

Effect of Inhibitors on the Corrosion Behaviour of Cold-Rolled Mild Steel

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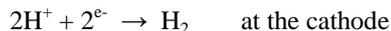
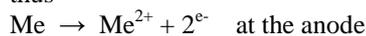
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Abstract – The effect of the following inhibitors, sodium nitrite (NaNO_2), potassium chromate (K_2CrO_4), potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), sodium benzoate ($\text{NaC}_6\text{H}_5\text{CO}_2$) and sodium hypophosphate (Na_2HPO_4) on the corrosion behaviour of cold-rolled mild steel in chloride solution was investigated using the conventional weight loss method. The results showed that the inhibitors with the exception of $\text{NaC}_6\text{H}_5\text{CO}_2$ tend to accelerate corrosion. It was observed that the weight losses for the deformed specimens decreased with increase in the concentration of inhibitors and increase in the degree of deformation. Also the optimum concentration of inhibitors to practically effect complete protection is higher for the base material and this is due to the greater adsorption of the inhibitors on the surface of the deformed specimen resulting from cold rolling.

Keywords – Inhibitors, Corrosion Behaviour, Cold-Rolled Mild Steel, Potassium Dichromate And Sodium Benzoate.

I. INTRODUCTION

A corrosion inhibitor has been defined as a substance which, when added in small amounts to an environment potentially corrosive to a metal or alloy in contact with it is capable of reducing corrosion rate or even preventing its occurrence [1] and [2]. In the usual type of corrosion the metal or alloy passes into solution at the anode of the corrosion cell while hydrogen is eliminated at the cathode thus



The two processes have equivalent relationship and together constitute electrochemical corrosion. Dissolved oxygen in the electrolyte functions by removing the hydrogen from the cathode. This promotes the corrosion by depolarising the cell. The function of corrosion inhibitors therefore is to prevent or retard the operation of this mechanism.

Types of Inhibitors

The use of inhibitors is one method of preventing corrosion through cathodic[3] and [4], anodic protection [5] and coating [6]. There are basically three main types of inhibitors namely: anodic, Cathodic and adsorption or mixed inhibitors [7].

Anodic inhibitors modify anodic reactions. They restrain the reaction (the passage of metals into solution) at the anode by forming insoluble substances at the anode. Reference[8], [9] and [2] have shown that chromates and nitrate behave in this way. Reference[10] demonstrated the possibility of sodium benzoate acting in the same respect. Cathodic inhibitors influence cathodic reactions [3]. They tend to produce insoluble reaction products which stifle the reaction at the cathode by supplying an ion that forms a basic salt or hydroxide which, by forming in situ at the cathode prevents further attack.

Adsorption inhibitors form an adsorbed screen over corrosion area and by preferential action can act on the anode or cathode or both [11]. They frequently consist of substances

with large molecules and may be present in such quantity as to form an enveloping screen over the metal surface. They may also be adsorbed on the initial corrosion products after corrosion has commenced. In this way the active areas are enclosed and the attack suspended.

Effect of electrolyte

Reference [12] observed chloride ions induce corrosion of steel even in concrete. This was supported by [13] who observed that corrosion of steel in the presence of chloride ions is higher than in its absence and thus may reduce the effectiveness of some inhibitors. However he concluded that some measure of inhibition can be achieved increasing the amount of the inhibitor. In examining the effect of electrolytes such as SO_4^{2-} , Cl^- , etc to four inhibitors, CrO_4^{2-} , TcO_4^{2-} , MoO_4^{2-} and WO_4^{2-} [14] observed that an unstable state exists at the metal solution interface and that the mechanism of corrosion is reversible with the addition or removal of electrolyte.

Effect of Cold work

When a material is deformed there is an increase in the number of dislocation lines that can be associated with characteristic steps due to the shift of slip planes resulting from the deformation. The effect of cold work on corrosion of metals is not well understood and in some cases contradictory data have been published. Some workers have found cold work to increase corrosion and some found no difference while others reported a decrease. Reference [15] in summarising the available evidence on the effect of plastic deformation on corrosion concluded that there was no consistent change in the rate of corrosion with stress rather the effect was quite specific both to metal and environment. Reference[16] in their work on

the effect of cold work on pure iron and iron-carbon alloys in de-aerated hydrochloric acid stated that while pure iron corroded at the same rate whether cold worked or not, cold working iron-carbon alloys showed increase in corrosion rate [17].

This work is on the effect of inhibitors on the corrosion behaviour of cold-rolled mild steel in chloride solution.

II. MATERIALS AND METHOD

Material: Mild steel with the chemical composition shown in Table 1

Corroding medium: Potassium chloride (KCl)

Inhibitors: Potassium chromate ($K_2Cr_2O_4$), sodium nitrite ($NaNO_2$), potassium dichromate ($K_2Cr_2O_7$), sodium benzoate ($NaC_6H_5CO_2$) and sodium phosphate (Na_2HPO_4).

Element	C	Si	Mn	P	S	Cu	Fe
%Composition	0.140	0.220	0.500	0.04	0.04	0.045	Balance

Method

Specimens of mild steel were cut from steel sheet with the chemical composition shown in Table 1 and deformed to 30% and 74% by cold rolling using manually operated two-high mill. The surfaces of the specimen were cleaned using emery paper, washed with distilled water, degreased in benzene, dried, weighed to 0.10mg and used immediately. All solutions were prepared by dissolving various quantities (0.01-0.4mg) of the inhibitors and 4g KCl in 100ml and in 500ml of distilled water respectively. The specimens were totally immersed (resting on the bottom and against the side of the beaker) in 40ml of different unstirred mixtures of equal volumes of the inhibitors and KCl contained in 100ml beaker. One specimen totally undeformed immersed in 40ml of KCl was used as control. The specimens were immersed for five days in a cupboard whose temperature was maintained at 27°C with the aid of air conditioners.

At the end of the test the specimens were washed in distilled water and methanol successively, dried and weighed. Weight loss measurements were carried out using sensitive electronic balance following the procedures and precautions described by [19] and [2] first with the corrosion products and after the corrosion products were cleaned off.

The tests were carried out in duplicate, two final weight loss values recorded and the mean values determined.

III. RESULTS AND DISCUSSION

Results

The experimental results are shown in Figures 2-4.

Table 2: Shows the x-values are the concentrations of inhibitors in g/100ml

X-Values	NaNO2	Na2HPO4	NaC6H5CO2	K2CrO4	K2Cr2O7
0	5.5	5.5	5.5	5.5	5.5
0.01	6.7	5.65	5.7	6.2	6.8
0.02	5.2	6.1	5.5	6.65	6.9
0.05	3	4.45	4.8	7.4	6.7
0.1	1.65	3.5	4.5	8.3	6.2
0.2	0.45	3	3.4	6.8	5.45
0.3	0.4	2.6	3	5.6	4.3
0.4	0.2	2.3	2.6	4.7	3.5

Table 3: Shows the results of the x-values deformed for 30%

X-Values	NaNO2	Na2HPO4	NaC6H5CO2	K2CrO4	K2Cr2O7
0	5.1	5.1	5.1	5.1	5.1
0.02	5.9	3.7	3.8	4.4	6.2
0.05	3.1	3	4.1	6.45	5.7
0.1	0.7	5.1	4.5	7.5	5
0.2	0	4.5	3.5	8.8	3.9

Table 4: Shows the results of the x-values deformed for 74%

X-Values	NaNO2	Na2HPO4	NaC6H5CO2	K2CrO4	K2Cr2O7
0	4.5	4.5	4.5	4.5	4.5
0.02	7.55	3.9	3.55	3.45	2.1
0.05	5.3	4.55	5.05	8.3	2.55
0.1	2.35	7.75	4.7	6.6	7.2
0.2	0.15	6.45	3.3	5.5	5.8

Figure 1 represents the effect of the five inhibitors on the base (undeformed) mild steel in chloride solution. Figure 2 shows the effect of the inhibitors on the cold-rolled specimen deformed 30% and Figure 3 shows the results obtained with specimens deformed 74%.

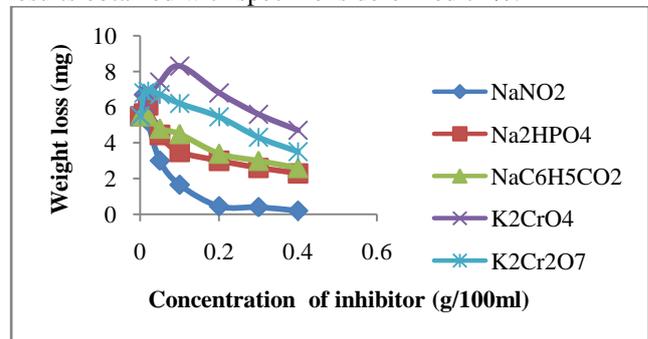


Fig.1. Effect of inhibitor concentration on undeformed specimen.

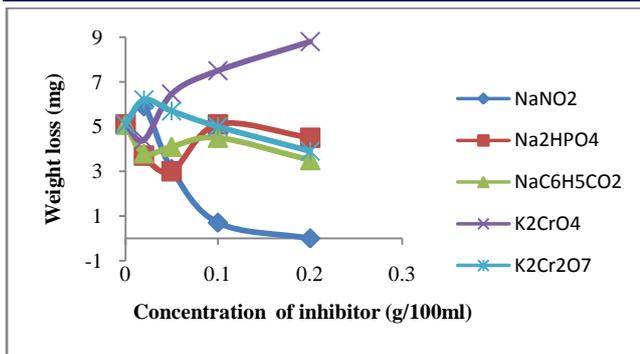


Fig.2. Effect of inhibitor concentration on specimen deformed 30%.

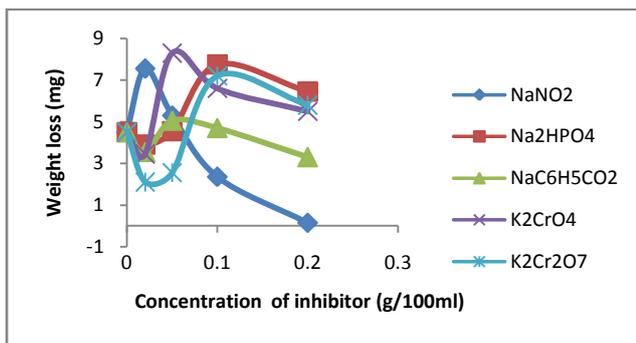


Fig.3. Effect of inhibitor concentration on specimen deformed 74%.

Discussion of Results

In Figure 1 all five inhibitors seem to accelerate corrosion at low concentrations up to 0.02. However as concentration increased above 0.02 the weight loss continued to decrease, as observed by [11], except for K_2CrO_4 which showed continuous increase up to concentration of 0.10.

This initial rise in the rate of corrosion in the presence of low inhibitor concentrations (Figure 1) could be due to the instability of the initial protective films formed and the fact that at such low concentrations the inhibitors were insufficient to plug all the corrosion sites, giving rise to large cathode area. Since corrosion reactions are under cathodic control, the larger cathode area, which includes all plugged areas, raises the anodic dissolution rate resulting in increase in corrosion rate. This is in agreement with the findings of [12]. $NaNO_2$ practically completely stopped the corrosion process at concentration of 0.40. The other inhibitors would need higher concentrations to arrest the process.

Figures 2 and 3 show the results of specimens deformed 30% and 74% respectively.

From Figure 2 it can be observed that $NaNO_2$ and $K_2Cr_2O_7$ showed initial rise in weight loss up to about 0.02 but as concentrations increased the weight loss values continually reduced. The others K_2CrO_4 , $NaHPO_4$ and $NaC_6H_5CO_2$ showed initial decrease in weight loss, up to about 0.02, demonstrating some level of protection. However, while K_2CrO_4 showed a continuous rise in weight loss above the concentration of 0.02, $NaHPO_4$ and

$NaC_6H_5CO_2$ showed only a slight rise. $NaNO_2$ practically terminated the corrosion process at concentration of 0.20.

The initial decrease in weight loss shown by K_2CrO_4 , $NaHPO_4$ and $NaC_6H_5CO_2$ could be attributed to the fact that adhesion of adsorbed inhibitors is better on the slip steps created by cold work and resulting in a more effective coverage of specimen surface. This could correspond to incubation period. On the other hand the subsequent rise observed could be attributed to the formation of soluble complexes which were no longer protective or due to the breakdown of the initial protective film formed. This confirms the findings of [9]. Also the continuous rise in weight loss exhibited by K_2CrO_4 above 0.02 may be due to the areas of weakness, such as cracks resulting from the cold work or pores extending through the film, penetrated by the corroding medium (KCl), attacking the metal at the base and destroying any protective film formed. This supports the observations of [9] and [16].

Figure 3 presents the results for specimen deformed 74%. It can be observed that except for $NaNO_2$ all other inhibitors showed some degree of protective activity up to a concentration of 0.02 but their protective power was not strong enough to sustain the protection as weight loss started increasing above this concentration level and up to 0 [9] and [18]. $NaNO_2$ showed an initial increase in weight loss for concentrations up to 0.02 and then a continuous decrease until 0.20 when corrosion practically came to an end.

IV. CONCLUSION

The following conclusions were drawn from our investigation.

1. All inhibitors studied demonstrated the ability to perform corrosion inhibition in the presence of chloride ions. However the anodic inhibitors, except for sodium benzoate ($NaC_6H_5CO_2$), showed severe local corrosion at low concentrations.
2. Sodium nitrate ($NaNO_2$) seems to be the most effective in the medium studied being able to practically completely terminate at a much lower concentration than any of the others. This observation agrees with the conclusions of [12] and [16].
3. The higher the concentration of the inhibitors the higher the inhibition performance in the medium studied.
4. Cold working reduces the optimum concentration for complete protection since more of the inhibitors are adsorbed on the metal surface as a result of increase of dislocation lines.
5. In neutral solutions such as potassium chloride (KCl) cold working a material increases the effectiveness of inhibitor action because of the large number of slip steps created resulting in increase in adsorption of inhibitors on the surface of the metal.

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