Electrochemical dissolution of mild steel by alternating current

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The electrochemical dissolution of mild steel in hydrochloric acid and sulphuric acid by a.c. has been studied. It has been found that with sine wave a.c. (50 Hz) the dissolution efficiency increases with increase in concentrations of the acids and decreases with the progress of electrolysis. As current density increases an initial increase in the efficiency was noticed; but as current density increases further, the efficiency falls. With square wave a.c. of low frequency (0·5 Hz), the dissolution efficiency increases with increasing concentrations of the acids and also with increasing frequency. However the efficiency decreases with increasing current density and time of electrolysis.

1. Introduction

The influence of stray d.c. on the corrosion of buried or submerged structures is well known, but it is not widely appreciated that stray a.c. can also have similar deleterious effects. A review of the technical literature shows that numerous investigations have been made having a bearing on the a.c. electrolytic corrosion of iron, lead, copper, aluminium and other metals [1–4].

Apart from the corrosion of metals by a.c., the dissolution of certain metals by a.c. has also attracted the attention of a number of investigators. Such a method would be specially useful when the chemical dissolution of the metal is tedious, often involving a number of laborious operations. Studies on the dissolution of platinum group metals [5] and nickel [6, 7] by a.c. have been reported in the literature. In the present investigation the dissolution of mild steel in HCl and H_2SO_4 by sine wave a.c. and square wave a.c. has been studied.

2. Experimental

All the experiments were carried out in a glass beaker. Mild steel electrodes of rectangular shape (8 cm × 5 cm) were used. For each experiment 480 ml of acid solution was used as the electrolyte. The spacing between the electrodes was maintained at 2 cm. Stirring of the solution was done with the help of a magnetic stirrer. All the experiments were done at 30° C. The circuitry for the sine wave a.c. and square wave a.c. and the experimental technique followed were similar to that reported in an earlier paper [7].

3. Results

Fig. 1 shows the influence of H_2SO_4 and HCl concentration on the dissolution efficiency using sine wave a.c. (50 Hz). It may be seen that the efficiency increases with increase in the concentration of the acids. As the concentration of HCl increases from 0·2 N–2 N, the efficiency increases from 65%–92%. In the case of H_2SO_4, the efficiency increases from 80% at 0·2 N to 96% at 1 N H_2SO_4.

Fig. 2 shows the influence of current density on the dissolution efficiency. With HCl and H_2SO_4, there is an initial increase in efficiency with current density, but with further increase in current density there is a decrease in efficiency. Increase in the time of electrolysis resulted in a decrease in efficiency in both the acids. This is shown in Fig. 3.

With regard to the influence of concentration of acid and time of electrolysis, the results were similar when square wave a.c. of low frequency (0·5 Hz) was used. It was also noted that current efficiency increases with frequency of the square wave. Fig. 4 shows the influence of current density
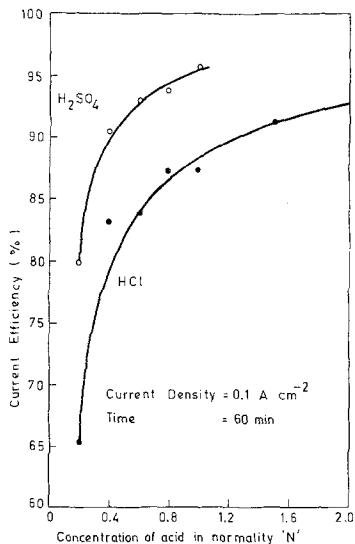
Fig. 1. Influence of concentrations of acids on dissolutions of mild steel by a.c. (sine wave, 50 Hz).

Fig. 3. Influence of time of electrolysis on dissolution of mild steel by a.c. (sine wave, 50 Hz).

on dissolution when square wave a.c. of low frequency is used. In this case, unlike that of sine wave a.c. there is a decrease in dissolution efficiency with current density from the beginning.

4. Discussion

When a.c. is passed across the cell containing the mild steel electrodes in a solution of sulphuric acid, the following reactions may take place at the anode
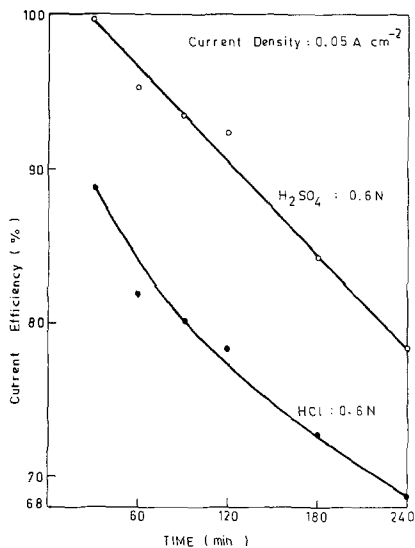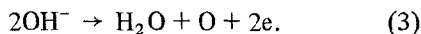
(Electrode 1) in the positive half-cycle depending upon the potential considerations.

$$Fe \rightarrow Fe^{2+} + 2e \qquad (1)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e \qquad (2)$$

$$2OH^- \rightarrow H_2O + O + 2e. \qquad (3)$$

During this interval, the reactions taking place at the cathode (Electrode 2) may be as follows
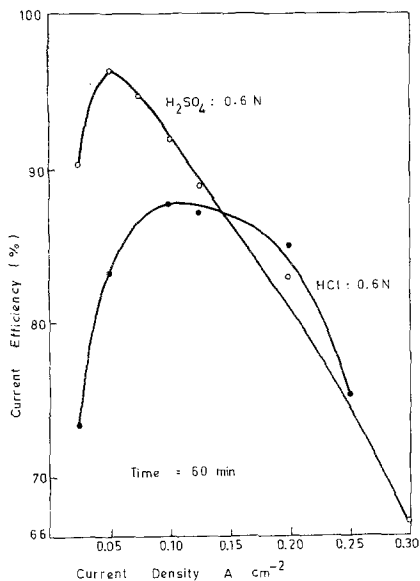

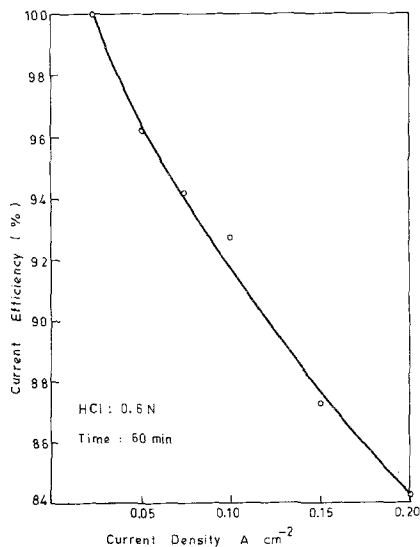Fig. 2. Influence of current density on dissolution of mild steel by a.c. (sine wave, 50 Hz).
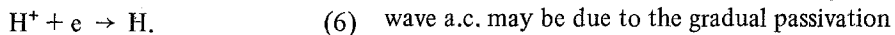

Fig. 4. Influence of current density on dissolution of mild steel by square wave (0·5 Hz).
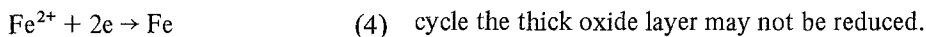
$$Fe^{2+} + 2e \rightarrow Fe \qquad (4)$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (5)$$

$$H^+ + e \rightarrow H. \qquad (6)$$
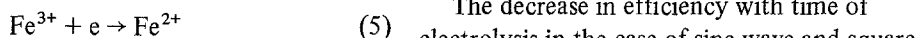
In the negative half-cycle, the situation will be exactly the reverse, Electrode 1 acting as cathode and Electrode 2 acting as the anode. When hydrochloric acid is used as the electrolyte, the discharge of chloride ions leading to Cl_2 evolution may also take place at the anode in addition to the reactions mentioned above. The ideal condition for successful dissolution of mild steel would be as follows. In the positive half-cycle only the metal dissolution reaction (Reaction 1) should take place. Reactions 2 and 3 will lead to a decrease in the dissolution of iron. In the negative half-cycle only the hydrogen evolution reaction should take place (Reaction 6).

The lower efficiency in dilute acids may be due to the passivation of the electrode due to the formation of an oxide during the electrochemical evolution of oxygen in the positive half-cycle. With increase in acid concentration, the passivation effect diminishes, probably due to the dissolution of the oxide in concentrated acids.

The initial increase in efficiency with current density when sine wave a.c. is used may be due to the reduction of the oxide in the negative half-cycle. But with further increase in the current density the oxidation of ferrous ions to ferric ions (Reaction 2) and the discharge of hydroxyl ions leading to oxygen evolution (Reaction 3) become more significant than at a lower current density. This leads to reduced efficiency for the dissolution of iron. Further, during the negative half-

cycle the thick oxide layer may not be reduced.

The decrease in efficiency with time of electrolysis in the case of sine wave and square wave a.c. may be due to the gradual passivation of the electrode due to the formation of the oxide film with the progress of electrolysis.

In the case of square wave a.c. the decrease in efficiency with increase in current density may be explained as follows. As current density increases, the formation of the oxide in the anodic half-cycle is enhanced. The duration of the positive half-cycle used was 1 s, which is a relatively long period. This results in the formation of a thick oxide layer on the electrode. This oxide layer is not completely removed in the cathodic half-cycle due to its thickness and hence the efficiency falls.

In the present investigation, frequencies up to 50 Hz only have been used. It may also be mentioned here that if the frequency is sufficiently high no effects of the a.c. would be observed since all current would pass via the double layer.

References

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