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Corrosion of mild steel in binary mixtures of acids

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ABSTRACT

Corrosion behaviour of mild steel in binary mixtures of dilute (IN) acids (H_2SO_4, HCl, HNO_3, H_3PO_4, H_2CrO_4) has been studied. In HCl: HNO_3 and H_3PO_4: HNO_3 mixtures when small amount of HCl or H_3PO_4 was added to HNO_3, it reduced the weight loss of mild steel considerably. In HCl: H_2SO_4 mixture, a small amount of HCl caused acceleration of attack. In H_2SO_4: H_3PO_4 mixture, attack in single acid was low but in 1:1 mixture the attack was very severe. In H_2SO_4: HNO_3 mixture and H_2CrO_4: HNO_3 mixture, the addition of H_2SO_4 or H_2CrO_4 to HNO_3 continuously deceased their attack. In H_2CrO_4: H_2SO_4 mixture, addition of H_2CrO_4 to H_2SO_4 had practically no effect. The addition of H_2CrO_4 to HCl had accelerating effect up to 1:1 ratio. Metal is not attacked in H_2CrO_4 and addition of H_3PO_4 to H_2CrO_4 had no detrimental effect.

Keywords: Corrosion, Mild steel, Passivity, weight loss, Acids.

INTRODUCTION

The problem of corrosion is of considerable importance, nowadays due to increase in uses of metals and alloys. Iron and ferrous alloys have been extensively used under different conditions in chemical and allied industries in handling alkalies, acids and salt solutions, leakage due to the faulty corrosion resistance of mild steel. The awareness of corrosion, its periodic monitoring, timely detection followed by maintenance and repairs is very important especially for buildings, structures and plants which are in contact with inflammable toxic chemicals. Proper corrosion control can save loss to the order of 20,000 crore or more and industrial accident can be averted. Iron and ferrous alloys have been extensively used under different conditions in chemical and allied industries in handling alkalies, acids and construction, which is extensively used in such situations [1].

Acid solutions are generally used for the removal of rust and scale in several industrial processes. Sulphuric acid is often used as a pickling acid for steel and its alloys [2]. Mild steel is employed widely in most industries due to its low cost and availability in ease for the fabrication of various reaction vessels such as cooling tower tanks, pipelines, etc [3].

In industry many metal finishing processes involve the use of more than one acid in mixture for removal of rust, corrosion products or foreign residues and for etching or pre treatment of metals.

It has been found that the solution rate of rust is highest in hydrochloric acid, nearly twice as slow in sulphuric acid and three times as slow in phosphoric acid .On the other hand, from the point of view of metal attack the metal dissolves most rapidly in aqueous sulphuric acid, some what more slowly in hydrochloric acid and slowest of all in phosphoric acid .Accordingly, for pickling, where complete removal of rust with least attack on metal is required, a mixture of 4N solution of 60:20:20 HCl : H_2SO_4 : H_3PO_4 is used with advantage . The pickling of steel in oxidising acid is expected to produce a metal surface without any absorbed hydrogen, as would be the case when the acid (non-oxidising) is hydrogen evolution type which causes hydrogen embrittlement or blisters of pickled metals. Mixtures of acids eg. H_2SO_4 + HCl or H_2SO_4 + HNO_3 may thus be used with advantage for pickling [4].

Another mixture of acid possessing industrial interest is that produced in the chamber process in making H_2SO_4, the mixture being 10% nitrogen oxide, expressed as HNO_3 in H_2SO_4 [5].

In addition to the industrial applications of mixed acids, investigations on the corrosive effect of acid mixtures on metals provide attractive theoretical interest in view of the differences in the electrochemical characteristics of metal corrosion process in oxidising and non-oxidising acids and the possibilities of formation, retention and breakdown of passive films in different mixtures. We have come across only on reference [6] reporting the mechanism of corrosion of iron in mixtures of dilute solutions of HCl and $HNO_{3.}$ Clearly much further work is wanted on this topic to cover mixtures of other acids over a wide range of concentration.

The present investigation deals with the behaviour of iron in mixtures of dilute (1N) solutions of HCl + H_2SO_4, HCl + HNO_3, H_2SO_4 + HNO_3, HCl + H_3PO_4, HCl + H_2CrO_4, H_2SO_4 + H_3PO_4, H_2SO_4 + H_2CrO_4, H_3PO_4 + H_2SO_4, HNO_3 + H_3PO_4, HNO_3 + H_2CrO_4 used in different proportions.

MATERIALS AND METHODS

Mild steel specimens (1.25 x 2.5) cm^2, cut from a single sheet of cold – rolled steel were used. All specimens were polished with 0,00,000 emery 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 solution.

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 with mixtures of dilute acids various proportion (0 to 100) of one of the acids were taken with various proportions (100 to 0) of the other.

The present investigation deals with the behaviour of iron in mixtures of dilute (1N) solutions of HCl + H_2SO_4, HCl + HNO_3, H_2SO_4 + HNO_3, HCl + H_3PO_4, HCl + H_2CrO_4, H_2SO_4 + H_3PO_4, H_2SO_4 + H_2CrO_4, H_3PO_4 + H_2SO_4, HNO_3 + H_3PO_4, HNO_3 + H_2CrO_4 used in different proportions.

RESULTS AND DISCUSSION

The corrosion rates of mild steel in mixtures of various proportions of 1N solutions of HCl and H_2SO_4 are shown in Table1& fig.1. The addition of 20% HCl to H_2SO_4 caused acceleration in corrosion values [7, 8]. Further addition of HCl to H_2SO_4 considerably reduced the metal attack. From the fig, it can be concluded that corrosion behaviour of mild steel in the mixture of HCl and H_2SO_4 is not very systematic [9, 10]. The dotted line shows the expected corrosion rate in mixture of acids. It is evident from the figure that mixture is generally corrosive, as most of the points lie above the dotted line [11].

Results obtained in mixtures of 1N HCl with 1N HNO_3 are shown in Table 2 & Fig 2. The rate of attack in HNO_3 alone was much higher than in HCl. The introduction of 30 parts of HCl into HNO_3 caused a sharp decline in weight loss value, which was further reduced at a slower rate on addition of more HCl. 30% HCl brought down the weight loss from 2.637 to 0.592 mg/dm^2. It is obvious that HCl addition has inhibitive effect, as in every case weight loss values are less than the expected values (shown by dotted line) [12].

Corrosion of steel in mixtures of 1N HNO_3 with 1N H_2SO_4 are shown in Table 3 & Fig 3. The results show that the dissolution of mild steel in 1N HNO_3 alone was approximately 9 times more than in 1N H_2SO_4 alone. As the concentration of H_2SO_4 was increased further, weight loss decreased. When 70% H_2SO_4 was added to 30% HNO_3 weight loss decreased considerably (from 2.522 to 0.416 mg/dm^2). From the fig.3, it is concluded that H_2SO_4 has an inhibitive effect on HNO_3, as weight loss is less than the expected value (dotted line) [13].

Corrosion of mild steel in mixture of 1N H_3PO_4 + 1N HNO_3 is shown in Table 4 & Fig 4. Corrosion rate of mild steel in 1N HNO_3 is about 15 times more than in 1N H_3PO_4 alone. Addition of 20% H_3PO_4 to HNO_3 reduced the weight loss from 2.5504 to1.312 mg/dm^2. Further addition of H_3PO_4 reduced the weight loss gradually. When 50% H_3PO_4 was added to 50% HNO3, there was reduction in weight loss by about 8 times, than that in HNO_3 alone. Thereafter there was a slow decrease in weight loss. Thus H_3PO_4 has an inhibitive effect on HNO_3.

Corrosion of mild steel in mixtures of 1N H_3PO_4 and 1N HCl are shown in Table 5 & Fig 5. Corrosion values decreased as HCl was added to H_3PO_4. Minimum weight loss value was obtained when 40 parts of HCl was added to 60 parts of H_3PO_4. Percentage protection obtained in this mixture was 85%. After that the weight loss increased. Maximum weight loss was obtained in 30 HCl: 70 H_3PO_4. Further increase in HCl quantity reduced the weight loss. The weight loss is not in a systematic order, in some ratio inhibition and in some ratio acceleration in corrosion is obtained [14, 15, and 16].

Table 6 & Fig 6 show the weight loss in mixtures of (1N) H_2SO_4 and H_3PO_4. There was maximum corrosion in mixture of 40 parts of H_3PO_4 and 60 parts of H_2SO_4. As the volume of H_3PO_4 increased further there was a decline in weight loss. In the mixture from 70% H_3PO_4 + 30% H_2SO_4 to 100% H_3PO_4, the curve was horizontal, indicating thereby small quantity of H_2SO_4 in H_3PO_4, had no effect. It is evident from the fig.6 that addition of H_3PO_4 to H_2SO_4 has detrimental effect for mild steel [17].

Corrosion rates of mild steel in mixtures of 1N H_2CrO_4 and 1N HNO_3 are shown in Table 7 & fig 7. The addition of H_2CrO_4 to HNO_3 inhibits corrosion. There was a sharp decrease till 30 parts of H_2CrO_4 was added to 70 parts of HNO_3. Weight loss reduced from 1.8 mg/dm^2 to 0.045 mg/dm^2. Percentage protection obtained was 97.5%. Further increase of chromic acid maintained mild steel in passive condition. It is obvious that H_2CrO_4 content $\geqq$ 30% in HNO_3 renders mild steel passive. This is due to the fact that H_2CrO_4 and HNO_3 both are oxidising acids. Addition of H_2CrO_4 makes HNO_3 so strong oxidising agent that it passivates mild steel.

Corrosion of mild steel in mixtures of 1N H_2CrO_4 and 1N H_2SO_4 is shown in Table 8 & Fig 8. It was seen from figure that as 10 parts of H_2CrO_4 was introduced to 90 parts of H_2SO_4, there was increase in corrosion value from 249.6 to 627.2 mg/dm^2. Corrosion value increased further and it was maximum in 30% H_2CrO_4. When H_2CrO_4 was increased to 50%, weight loss was minimum and this trend continued up to 90% H_2CrO_4 and 10% H_2SO_4. In 100% H_2CrO_4 also there was no weight loss. H_2CrO_4 is a strong oxidising agent and passivates mild steel in H_2SO_4, when present in higher concentration [18, 19].

Table 9 & Fig 9 shown the curve obtained when (1N) H_2CrO_4 and (1N) HCl are mixed together. When H_2CrO_4 was added to HCl, initially there was an increase in weight loss till 40 parts of H_2CrO_4 was added to 60 parts of HCl. Thereafter the weight loss decreased gradually. There was no weight loss in 100% $H_2CrO_{4.}$ Fig 9 shows that mixture of 1N H_2CrO_4 and 1N HCl is highly detrimental for mild steel.

In the mixture of (1N) H_3PO_4 and (1N) H_2CrO_4 there was no corrosion effect as shown in Table 10 & fig 10. Only in 100% H_3PO_4 there was a negligible weight loss. Addition of smallest quantity of H_2CrO_4 to H_3PO_4 rendered mild steel passive. Further addition of H_2CrO_4 had no effect on corrosion rate. It is evident from the Fig.10 that H_3PO_4: H_2CrO_4 mixture is a passivating mixture for mild steel.

Table 1

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$HCl + H_2SO_4$	
O + 100	483.2
10 + 90	432.0
20 + 80	784.0
30 + 70	640.0
40 + 60	380.8
60 + 40	108.8
80 + 20	268.8
90 + 10	128.0
100 + 0	35.2

Table 2

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$HCl + HNO_3$	
O + 100	2.637
10 + 90	1.728
30 + 70	0.592
40 + 60	0.480
50 + 50	0.320
70 + 30	0.200
90 + 10	0.99
100 + 0	0.035

Table 3

5.Volume of Acid (cc)	Weight Loss (mg/dm^2)
$HCl + H_3PO_4$	
O + 100	217.6
30 + 70	147.2
40 + 60	32.0
60 + 40	150.4
70 + 30	313.6
80 + 20	25.6
100 + 0	44.8

Table 4

6.Volume of Acid (cc)	Weight Loss (mg/dm^2)
$H_3PO_4 + H_2SO_4$	
O + 100	99.2
20 + 80	208.0
30 + 70	339.2
40 + 60	592.0
50 + 50	336.0
70 + 20	51.2
100 + 0	70.4

Table 5

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$H_2SO_4 + HNO_3$	
O + 100	2.522
10 + 90	1.808
30 + 70	1.616
50 + 50	1.107
70 + 30	0.416
80 + 20	0.326
90 + 10	0.278
100 + 0	0.237

Table 6

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$H_3PO_4 + HNO_3$	
O + 100	2.5504
20 + 80	1.312
30 + 70	0.8
40 + 60	0.438
50 + 50	0.310
80 + 20	0.227
100 + 0	0.169

Table 7

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$H_2CrO_4 + HNO_3$	
O + 100	1.8048
10 + 90	1.5296
20 + 80	1.161
30 + 70	0.045
40 + 60	0.006
50 + 50	0.006
70 + 30	0.003
80 + 20	NIL
100 +0	NIL

Table 8

Volume of Acid (cc)	Weight Loss (mg/dm^2)
$H_2CrO_4 + H_2SO_4$	
O + 100	249.6
10 + 90	627.2
30 + 70	742.4
50 + 50	4.8
60 + 40	NIL
70 + 30	NIL
80 + 20	NIL
90 +10	NIL
100 + 0	NIL

Table 9 **Table 10**

Volume of Acid (cc)	Weight Loss (mg/dm^2)	Volume of Acid (cc)	Weight Loss (mg/dm^2)
H_2CrO_4 + HCl		H_3PO_4 +H_2CrO_4	
O + 100	89.6	O + 100	NIL
10 + 90	102.4	10 + 90	NIL
20 + 80	26204	20 + 80	NIL
30 + 70	419.2	30 + 70	NIL
40 + 60	585.6	40 + 60	NIL
50 + 50	582.4	50 + 50	NIL
60 + 40	438.4	60 + 40	NIL
70 + 30	329.6	70 + 30	NIL
90 + 10	3.2	90 +10	NIL
100 + 0	NIL	!00 + 0	NIL

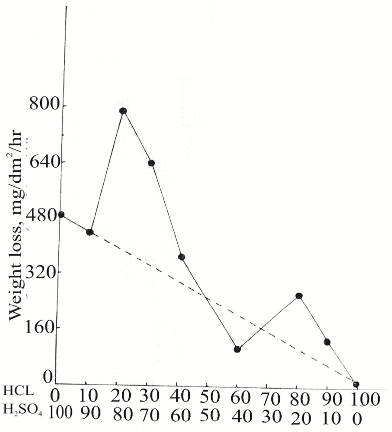

Fig. 1 CORROSION OF MILD STEEL IN MIXTURES OF (1N) HCL AND (1N) H_2SO_4 (RT,1hr)

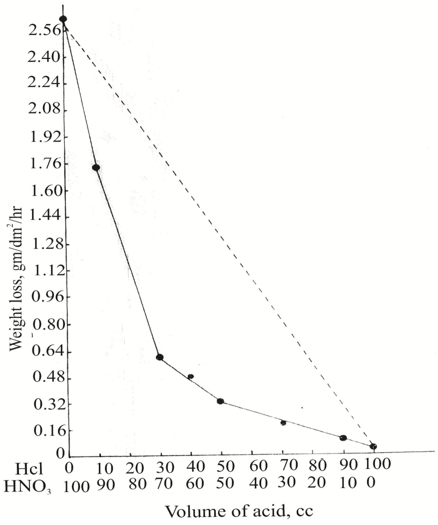

Fig. 2 CORROSION OF MILD STEEL IN MIXTURES OF (1N) HCl AND (1N) HNO_3 (RT,1hr)

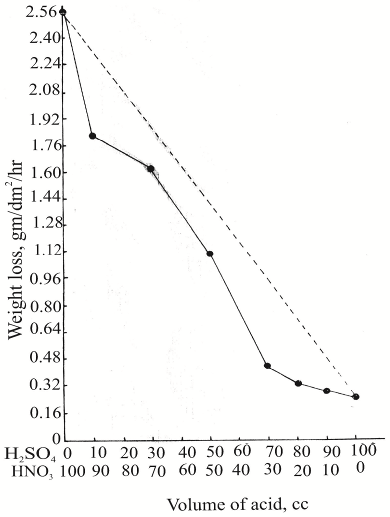

Fig. 3 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_2SO_4 AND (1N) HNO_3 (RT,1hr)

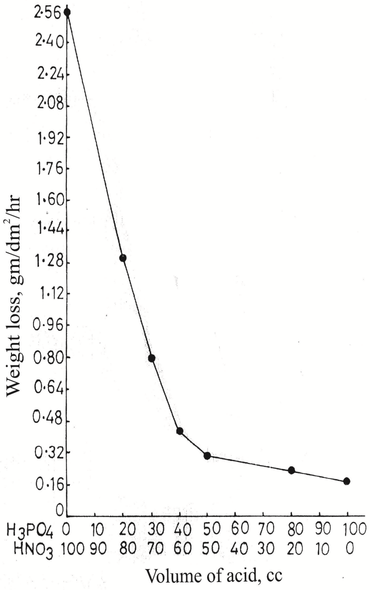

Fig. 4 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_3PO_4 AND (1N) HNO_3 (RT,1hr)

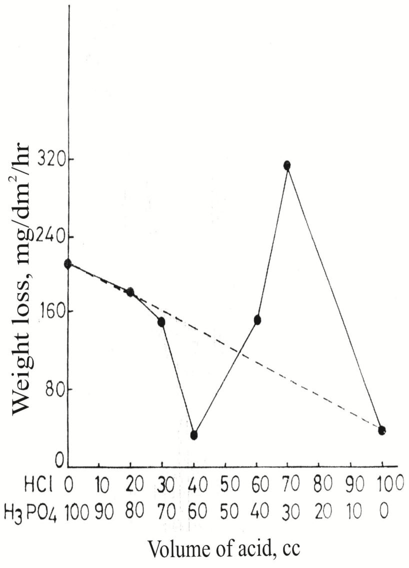

Fig. 5 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_3PO_4 AND (1N) HCl (RT,1hr)

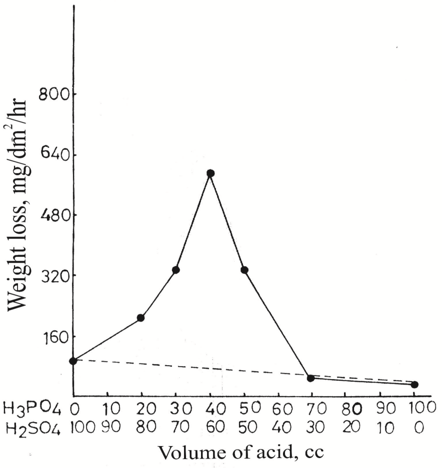

Fig. 6 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_2SO_4 AND (1N) H_3PO_4 (RT,1hr)

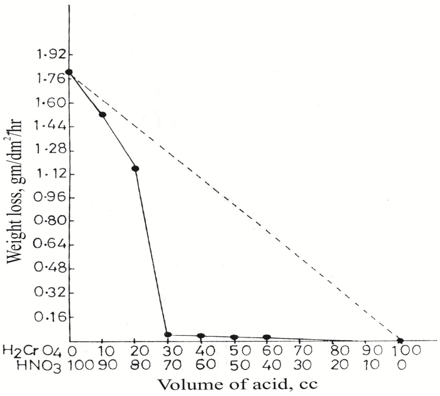

Fig. 7 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_2CrO_4 AND (1N) HNO_3 (RT,1hr)

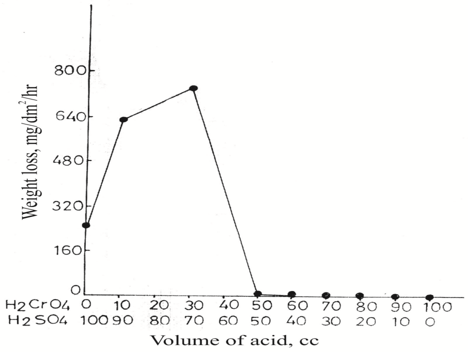

Fig. 8 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_2CrO_4 AND (1N) H_2SO_4 (RT,1hr)

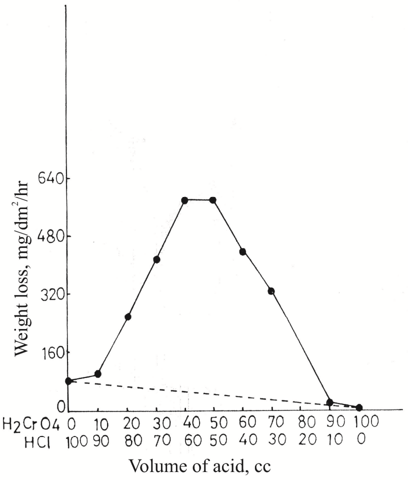

Fig. 9 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_2CrO_4 AND (1N) HCl (RT,1hr)

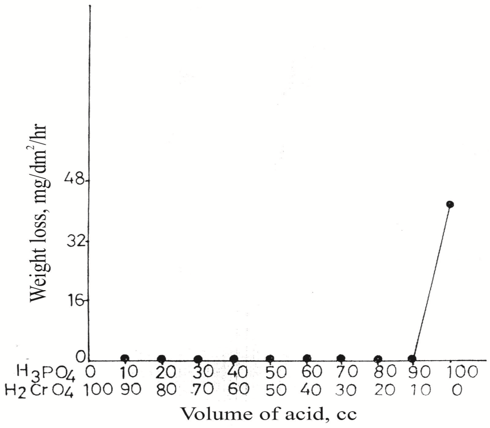

Fig. 10 CORROSION OF MILD STEEL IN MIXTURES OF (1N) H_3PO_4 AND (1N) H_2CrO_4 (RT,1hr)

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