

CORROSION BEHAVIOUR OF MILD STEEL IN SULPHURIC ACID - EFFECT OF HALIDES

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The effect of halide ions on the corrosion behaviour of mild steel in sulphuric acid medium was studied. Weight loss and polarization studies were carried out in 1 M sulphuric acid and at various concentration of the halide ions (chloride, bromide and iodide). The results revealed that corrosion of mild steel is more in acid medium without halide ions. Halide ions reduce the rate of corrosion and the inhibition efficiency is found to be in the order iodide > bromide > chloride.

Keywords: Mild steel, corrosion, sulphuric acid, halide ions and inhibition.

INTRODUCTION

Pickling of metals by acids is a widely practiced process in many industries for the removal of scales and corrosion products. Presence of halides in acids either as impurities or as additives is known to stimulate the dissolution of metals. Among the halides, the effect of chloride on the dissolution of iron and steel is widely studied [1-7]. But very few studies have been reported on the effect of other halides [8-10]. Hence, attempts have been made in this investigation to study the effect of chloride, bromide and iodide ions in the concentration range of 10^{-4} to 10^{-1} M on the corrosion behaviour of mild steel in 1 M sulphuric acid by chemical immersion and electrochemical methods.

EXPERIMENTAL

Mild steel specimens were cut to the size of 5 x 15 cm from the steel sheets having the following percentage composition Fe = 99.57, C = 0.098, Mn = 0.179, P = 0.002, Si = 0.024, S = 0.01, Cr = 0.0023, Ni = 0.018, Mo ≤ 0.001.

The specimens were numbered, pickled, mechanically polished and degreased before use. For electrochemical studies, the specimens were lacquered so as to expose 1 Sq.cm. area. All the chemicals were of analytical reagent grade and double distilled water was used to prepare the electrolyte.

Immersion tests were carried out in glass beaker containing the solution and electrochemical studies

in glass cell (three electrode polarization cell) equipped with a platinum counter electrode and a saturated calomel electrode as reference electrode. The impedance, linear polarization and Tafel polarization measurements were automatically controlled by a potentiostat, a frequency response analyzer (Solartron, 12893 UK) and a IBM personal computer. The data were analyzed using computer software (ZP/OJ Connore). For the impedance measurements sine wave of amplitude 10 mV in the frequency range of 10 KHz to 100 mHz were superimposed at the open circuit potential. For linear polarization and Tafel polarization the scan rate was 0.1 and 1 mV/sec respectively. Using the software the electrochemical parameters such as corrosion current (I_{corr}), open circuit potential (OCP), polarization resistance (R_p) and Tafel slopes (b_a and b_c) were estimated.

The corrosion current density I_{corr} is inversely proportional to the charge transfer resistance R_p by the relationship.

$$i_{corr} = \frac{b_a b_c}{2.303 (b_a + b_c)} \times \frac{1}{R_p} \quad (1)$$

where b_a and b_c were experimentally determined anodic and cathodic Tafel slope values respectively.

For immersion studies, the steel specimens were immersed for 1 hour in 1 M sulphuric acid containing various concentrations of chloride, bromide and iodide (10^{-4} to 10^{-1} M). From the

weight change the corrosion rate was calculated. The solution was analyzed for ferric ion content by photocolorimeter by thiocyanate method. The efficiency of inhibition was calculated using the formula.

$$\text{Efficiency of inhibition (I)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

where W_0 and W_1 are the weight loss of mild steel in acid free of halide and in acid with halide ion respectively.

RESULTS

Immersion studies

Table I shows the effect of halide ions on the corrosion rate of mild steel in 1 *M* sulphuric acid. It clearly indicates that addition of halide to the acid has reduced the corrosion rate. A steady decrease in corrosion rate is observed by increasing the concentration of halide. The extent of corrosion inhibition is found to depend on the nature and concentration of the halide ions. For a given concentration of halide ion, the degree of corrosion inhibition is in the order of

$$\text{Iodide} > \text{Bromide} > \text{Chloride} \quad (3)$$

TABLE I: Results of immersion studies of mild steel in sulphuric acid — Effect of halide ion

Type of halide	Concn (M)	Weight loss (gms)	Inhibition efficiency(%)
—	—	0.0351	—
Chloride	1×10^{-4}	0.0313	11.11
Chloride	1×10^{-3}	0.0314	10.60
Chloride	5×10^{-3}	0.0297	15.40
Chloride	1×10^{-2}	0.0277	21.00
Chloride	1×10^{-1}	0.0196	44.00
Bromide	1×10^{-4}	0.0305	13.00
Bromide	1×10^{-3}	0.0260	26.00
Bromide	5×10^{-3}	0.0253	28.00
Bromide	1×10^{-2}	0.0207	42.00
Bromide	1×10^{-1}	0.0147	58.00
Iodide	1×10^{-4}	0.0161	54.00
Iodide	1×10^{-3}	0.0109	69.00
Iodide	5×10^{-3}	0.0095	73.00
Iodide	1×10^{-2}	0.0042	88.00
Iodide	1×10^{-1}	0.0021	94.00

Polarization measurements

The polarization curves are illustrated in Fig. 1 and show the effect of iodide ions on the corrosion behaviour of mild steel in sulphuric acid.

The corrosion parameters deduced from Tafel polarization such as corrosion current (i_{corr}), corrosion potential (E_{corr}) and Tafel constants b_a and b_c are given in Table II. From the I_{corr} values, the percentage degree of protection (inhibition efficiency, I.E.) is calculated by

$$\text{I.E.} = \frac{I_{\text{corr}}(\text{acid}) - I_{\text{corr}}(\text{acid with halide})}{I_{\text{corr}}(\text{acid})} \times 100 \quad (4)$$

This value has been taken to present the relative effects of the halide ion on the corrosion of mild steel in sulphuric acid.

The Tafel plots exhibit a well defined Tafel region extending over more than a decade in the current axis. The anodic and cathodic Tafel slopes are found to be 85 ± 10 mV/decade and $90 + 15$ mV/decade respectively and these values are not affected by the presence of halide ion.

The polarization resistance values (R_p) calculated as the slope of the current potential curve near the corrosion potential by the linear polarization method are tabulated in Table III.

The results show that addition of halide ions increases the R_p value (i.e. decreases the corrosion rate) and the inhibition efficiency is more for iodide than for other two halides.

Impedance studies

The Nyquist impedance plots for steel in sulphuric acid with and without iodide additions are shown in Fig. 2.

It may be observed from Fig. 2 that they are single depressed semicircle (capacitive loop) and are not typical semicircle i.e. the centre of the semicircle does not lie on the real axis but shifts below the real axis. Addition of halide increases the diameter of the semicircle (higher R_p value) and the effect is more in the case of iodide.

The parameters R_p , I_{corr} and percentage inhibition efficiency are summarized in Table III. The values show that in acid solution without halide, the R_p is lesser. Addition of halide increases the R_p . This is in accordance with the other results. The variation of inhibition efficiency with the concentration of halides determined by impedance data exhibits the same trend with other methods.

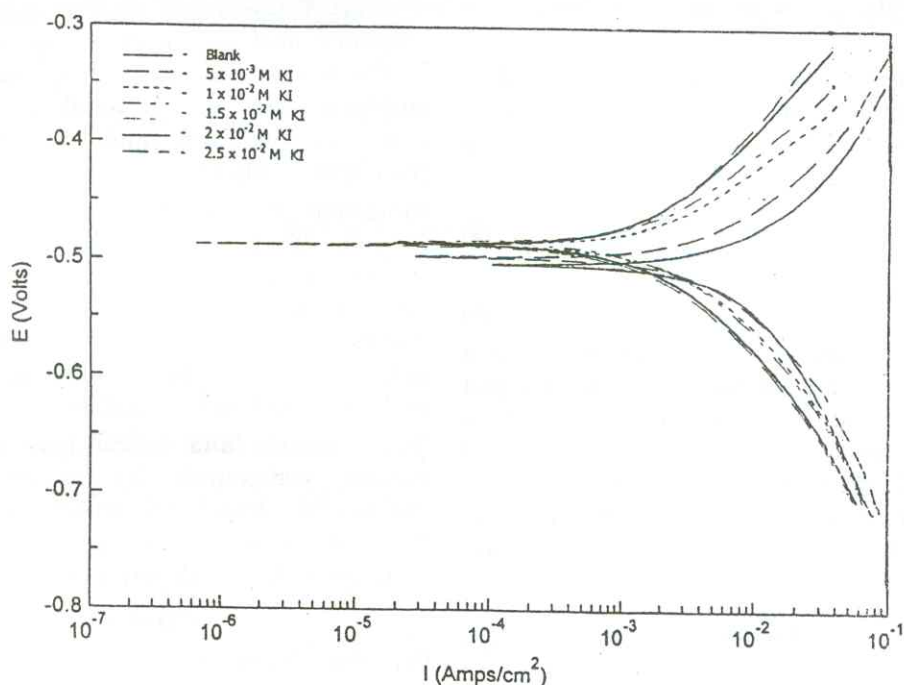


Fig. 1: Potentiodynamic polarization of mild steel in 1 M H₂SO₄ — Effect of iodide ions

The highest inhibiting effect is observed for iodide ion.

DISCUSSION

All the experimental results clearly indicate that the corrosion rate is more in sulfuric acid and addition of halide ion reduced the rate of

TABLE II: Results of electrochemical studies — Tafel polarization

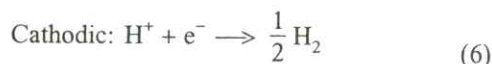
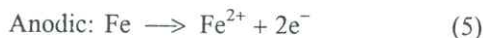
Type of halide	Concn (M)	E _{corr} (mV)	I _{corr} (mA)	b _a (mV)	b _c (mV)	I.E. (%)
—	—	-502	3.720	60	110	—
Chloride	1 x 10 ⁻³	-482	2.900	60	80	22.0
Chloride	5 x 10 ⁻²	-478	2.400	55	80	35.5
Chloride	1 x 10 ⁻²	-470	3.000	65	100	19.0
Bromide	5 x 10 ⁻²	-484	4.830	84	151	30.0
Bromide	5 x 10 ⁻³	-477	2.450	70	110	34.0
Bromide	1 x 10 ⁻²	-474	3.470	90	130	7.0
Bromide	2 x 10 ⁻²	-472	3.360	96	138	10.0
Iodide	1 x 10 ⁻³	-495	3.014	85	104	19.0
Iodide	5 x 10 ⁻³	-483	1.320	79	74	64.0
Iodide	1 x 10 ⁻²	-482	1.220	79	83	67.0
Iodide	1.5 x 10 ⁻²	-482	1.010	88	89	73.0
Iodide	2 x 10 ⁻²	-478	0.930	76	95	75.0

TABLE III: Results of electrochemical studies — LPR and impedance

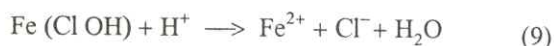
Type of halide	Concn (M)	Polarisation resistance (Ω)		Corrosion current (mA)		Inhibition efficiency (%)	
		LPR	Impe-dance	LPR	Impe-dance	1	2
—	—	3.88	4.50	6.70	8.60	—	—
Chloride	1 x 10 ⁻³	4.74	3.00	5.48	4.30	18	50
Chloride	5 x 10 ⁻³	4.66	3.00	5.57	4.30	17	50
Chloride	1 x 10 ⁻²	5.14	3.50	5.00	2.89	25	66
Bromide	1 x 10 ⁻³	3.67	2.80	7.00	4.64	7	46
Bromide	5 x 10 ⁻³	5.47	5.00	4.75	2.60	29	70
Bromide	1 x 10 ⁻²	6.74	5.25	3.86	2.48	42	71
Bromide	12 x 10 ⁻²	6.60	6.00	3.94	2.17	41	75
Iodide	1 x 10 ⁻³	—	5.00	—	2.76	68	70
Iodide	5 x 10 ⁻³	8.57	7.50	3.00	1.73	55	80
Iodide	1 x 10 ⁻²	8.59	9.50	3.00	1.37	55	84
Iodide	12 x 10 ⁻²	12.74	13.00	2.00	1.00	70	88

corrosion. The extent of inhibition depends on the nature and concentration of halide ions. For a given concentration of halide ions the degree of inhibition is in the order of iodide > bromide > chloride.

The inhibiting effect of halide can be explained as due to adsorption of halide. The corrosion of steel in acidic solution is the sum of the following reaction.



However, each of the reactions proceeds with many consecutive steps depending on the pH and the type of anion present in the solutions. There are two main theories based on the works of Heusler [2] and Bockris [3]. Both the theories indicate the participation of (OH⁻) ions directly. Anodic dissolution of iron in acidic solution could be written as



Adsorption of halide ions on the electrode surface affect the kinetics of dissolution of steel [5-7].

Hackerman *et al.* [8] suggested that the halide ion in general and especially iodide ions affect the steel dissolution in acid solution by a strong

interaction with the metal surface, possibly through chemisorption. Anion adsorption is found to be greater for iodide and bromide than chloride. Moreover, the lower corrosion rate for steel in sulphuric acid containing halide ions might be due to the formation of (Fe OH)_{ads} species whereas in sulphuric acid free of halide ion, only hydroxide ions are involved and so the formation of [Fe(OH)]_{ads} [9].

Inhibition of corrosion by halides are also reported in some other works [5-8] and according to them, the inhibiting effect of the anions depends upon the deformability of the anion, which enables to displace the existing adsorbed species. The deformability of the halides is in the order of chloride < bromide < iodide.

Both bromide and iodide ions are able to form surface compounds by covalent linkage and explains the higher inhibition shown by these ions. When the adsorption is strong enough to result in hydrolysis, then inhibition is more.

CONCLUSION

On the basis of the studies, the following conclusions can be drawn.

- Corrosion rate of steel is more in sulfuric acid free of halide.
- Halide addition reduces the rate of corrosion in sulfuric acid.
- The order of inhibition efficiency is Iodide > bromide > chloride.
- Halides inhibit the rate of corrosion by getting adsorbed on the reaction sites.

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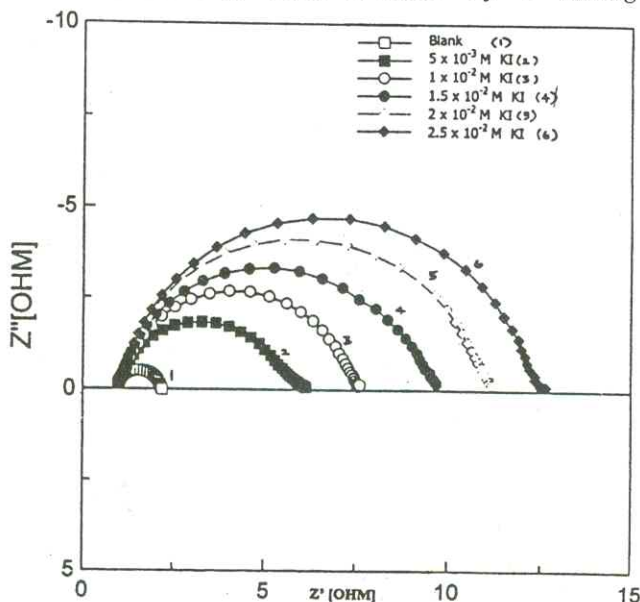


Fig. 2: Nyquist plot of mild steel in 1 M H₂SO₄
Effect of iodide ions