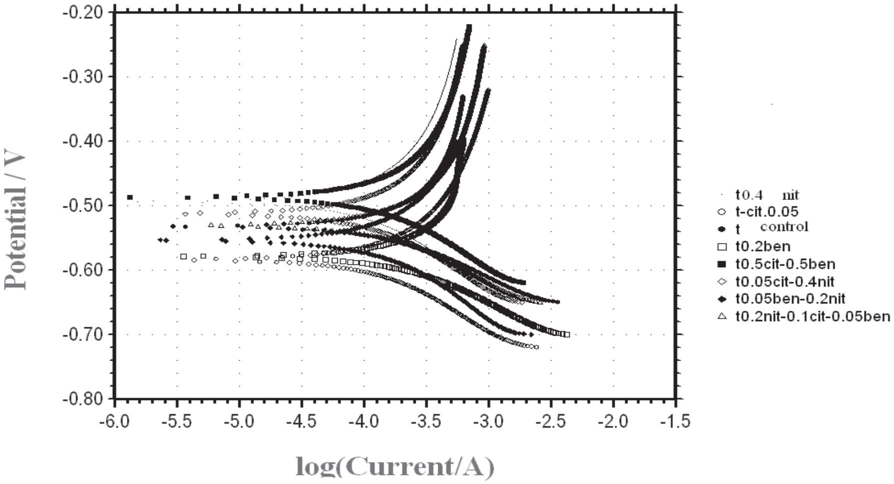

Fig. 2. Tafel plot of mild steel specimens exposed to control and various inhibiting systems for the immersion period of initial

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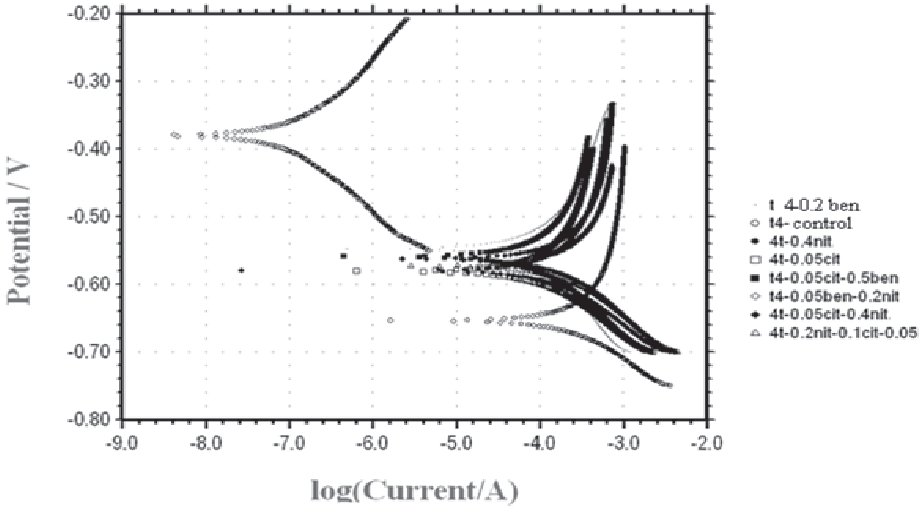

Fig. 3. Tafel plot of mild steel specimens exposed to control and various inhibiting systems for the immersion period 4hrs

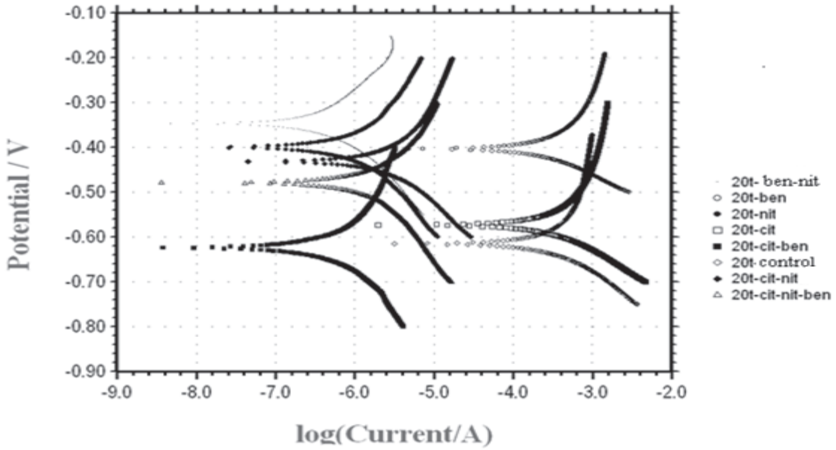

Fig. 4. Tafel plot of mild steel specimens exposed to control and various inhibiting systems for the immersion period 20days

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3. 3. Electrochemical Impedance Spectroscopic Technique

Polarisation resistance R_p(K.Ω), corrosion rate (mmpy) and inhibition efficiency (%) calculated for control, various inhibitors and for various mixed inhibitor added systems (from Fig.6-9) were reported in Table 4. The initially measured R_p value for control system was 0.386 K.Ω after 100th days of exposure, the R_p value decreased to 0.126 K.Ω. This observation was made due to the permeation of chloride ion into the passive film casues depassivation. On the otherhand, the R_p values measured after 100th days of exposure for mixed inhibitor systems added systems showed gradual increase in R_p values from 0hr, 4hr, 20 days and 100 days of exposure when compared with individual inhibitor systems. The inhibition efficiencies were found to be 99.3, 99.3, 99.7 and 99.3 for 0.05M sodium citrate + 0.05M sodium benzoate, 0.05M sodium citrate + 0.4M sodium nitrite, 0.05M sodium benzoate + 0.2M sodium nitrite and 0.2M sodium nitrite+0.1M sodium citrate +0.05M sodium benzoate inhibitor

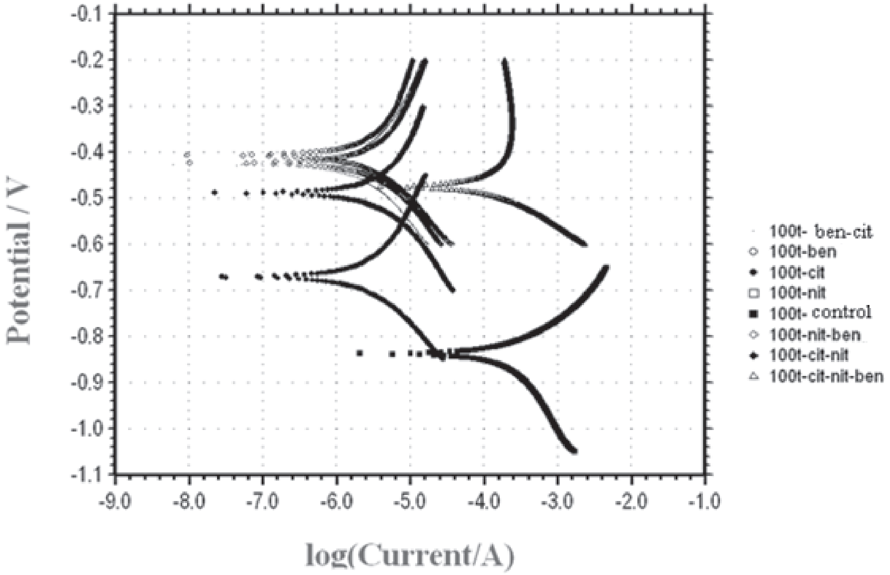

Fig. 5. Tafel plot of mild steel specimens exposed to control and various inhibiting systems for the immersion period 100days

Table 2. Tafel polarization technique

System studied	Period of immersion	Ba mV/Dec	Bc mV/Dec	E_{corr} mV vs Ag/AgCl	I_{corr} (mA/cm^2)	Corrosion rate (mmpy)	I.E (%)
Control	0 hr	40	50	-488	0.1933	2.2616	--
	4 hr	100	120	-572	0.4211	4.9269	--
	20 days	100	60	-375	0.4858	5.6838	--
	100 days	120	140	-412	0.2522	2.9507	--
Nitrite	0 hr	180	60	-482	0.0175	0.2048	90.9
	4 hr	90	40	-524	0.1778	2.0803	57.8
	20 days	40	40	-400	0.0070	0.0819	98.6
	100 days	80	50	-403	0.0012	0.0140	99.5
Citrate	0 hr	160	80	-540	0.0125	0.1463	93.5
	4 hr	100	80	-509	0.0562	0.6575	86.7
	20 days	180	100	-535	0.4298	5.0287	11.5
	100 days	140	120	-657	0.0022	0.0257	99.1
Benzoate	0 hr	160	60	-497	0.2720	3.1824	--
	4 hr	190	110	-509	0.0438	0.5125	89.6
	20 days	160	60	-420	0.3418	3.9991	29.6
	100 days	160	80	-370	0.0018	0.0211	99.3
Citrate-benzoate	0 hr	100	60	-470	0.1036	1.2121	46.4
	4hr	140	60	-521	0.0034	0.1256	97.5
	20 days	120	80	-625	0.0005	0.0059	99.8
	100 days	140	100	-820	0.0013	0.0152	99.5
Citrate-nitrite	0 hr	160	100	-463	0.1163	1.3607	90.1
	4 hr	160	100	-499	0.1931	2.2593	54.1
	20 days	80	60	-431	0.0025	0.0293	99.5
	100 days	140	100	-447	0.0032	0.0374	98.7
Benzoate-nitrite	0 hr	140	100	-521	0.0572	0.6692	70.4
	4 hr	120	100	-381	0.0009	0.0105	99.8
	20 days	80	80	-555	0.0003	0.0035	99.9
	100 days	100	80	-399	0.0024	0.0281	99.0
Citrate-nitrite-benzoate	0 hr	190	90	-494	0.2306	2.6981	--
	4 hr	120	80	-533	0.1709	1.9995	59.4
	20 days	100	60	-430	0.1671	1.9551	33.7
	100 days	120	140	-492	0.0003	0.0035	99.9

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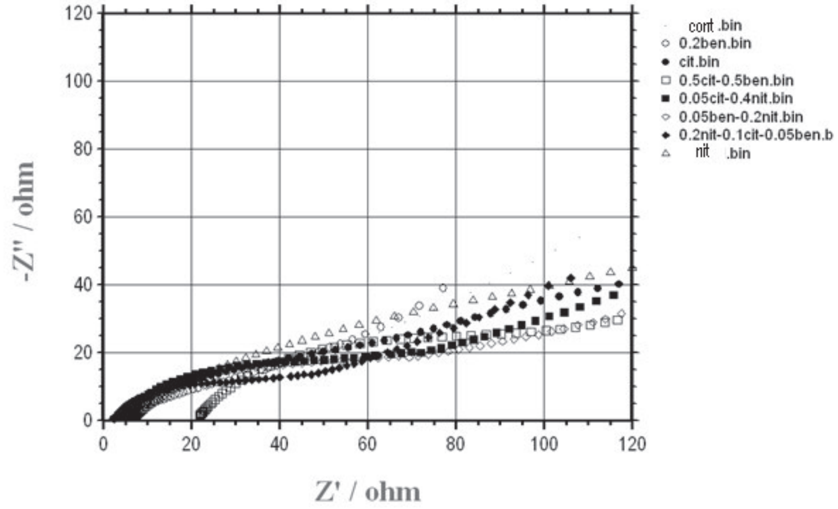

Fig. 6. Nyquiste plot of mild steel specimens exposed to control +various inhibitors for the immersion period of 0 days.

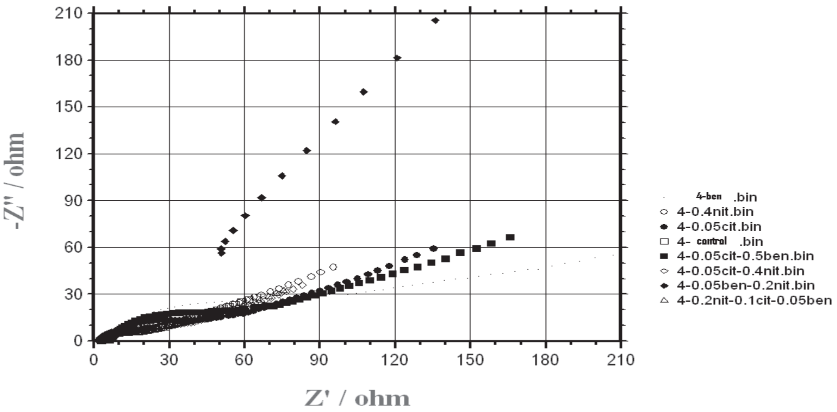

Fig. 7. Nyquiste plot of mild steel specimens exposed to control +various inhibitors for the immersion period of 4 hrs.

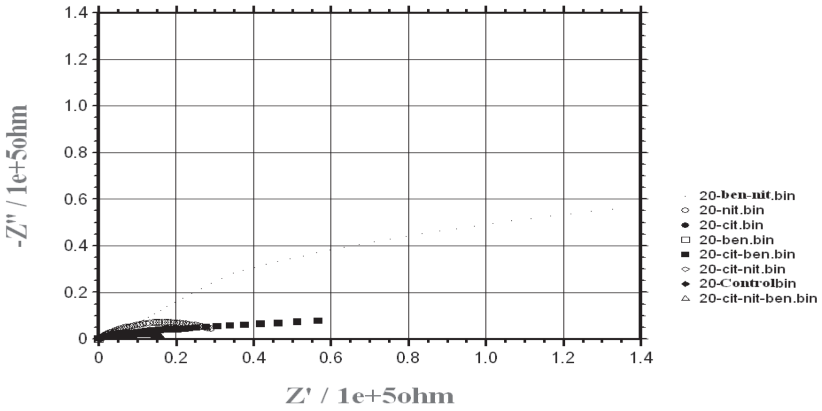

Fig. 8. Nyquiste plot of mild steel specimens exposed to control +various inhibitors for the immersion period of 20 days.

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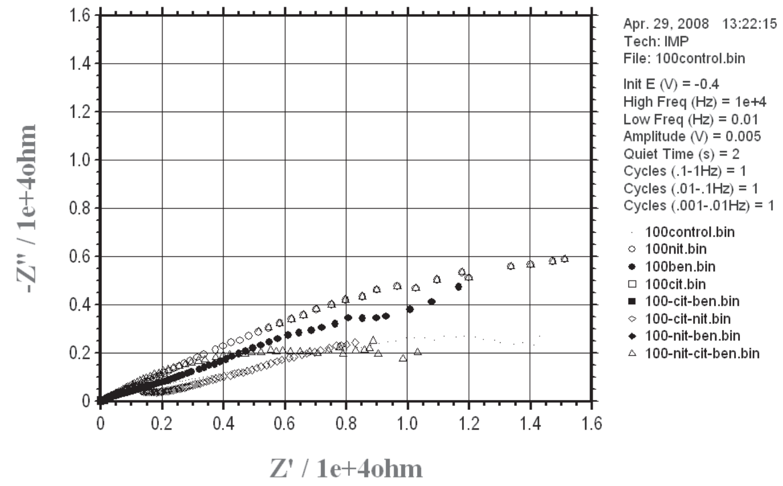

Fig. 9. Nyquiste plot of mild steel specimens exposed to control +various inhibitors for the immersion period of 100 days.

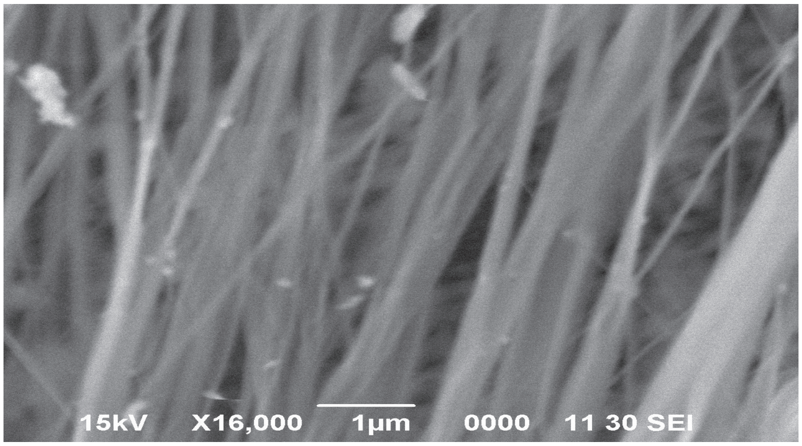

Fig. 10. Mild steel specimens after 100 days of exposure in chlorine contaminated alkaline solution

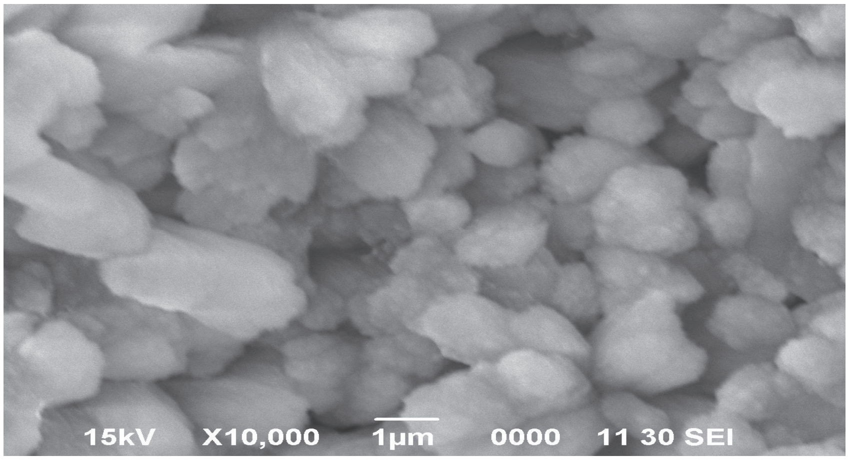

Fig. 11. Mild steel specimens after 100 days of exposure in control + Citrate-benzoate inhibitive systems

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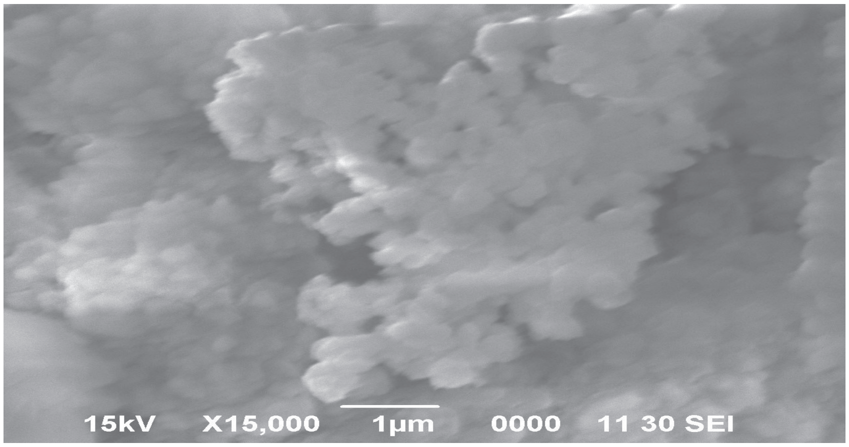

Fig. 12. Mild steel specimens after 100 days of exposure in control + Citrate-nitrite inhibitive systems

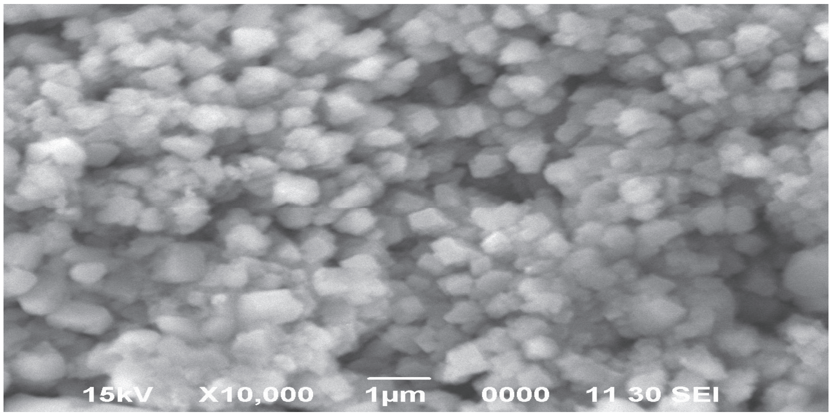

Fig. 13. Mild steel specimens after 100 days of exposure in control + benzoate-nitrite inhibitive systems.

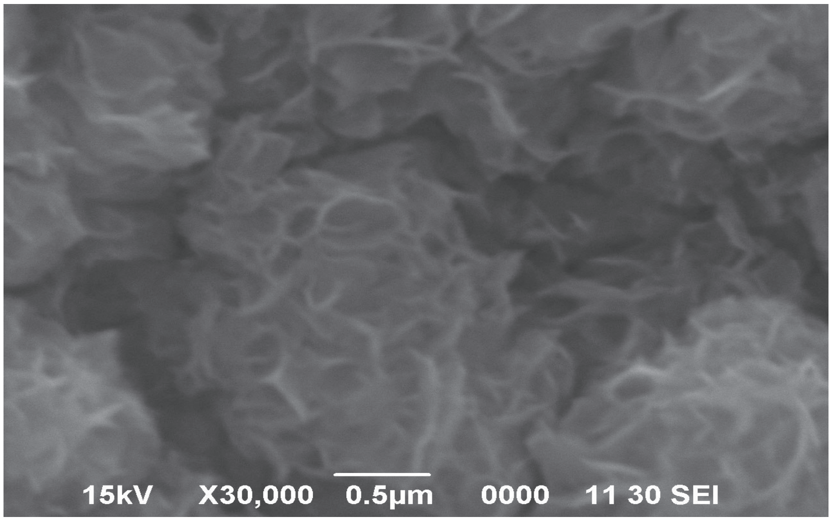

Fig. 14. Mild steel specimens after 100 days of exposure in control + citrate-benzoate-nitrite inhibitive systems.

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Table 3. Electrical Impedance Spectroscopic technique

System studied	Period of immersion	R_p K.Ω	Stern geary constant (mV / dec)	I_{corr} (mA/cm^2)	Corrosion rate (mmpy)	I.E (%)
Control	0 hr	0.386	20	0.0518	0.6112	--
	4 hr	0.367	30	0.0817	0.9641	--
	20 days	0.719	16	0.0223	0.2631	--
	100 days	0.126	28	0.2222	2.6220	--
Nitrite	0 hr	0.352	10	0.0284	0.3351	45.2
	4 hr	0.736	12	0.0163	0.1923	80.0
	20 days	35.65	09	0.0002	0.0024	99.1
	100 days	16.16	13	0.0008	0.0094	99.6
Citrate	0 hr	0.285	23	0.0807	0.9523	--
	4 hr	0.358	19	0.0531	0.6266	35.0
	20 days	0.480	28	0.0583	0.6879	--
	100 days	5.698	28	0.0049	0.0578	97.8
Benzoate	0 hr	0.580	19	0.0328	0.3870	36.7
	4 hr	0.556	24	0.0432	0.5098	47.1
	20 days	0.333	19	0.0570	0.6726	--
	100 days	13.20	23	0.0017	0.0201	99.2
Citrate-benzoate	0 hr	0.872	16	0.0183	0.2159	64.7
	4 hr	0.419	18	0.0429	0.5062	47.5
	20 days	71.76	21	0.0003	0.0035	98.7
	100 days	16.58	25	0.0015	0.0177	99.3
Citrate-nitrite	0 hr	0.529	27	0.0510	0.6018	01.5
	4 hr	0.481	27	0.0561	0.6620	31.3
	20 days	13.39	15	0.0011	0.0130	95.0
	100 days	15.59	25	0.0016	0.0189	99.3
Benzoate-nitrite	0 hr	0.287	25	0.0871	1.0280	--
	4 hr	126.5	24	0.0002	0.0024	99.8
	20 days	339.6	17	0.00005	0.0006	99.8
	100 days	25.88	19	0.0007	0.0083	99.7
Citrate-nitrite-benzoate	0 hr	0.776	27	0.0348	0.4106	32.8
	4 hr	0.411	21	0.0511	0.6030	37.5
	20 days	19.19	28	0.0015	0.0177	93.3
	100 days	10.03	16	0.0016	0.0189	99.3

systems exposed to 100th days of exposure respectively. This was due to the synergistic action of nitrite with citrate and benzoate systems.

4. CONCLUSIONS

From the above studies conducted, the following broad conclusions were drawn, The mixed inhibitors containing nitrite as one of the inhibitor maintaining the passivity even in presence of high chloride concentration of 0.5M NaCl. The combination of nitrite ions with other inhibitive systems showed the synergism that enhanced the durability through repassivation. Especially in the case of citrate-nitrite-benzoate system, significant improvement in passivity on mild steel was observed. Further the nanofibrous coating of -Fe_2O_3 appeared on mild steel enhanced the durability through barrier type protection. The results obtained from gravimetric method confirm that the 100 days exposure of

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mild steel in nitrite with citrate, nitrite with citrate and benzoate mixed inhibitors showed the maximum inhibition efficiency of 98% in comparison with nitrite inhibitive system alone (41.5%). The maximum corrosion resistance performance of these mixed inhibitors system was due to the formation of thick layer of nano γFe_2O_3 fibrous film on steel surface.

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