# Corrosion Behaviour of Mild-Steel in Acid Environments - Plain and Binary Acid Mixtures

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Corrosion rate of mild-steel decreases in presence of lower concentration of nitric acid in hydrochloric acid. But, at equal concentrations of binary acid mixture, the rate is higher than in plain hydrochloric acid but lower than that in plain nitric acid. At lower concentration of nitric acid, probably nitrate ion develops a passivating effect on the corroding surface. At higher concentration of nitric acid in binary acid mixture, the formation of nitrous acid and nitrogen dioxide might be destroying passivating effect of nitric acid.

The polarization data and shift in corrosion potentials in less noble direction reveal the effect of nitrate ion in lower concentration of nitric acid. $b_a$ and $b_c$ values indicate that nitrate ion affects the corrosion half reactions almost equally in binary acid mixtures containing lesser concentrations of nitric acid. It has been observed that when acid concentrations are equal in binary acid mixture, both anode and cathode polarise to a large extent. Result of corrosion rate determination by weight-loss and polarization technique have shown good agreement within ± 1.0% of error.

Mild-steel is one major material of construction extensively used in chemical and allied industries for handling alkalies, acids and salt solutions [1]. The study of corrosion of mild-steel in nitric acid is a subject of practical significance, since the acid is highly corrosive and extensively used in various industrial operations. Effect of nitric acid vapour on corrosion behaviour of mild-steel using thermometric technique has been discussed. Here reaction number had been calculated [2]. Uchida [3] evaluated corrosion resistance of newly developed corrosion resistance material to binary acid mixtures (such as $HNO_3 + H_2SO_4$ etc.) and found mixed acids more corrosive than any single acid. Austin [4] reported effect of binary mixture of different acids. It has been reported that corrosion rate of alloys is a function of (a) acid mixture, (b) temperature and (c) composition of alloys [5]. Effect of binary acid mixture using thermometric technique on corrosion behaviour of brass has been investigated by Oza and others [6]. Anodic behaviour of mild-steel in acids containing nitrate ion have been reported by Abdel All and Wahdan. According to them, passivating oxide film present on mild-steel was attacked by nitrate ion [7]. The kinetics of reaction in acid solutions were studied by Hausler and Bonhoffer. From Tafel slopes and from electrochemical reaction orders, a catalytic mechanism involving transfer of ferrous ion ($Fe^{+2}$) in one step was postulated [8]. Potentio-kinetic polarization curves for mild-steel in acidic medium has been discussed [9]. Tafel intercept and linear polaisation technique have been tried by Mehta [10].



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The present communication deals with the corrosion behaviour of mild-steel in single and binary acid mixtures.

## EXPERIMENTAL

### Weight Loss Measurements

Commercial mild-steel specimens (composition S-0.05%, P-0.02%, Mn-0.70%, C-0.27%, Si-0.35%) of 5.5x2.5x0.2 cm size were used. All the chemicals used were of A.R. grade. The solutions were prepared from freshly double-distilled water. Different concentrtions of hydrochloric and nitric acid were studied separately as well as in presence of each other. Samples were completely immersed in 200 ml of the acid solutions. At the end of the immersion period, the specimens were removed carefully, washed with water, dried and finally weighed. Results were computed from average of duplicate experiments.

### Galvanostatic Polarization Measurements

Cylindrical specimen of 6 mm diameter commercial mild-steel rod embeded in Teflon in order to obtain exposed surfaced area of 0.6838 sq.cm. Each electrode was mechanically polished with increasingly finer grade (180, 220, 320, 400, 500, 600) emery paper. The specimens were washed, rinsed with distilled water and dried with rectified spirit after each polishing operation as per standard metallographic practice. Each experiment was carried out with a newly polished electrode and with a fresh portion of the test solution. Galvanostatic polarization studies were carried out using an electronic Galvanostat /Potentiostat Model CL-95. The reference electrode is a saturated calomel electrode and the counter electrode is in the form of platinum foil.

## RESULTS AND DISCUSSION

### Weight Loss Method

From Fig.1(a) and (b) it is clear that there exists a linear relationship between corrosion rate and acid concentration particularly at lower acid concentrations. With increase in acid concentration, however, corrosion rate increases many fold. Corrosion rate of mild-steel in hydrochloric acid solution may be attributed to the presence of chloride ion ($Cl^-$) and hydrogen ions ($H^+$) beyond a thereshold limit. It is interesting to note that corrosion observed is almost uniform type. At higher concentations of nitric acid, corrosion rate is found nearly three times higher than that with hydrochloric acid solution of the same strength. Higher corrosion rate with increase in nitric acid concentrtion may by attributed to the autocatalytic formation of nitrous acid, which may destroy passivating effect.

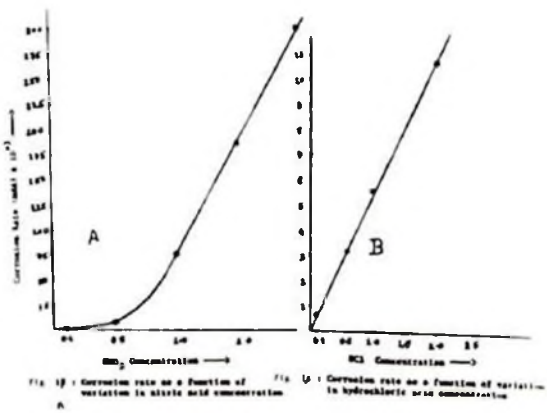



**Fig 1 Corrosion rate as a Function of Acid Concentration**
A. $HNO_3$; B. HCl

**Table 1**

**Corrosion Rate of Mild-steel in Different Acid Solutions by Weight loss Method**

Effective area of the Specimen = 30.7 $cm^2$
Temp. 27±1°C; Immersion Period = 24 hrs

| Concentration (M) | Corr. rate x $10^2$ (mdd) | |
|---|---|---|
| **Single Acid** | **HCl** | **$HNO_3$** |
| 0.1 | 6.03 | 32.61 |
| 0.5 | 32.08 | 61.79 |
| 1.0 (2 hr immersion) | 56.87 | 768.23 |
| 2.0 (1 hr immersion) | 108.23 | 3010.08 |
| **Acid Mixture (HCl + $HNO_3$)** | | |
| 0.1 + 0.01 | 3.30 | |
| 0.1 + 0.02 | 3.97 | |
| 0.1 + 0.05 | 5.89 | |
| 0.1 + 0.1 | 8.99 | |
| 0.5 + 0.05 | 4.72 | |
| 0.5 + 0.1 | 7.55 | |
| 0.5 + 0.2 | 17.27 | |
| 0.5 + 0.5 | 42.42 | |

Results in Table 1, indicate that when nitric acid is added to 0.1 M hydrochloric acid solution, corrosion rate of mild-steel is lower than in single acid. Higher corrosion rate in 0.1 M + 0.1 M binary acid mixture than that in 0.1 M hydrochloric acid solution can be explained considering the autocatalytic formation of nitrous acid and nitrogen dioxide as under:

$$2H^+ + HNO_3 + 2e^- \longrightarrow HNO_2 + H_2O \quad ..(1)$$
$$2HNO_2 \longrightarrow NO_2 + H_2O + NO \quad ...(2)$$

Corrosion rate in 0.1 M binary acid mixture is lower than in 0.1 M $HNO_3$ solution; this may be due to: (1) dilution effect in the mixture, and (2) passivating effect of nitric acid at this concentration. Corrosion rate in $HNO_3$ is higher probably due to the distruction of passivating effect of nitric acid by $HNO_2$ and NO formed. Similar behaviour is also observed with binary acid (0.5 M) solution with different concentration of nitric acid [Fig.-2(a) and 2(b)].

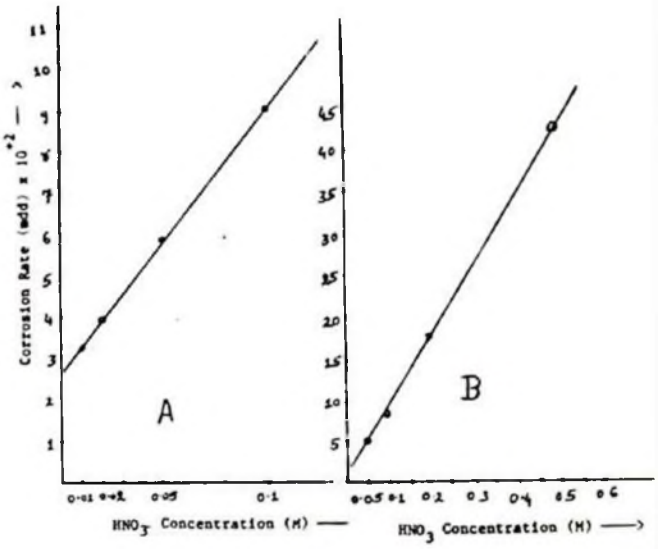



**Fig 2. Corrosion rate as a Function of Variation in Nitric Acid Concentration in Presence of Hydrochloric Acid**
A. 0.1 M HCl; B. 0.5 M HCl

**Polarization Method**

Galvanostatic cathodic and anodic polarization measurements were carried out at different concentrations of plain hydrochloric acid, nitric acid and in their binary mixtures.

The corrosion rate can be determined from corrosion current measurements using the following equation:

$$i_{corr} = 0.96\ W$$

**Table 2**

**Tafel parameters and corrosion rate of mild-steel in HCl and $HNO_3$ Individually and in Binary Mixture**

| Concentration $HCl + HNO_3$ M | OCP vs SCE mV | Corr.C.D. x $10^{-5}$ Amp/cm² | Tafel Slope mV/decade $b_a$ | $b_c$ | Corr.rate(MDD) Wt.loss | Polar. |
|---|---|---|---|---|---|---|
| 0.1 + 0 | 575 | 24 | 120 | 160 | 603.2 | 600.0 |
| 0.1 + 0.01 | 556 | 13 | 125 | 165 | 330.6 | 325.0 |
| 0.1 + 0.1 | 438 | 36 | 90 | 135 | 899.6 | 900.0 |
| 0 + 0.1 | 568 | 130 | 130 | 165 | 3261.0 | 3250.0 |
| 0.5 + 0 | 554 | 130 | 110 | 155 | 3208.0 | 3250.0 |
| 0.5 + 0.05 | 553 | 18 | 105 | 150 | 472.3 | 450.0 |
| 0.5 + 0.5 | 526 | 170 | 95 | 150 | 4242.6 | 4250.0 |
| 0 + 0.5 | 485 | 250 | 100 | 140 | 6179.0 | 6250.0 |

where, $i_{corr}$ is the corrosion current (mA/cm²) and W is the corrosion rate (mg/cm²/h) which can be calculated over a period of hours [11].

Polarization data presented in Table 2, indicate a decrease in corosion current density in hydrochloric acid solutions containing 0.01 M nitric acid. Values of cathodic and anodic over-potentials in binary acid mixture (0.1 M HCl + 0.01 M $HNO_3$) indicate nearly equal effect of nitric acid on anodic oxidative reaction and cathodic reduction reaction. Increase in corrosion rate in binary acid solutions of equal molarity is evident from increase in corrosion current density values. Moreover, cathodic and anodic overpotentials drop considerably (Fig.3 A & B). But, the magnitude of values are somewhat more significant at higher acid concentration (Fig 3B). Corrosion rate from weight-loss determinations as well as polarization technique have shown good agreement within permissible range of error.

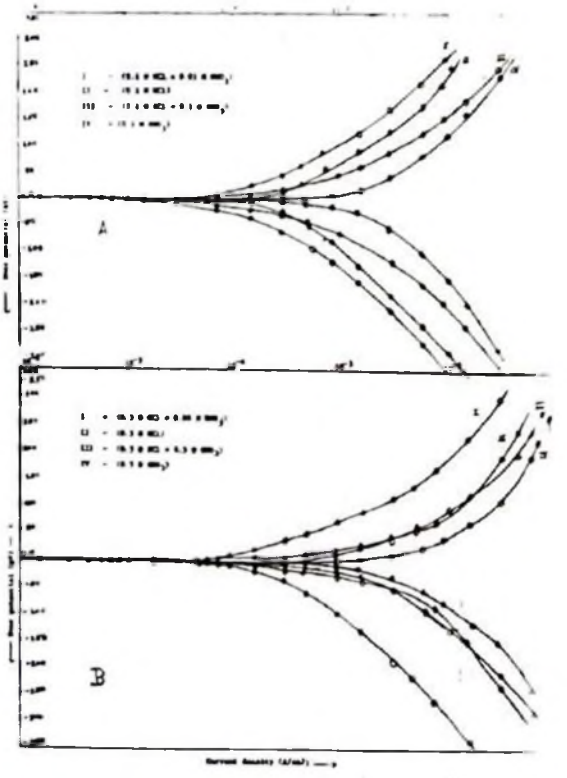



**Fig 3. Effect of Current Density on Cathod and Anode Potentials of Mild-steel in Different Acid Media**
A. 0.1 M asid; B. 0.5 M asid with different amounts of $HNO_3$

## CONCLUSION

1. Corrosion rate of mild-steel increases with increase in acid concentration.

2. Corrosion of mild-steel in plain nitric acid solutions may be due to (i) nitrate ion, (ii) hydrogen ion and nature of complex reactions taking place.

3. Nitric acid (lesser concentrations) in binary acid mixture, reduces corrosion rate by developing passivating effect on the corroding surface. However, when nitric acid is present with equimolar concentration in binary acid mixture, corrosion rate is enhanced by destroying passivating effect of nitric acid.

4. Higher corrosion rate in presence of higher concentation of nitric acid may be attributed to the formation of nitrous acid and nitrogen dioxide.

5. It is apparent from the results of polarization study that presence of nitric acid in a binary acid mixture, affects anodic dissolution and cathodic reduction reactions almost equally.

6. Data on corrosion rate obtained by weight-loss method and polarization technique agree with each other within permissible range.

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