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Metal attack and dissolution of scale by mixtures of acids

Shalini Srivastava

Department of Chemistry, Shia P.G. College(An Associated College of Lucknow University), Lucknow.(U.P.), India

ABSTRACT

Calcareous deposits are formed on boiler surfaces by continuous use of natural water. Scales formed by natural water cannot be removed easily by using single acid. Mixtures of acids were taken to observe metal attack by acids and descaling. Experiments were conducted in such a manner that the quantity of one acid was gradually increased and the ratio of two acids was kept constant. When HNO_3 *concentration was changed, lower concentration decreased rate of corrosion but higher quantities increased it in* **HCl** + H_2CrO_4 *mixture. Results obtained with different concentration of* **HCl** *showed acceleration in rate of corrosion in lower concentration of* HNO_3, H_2CrO_4 *mixture. Even in higher concentration weight loss was appreciable. In* H_2CrO_4 **HCl**, HNO_3 *(90+5+5) respectively mixture is advantageous i.e. corrosion rate is minimum 0.064 gm/dm*^{2} *and scale dissolution is maximum (0.14 gm/minute).:*

Keywords: Corrosion, Scales, Metal Attack, H_2CrO_4, Passivity

INTRODUCTION

Acids can usually be classified as being either oxidizing or non-oxidizing type : the former is represented by concentrated HNO_3 and H_2SO_4 and the later by HCl of all concentrations. The attack on mild steel is dependent on the nature of the acid and the operating conditions. The mechanism of attack is different for oxidizing and non-oxidizing acids. In dilute solution the metal is attacked in all cases and no passivation is possible. In concentrated acid mixtures containing oxidizing acids, passivity is possible provided the other acid component does not cause breakdown of passivity.

Putilova [1] has shown the effect of the mixture of dilute acids (HCl, H_2SO_4, H_3PO_4), on its capacity for rust removal as well as attack on metal. A mixture of 60:20:20 of (4NHCl, H_2SO_4, H_3PO_4), were found most satisfactory for picking of steel. Nitro mixtures containing concentrated HNO_3 and H_2SO_4, have been extensively investigated. Nitro mixtures are passive towards steel when they do not contain water. However, when such mixtures contain water a minimum concentration of H_2SO_4 is required for passivity.

Corrosion of mild steel in mixture of dilute and concentrated acids (HCl, H_2SO_4, HNO_3) has been studied under immersed condition. The data reveals acceleration, mutual reinforcement, breakdown of passivity and inhibition depending upon the nature of the mixtures [2]. The effects of binary combination of HNO_3, H_2SO_4, HCl and HF on the corrosion of Ni alloys and stainless steel were examined. Unexpectedly high corrosion rates occurred for some alloys in some combinations of acids [3].

The corrosion of stainless steel Al Si 304 (11109 – 50 – 5) in mixtures of HCl and HNO_3 under different operating conditions was studied. The rate of corrosion increases as the concentration of the reaction between stainless steel and the acid mixtures becomes exothermic. The maximum corrosion and maximum rise in temperature are observed for the combination 40:60, HCl : HNO_3. Hexamine was an effective inhibitor [4].

Nitric acid (0.15%) has been found to be a very good inhibitor for steel dissolution in 65% H_2SO_4 by corrosiometeric technique [5].

MATERIALS AND METHODS

Mild steel specimens (1.5 x 2.5 cm^2), cut from a single sheet of cold-rolled steel were used. All specimens are polished with 0,00,000 emerey paper, degreased with sulphur free toluene, followed by cleaning with methanol before experiments.

The chemicals were of reagent grade and distilled water used for making the solutions.

The metal panels were cleaned, weighed and fully immersed in 100 cc acid solutions. After the tests they were withdrawn, rinsed, treated with a water-displacing fluid to remove the last traces of acids, cleaned with toluene and reweighed, to determine the metal dissolution, from their losses in weight.

In the tests conducted Normal solutions of three acids were taken. The quantity of one acid was changed from 0-90 % and the other two acids were taken in equal proportions.

The rate of dissolution of scales in mixtures of acids was also studied. Scale was prepared by boiling tap water in an aluminium container. It was analysed and found to contain $CaCO_3$. Then 1 gm of scale was taken and it was dissolved in various acid mixtures for two minutes. Scale was then collected on filter paper, washed with water, dried and kept in desiccators, filled with $CaCl_2$, overnight and then weighed next day. In mixtures of acids, that ratio of acid was taken, where there was least weight loss of mild steel.

DISSOLUTION OF SCALE

The rate of dissolution of $CaCO_3$ scale in mixtures of acids was determined by putting 1 gm scale in contact with acids for 2 minutes. From the weight loss which was attained in 1N solution of mixtures of these acids in different combinations those acid combinations were chosen in which weight loss was minimum. In these combinations scale dissolution rate was determined. Results have been given in Table 4.

In H_2CrO_4 rate of dissolution of scale was 74.7 mg/minutes, in HNO_3 it was 99.9 mg/minutes and in HCl it was 74.8 mg/minutes. Scale dissolution efficiency was 140.1 mg/minutes in H_2CrO_4, HCl, HNO_3 mixture (90+5+5), 135.1 in HNO_3, HCl, H_2CrO_4 (20+40+40), 137.0 in HCl, HNO_3, H_2CrO_4 (60+20+20).

There was negligible weight loss H_2CrO_4, HCl, HNO_3 mixture (6.4 mg/dm^2) while in other two mixtures it was appreciable. Thus we conclude that H_2CrO_4, HCl, HNO_3 is most advantageous mixture i.e. scale dissolution is maximum and corrosion rate is minimum.

TABLE 1 CORROSION OF MILD STEEL IN TERNARY MIXTURE OF 1N SOLUTION OF CHROMIC ACID + HYDROCHLORIC ACID + NITRIC ACID (1Hr, R.T.)

Volume of Acid (cc)	Weight loss (mg/dm^2)
H_2CrO_4 + HCl + HNO_3	
10 + 45 + 45	505.6
20 + 40 + 40	448.0
30 + 35 + 35	4.8
50 + 25 + 25	345.6
80 + 10 + 10	246.4
90 + 05 + 05	6.4

TABLE 2 CORROSION OF MILD STEEL IN TERNARY MIXTURE OF 1N SOLUTION OF HYDROCHLORIC ACID + NITRIC ACID + CHROMIC ACID (1Hr, RT.)

Volume of Acid (cc)	**Weight loss (mg/dm^2)**
HCl + HNO_3 + H_2CrO_4	
10 + 45 + 45	1027.2
30 + 35 + 35	854.4
40 + 30 + 30	816.0
60 + 20 + 20	432.0
70 + 15 + 15	451.2
80 + 10 + 10	601.6
90 + 05 + 05	742.4

TABLE 3 CORROSION OF MILD STEEL IN TERNARY MIXTURE OF 1N SOLUTION OF NITRIC ACID + HYDROCHLORIC ACID + CHROMIC ACID (1Hr, RT.)

Volume of Acid (cc)	Weight loss (mg/dm^2)
HNO_3 + HCl + H_2CrO_4	
10 + 45 + 45	470.8
20 + 40 + 40	358.4
40 + 30 + 30	432.0
50 + 25 + 25	460.8
60 + 20 + 20	508.8
80 + 10 + 10	723.2
90 + 05 + 05	1433.6

TABLE 4 RATE OF DISSOLUTION OF SCALE

Acid taken	Ratio of Acid Mixture (cc)	Rate of Corrosion (mg/dm^2)	Ratge of scale Dissolution (mg/minutes)
HCl	100	35.2	74.8
HNO_3	100	2521.6	99.9
H_2CrO_4	100	Nil	74.7
HCl + HNO_3 + H_2CrO_4	60 + 20 + 20	432.0	137.0
HNO_3 + HCl + H_2CrO_4	20 + 40 + 40	358.4	135.1
H_2CrO_4 + HCl + HNO_3	90 + 05 + 05	6.4	140.1

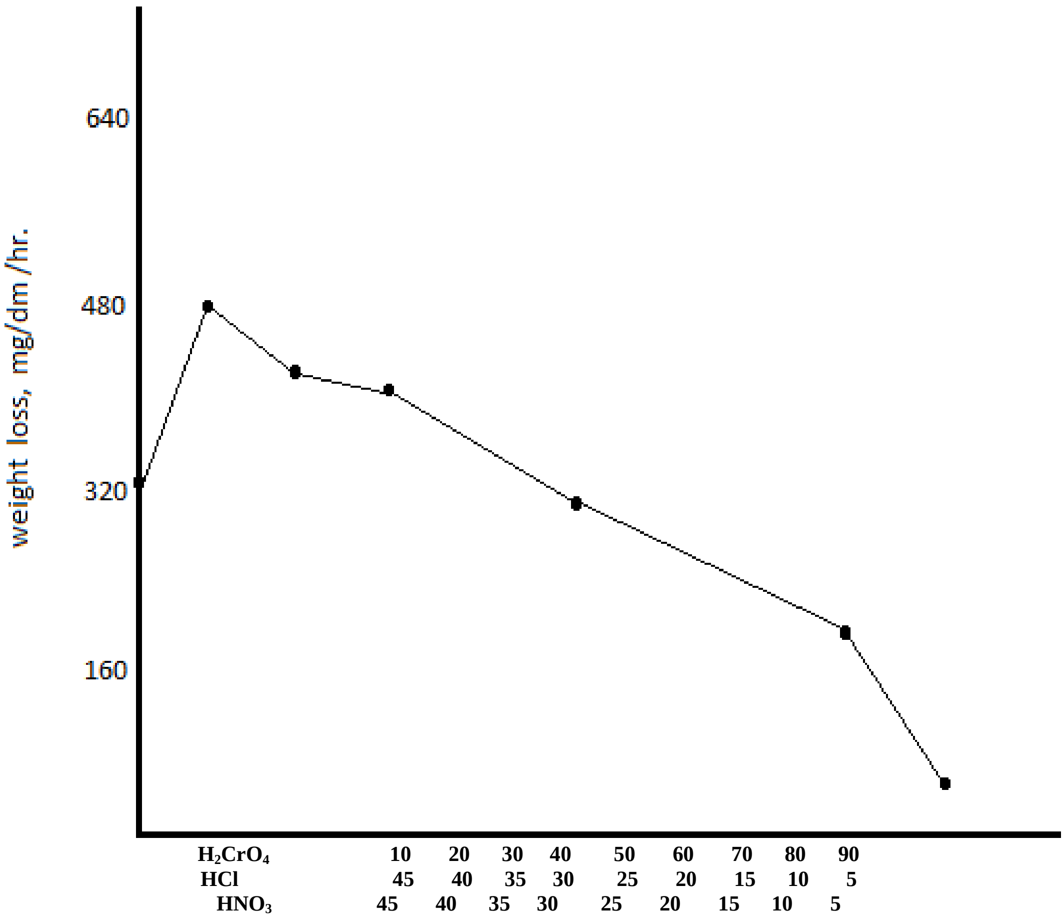

Fig. 1 CORROSION OF MILD STEEL IN MIXTURES OF 1N H_2CrO_4, HCl AND HNO_3 (RT, 1hr)

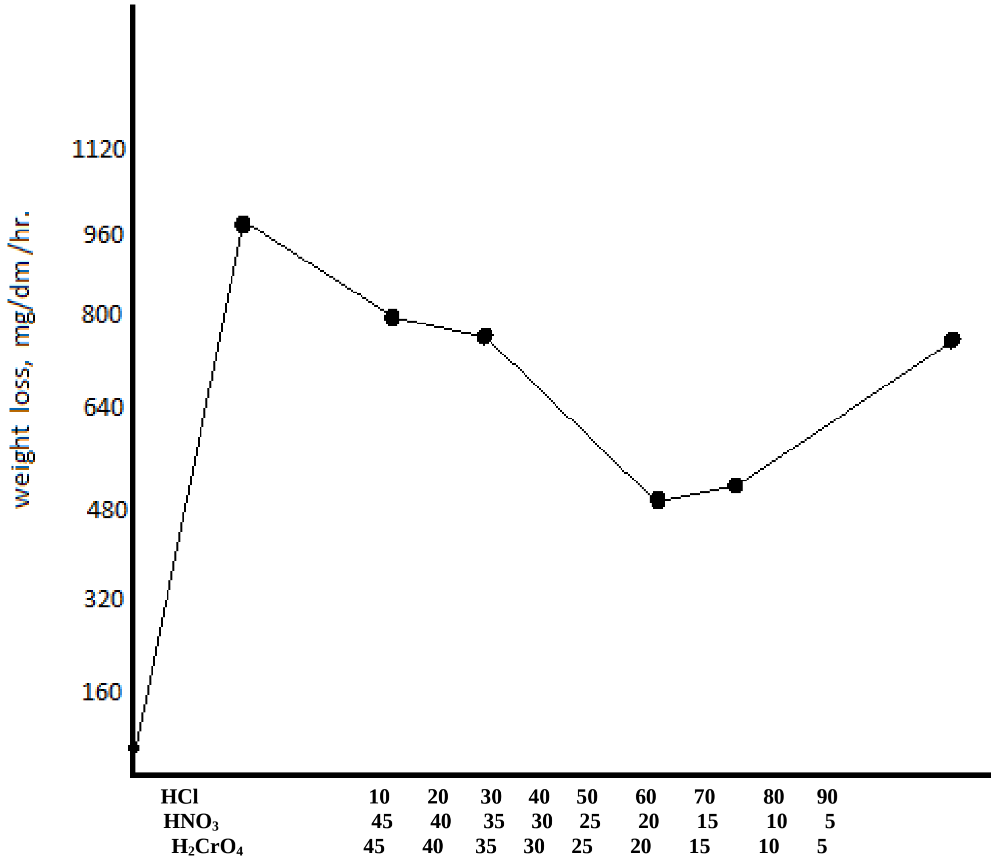

Fig. 2 CORROSION OF MILD STEEL IN MIXTURES OF 1N HCl, HNO_3 AND H_2CrO_4 (RT, 1hr)

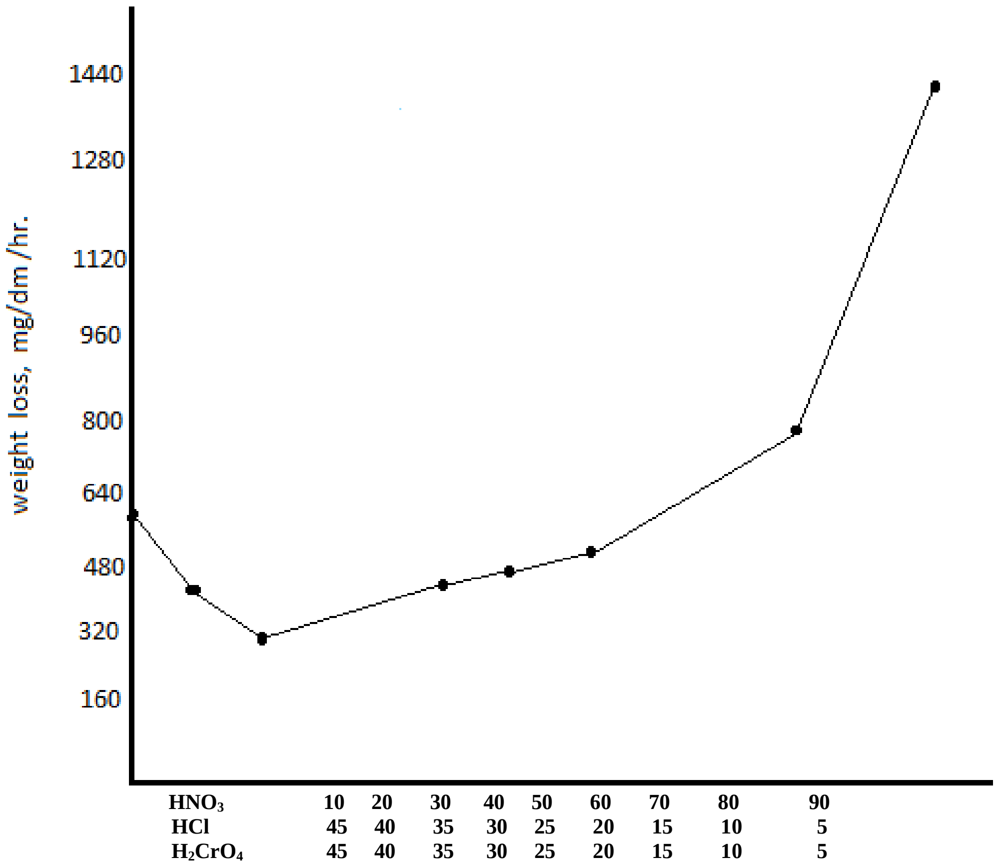

Fig. 3 CORROSION OF MILD STEEL IN MIXTURES OF 1N HNO_3, HCl, AND H_2CrO_4 (RT, 1hr)

RESULTS AND DISCUSSION

CHROMIC ACID + HYDROCHLORIC ACID + NITRIC ACID

Corrosion rate of mild steel in mixtures of 1N H_2CrO_4 is shown in figure 1, table 1.the quantity of H_2CrO_4 was changed in the experiment. Addition of 10 parts of H_2CrO_4 to HCl, HNO_3 mixture showed sharp increase in corrosion values from 320 to 505 mg/dm^2. Increase of further quantity of H_2CrO_4 decreased the weight loss gradually. In 90% H_2CrO_4 there was a sharp fall in weight loss.

It is evident that H_2CrO_4 is harmful for HCl, HNO_3 mixture in small amounts but beneficial in larger amounts.

HYDROCHLORIC ACID + NITRIC ACID + CHROMIC ACID

Corrosion rate of mild steel in mixtures of 1N HCl : HNO_3 : H_2CrO_4 is shown in fig 2, Table 2. Here quantity of HCl was changed in the experiment, in HNO_3 : H_2CrO_4 mixture of 1:1 there was practically no weight loss (6.4 mg/dm^2)When 10 part of HCl was added to the mixture corrosion rate increased from 6.4 to 1027 mg/dm^2. Increased quantity of HCl upto 60:20:20 HCl : HNO_3 : H_2CrO_4Thus addition of HCl is harmful to mild steel exposed to HNO_3, H_2CrO_4 mixture. This may be due to the fact that HNO_3 and H_2CrO_4 mixture being strongly oxidizing agents passivating the mild steel, Cl ions of HCl breaks the passivity and increases the attack.

NITRIC ACID + HYDROCHLORIC ACID + CHROMIC ACID

Corrosion rate of mild steel in mixtures of 1N HNO_3 : HCl : H_2CrO_4, where quantity of HNO_3 is changed is shown in fig.3, Table 3. Addition of 10 and 20 parts of HNO_3 to HCl : H_2CrO_4 mixture reduced the weight loss. Further addition of HNO_3 increased weight loss continuously. Weight loss value 20:40:40 HNO_3 : HCl : H_2CrO_4 was 358 mg and in 90:5:5 weight loss value was 1433.6 mg/dm^2. From the figure\ it is evident that addition of smaller quantities of HNO_3 causes inhibition in corrosion due to HCl : H_2CrO_4 mixture.

CONCLUSION

Mild steel is not attacked in H_2CrO_4. HNO_3 is a very strong oxidising agent. Its rate of corrosion is maximum in HNO_3.

1. HCl is harmful to mild steel in HNO_3, H_2CrO_4 mixture in all concentration.
2. Smaller quantities of HNO_3 inhibits the rate of corrosion in HCl : H_2CrO_4 mixture.
3. H_2CrO_4 is harmful for HCl, HNO_3 mixture in small amounts, in larger amounts H_2CrO_4 is beneficial for HCl, HNO_3 mixture. In this mixture H_2CrO_4 : HCl : HNO_3 (90+5+5) corrosion rate of mild steel is minimum and rate of scale dissolution is maximum.

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