Electrochemical dissolution of nickel in sulphuric acid by alternating current

K. DEO, S. G. MEHENDALE, S. VENKATACHALAM

Department of Metallurgical Engineering, Indian Institute of Technology, Bombay, India

The electrochemical dissolution of nickel in sulphuric acid by alternating current has been studied. Experiments with sine wave a.c. (50 cps) have shown that the dissolution efficiency increases with increase in concentration of sulphuric acid as well as current density. However, the dissolution efficiency increases with increase in concentration of sulphuric acid but decreases with increase in current density when square wave type a.c. of low frequency (0·5 cps) is used. Increase of frequency of square wave a.c. increases the dissolution efficiency.

1. Introduction

The use of modulated currents in electrochemical processes is well known. The modified Wohlwill gold refining process employs superimposed alternating current to facilitate anodic dissolution. Periodic current reversal has been used in the plating industry for more than twenty years to aid the production of bright coherent deposits. Its application to the electrorefining of copper is presently being studied.

Certain metals go into solution under the influence of alternating current. Such a method of electrochemical dissolution would be preferred industrially for those metals where chemical dissolution of the metals is tedious. The dissolution of nickel [1] and powdered metals of the platinum group [2] in hydrochloric acid under the influence of a.c. have been reported in the literature. In the present investigation the dissolution of nickel in sulphuric acid under the influence of a.c. has been studied.

2. Experimental

The experiments were carried out in a perspex cell (10 × 10 × 10 cm). Electrolytic nickel plates (7 × 4 cm) were used as the electrodes. The volume of the electrolyte used was 600 ml. The inter-electrode spacing was maintained as 1·5 cm. Stirring of the electrolyte was carried not with the help of a magnetic stirrer. All the experiments were carried out at room temperature.

The influence of the concentration of sulphuric acid and current density on the electrolytic dissolution of nickel was studied using alternating current (sine wave, 50 cps) and square wave type of current of low frequency (0·5 cps). In the latter case, the influence of change in frequency on the dissolution of nickel was also studied.

While studying the influence of current density on the dissolution of nickel, the total quantity of electricity passing through the cell was kept constant. The sine wave form of alternating current (50 cps) of desired amplitude was obtained directly from the mains using a step-down transformer and an autotransformer. The schematic representation of the sine wave form and the circuitry used to obtain this are given in Figs. 1a and b.

The nature of the square wave alternating current and the circuitry used to obtain this are shown in Figs. 2a and b. As shown in Fig. 2b, the current is fed to the electrolytic cell by two circuits alternatively. When contact n/c (normally closed) is closed and contact n/o (normally open) is open, electrode 1 becomes the anode and electrode 2 becomes the cathode. When this is reversed i.e. n/o is closed and n/c is open, electrode 1 becomes the cathode and electrode 2 becomes the anode. The contacts n/o and n/c are operated separately by a timer circuit (not shown in Fig. 2) in such a way that frequency as well as period of contact can be
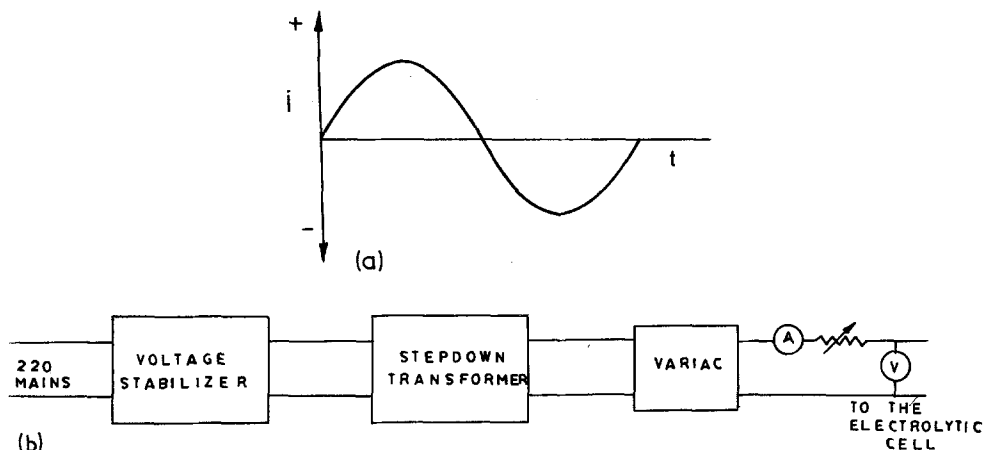
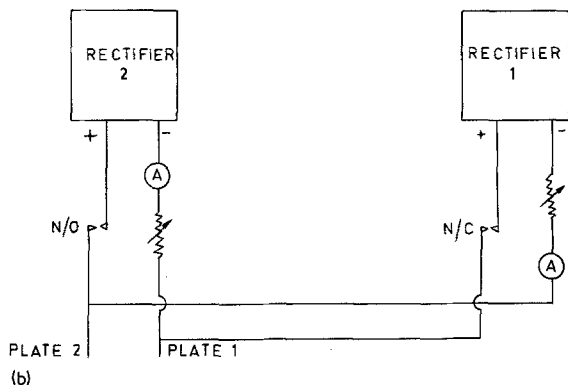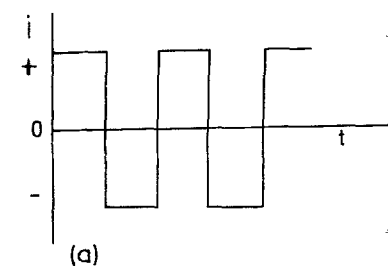Fig. 1. (a) Sine wave a.c. (b) Circuitry for sine wave a.c.

Fig. 2. (a) Square wave a.c. (b) Circuitry for square wave a.c.

controlled. By changing the values of the variable resistances in both the circuits, the values of the current in the forward and reverse direction can be changed.

The experimental procedure was as follows: the electrodes are weighed after thoroughly cleaning by washing and then drying, before and after electrolysis. The change in weight of the electrodes is noted. The current efficiency for the dissolution of nickel is calculated as shown below.

The theoretical amount of nickel that would be dissolved from both electrodes under the influence of a.c. (sine wave) is given by,

$$W = \left[\int_0^{T/2} (I_0 \sin \omega t)\, dt\right] t/T \cdot M/n \cdot 1/F$$

where W = theoretical amount of Ni that should be dissolved; t = total duration of electrolysis; I_0 = peak value of current; T = total period of one cycle; M = atomic weight of Ni; n = valency of Ni; F = Faraday = 96 500 A.s.
This equation reduces to

$$W = \frac{2\sqrt{2}}{\pi} \cdot \frac{M}{n \cdot F} \cdot I_{rms} t$$

where I_{rms} = effective current shown by a.c. ammeter in series with the electrolytic cell.

The theoretical amount of nickel that would be dissolved from both the electrodes under the influence of square wave type current is given by,

$$W = I \times t \times M/n \cdot 1/F$$

where I = current passed in positive or negative cycle. Hence the efficiency of electrochemical dissolution of nickel is given by,

$$\eta = \left(\frac{W_1}{W} \times 100\right) \%$$

where W_1 = actual amount of nickel dissolved from both electrodes.
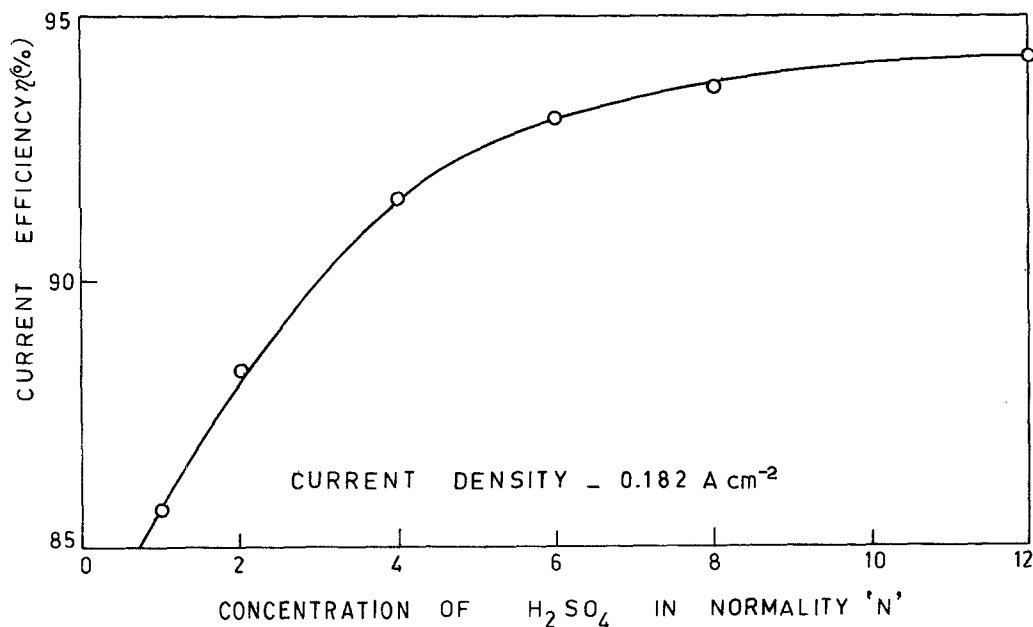
Fig. 3. Influence of concentration of H_2SO_4 on dissolution of Ni by a.c. (sine wave, 50 cps).

3. Results

Fig. 3 shows the influence of H_2SO_4 concentration on the dissolution efficiency using sine wave alternating current (50 cps). It may be seen that the dissolution increases with increase in concentration of sulphuric acid. When the concentration of H_2SO_4 was varied from $1-12$ N the current efficiency increased from $85-95\%$. Fig. 4 shows that in the case of sine wave alternating current the dissolution increases with increase in current density also. When current density was varied from $0.01-0.4$ A cm^{-2}, the efficiency increased from $58-95\%$.

In the case of square wave type current, when acid concentration was increased from $1-8$ N at a current density of 0.075 A cm^{-2}, dissolution efficiency increased from $45-95\%$. This is shown in Fig. 5. However, when the square wave is used, the dissolution efficiency decreases with increase in current density. The efficiency decreased from $97-50\%$ when current density was increased from $0.025-0.125$ A cm^{-2} (Fig. 6). This is in contrast to that observed with sine wave a.c. The cell voltage was found to have increased almost linearly with current density for both types of alternating currents. (Figs. 7a and b). Fig. 8 shows the influence of frequency of the square wave on the dissolution efficiency. When the frequency was changed from $0.017-0.5$ cps, efficiency increased from $90-100\%$.

4. Discussion

When a.c. is passed across the cell containing the nickel electrodes in a solution of sulphuric acid, the following reactions can take place at electrode-1 in the positive half cycle.

$$Ni \rightarrow Ni^{++} + 2e \tag{1}$$

$$2OH^- \rightarrow H_2O + O + 2e. \tag{2}$$
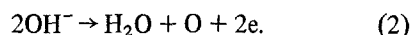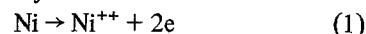
During this interval, electrode-2 acts as cathode and the following reactions can take place at that electrode.

$$Ni^{++} + 2e \rightarrow Ni \tag{3}$$

$$H^+ + e \rightarrow H. \tag{4}$$
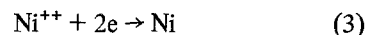
During the negative half cycle, the situation will be exactly the reverse, electrode-1 acting as cathode and electrode-2 acting as anode. The ideal condition for successful dissolution of nickel would be when only Reaction 1 takes place in the positive half cycle and only Reaction 4 takes place in the negative half cycle.

The lower efficiency of nickel dissolution in dilute sulphuric acid is apparently the consequence of the formation of insoluble oxide films during the electrochemical evolution of oxygen in the positive half cycle. With increase in concentration of sulphuric acid, this passivating effect diminishes and therefore dissolution efficiency increases. The
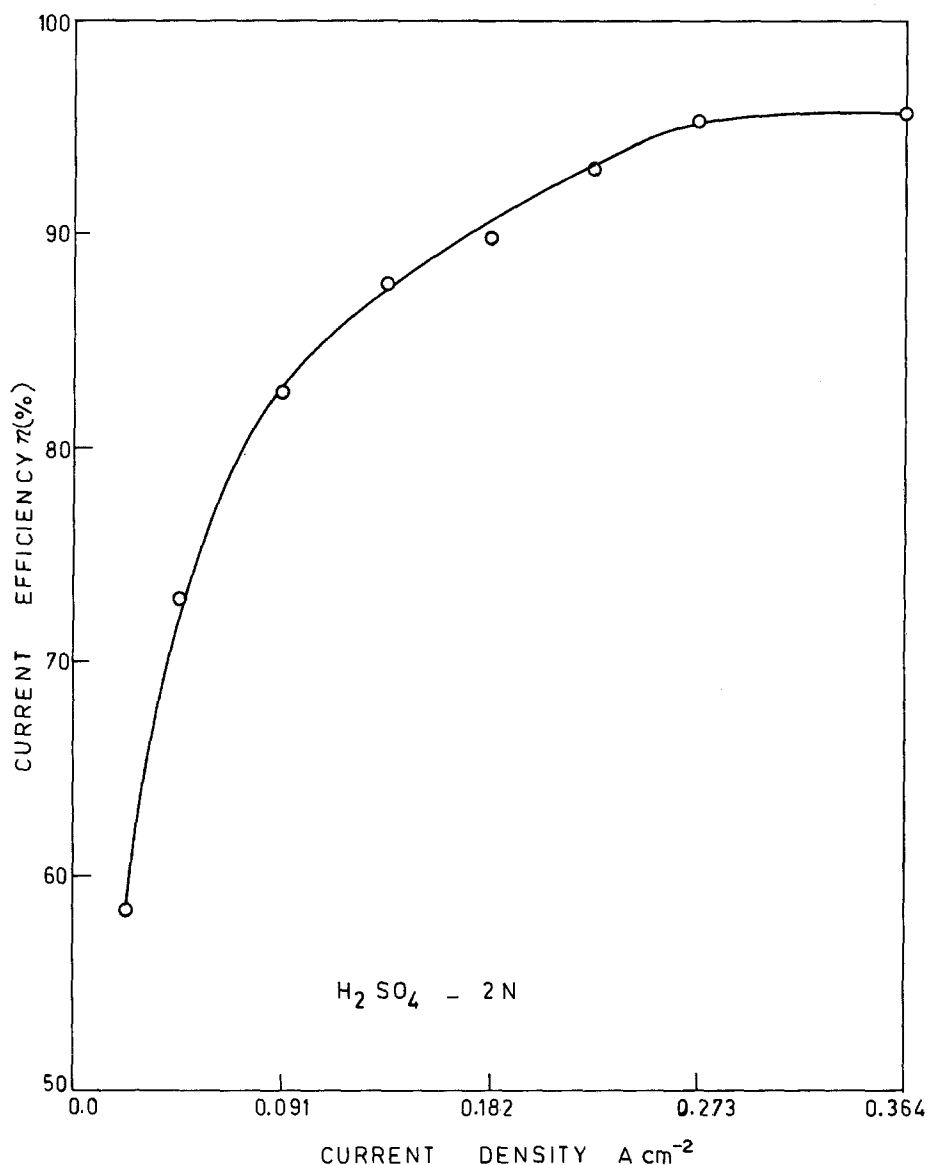
Fig. 4. Influence of current density on dissolution of Ni in H_2SO_4 by a.c.

reduction in passivation may be due to the ability of concentrated sulphuric acid to dissolve the oxide film.

With regard to the increase in dissolution efficiency with increase in current density, when the sine wave is used, the probable explanation may be as follows. During the cathodic half cycle, it is possible that the higher oxides of nickel get reduced to lower oxides which are soluble in sulphuric acid. This may occur only at the higher current densities. It is also possible that the nickel oxide gets reduced to nickel ions as follows:

$$NiO_2 \cdot 2H_2O + 4H^+ + 2e \rightarrow Ni^{++} + 4H_2O.$$
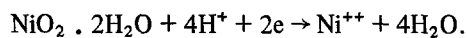
Furthermore, the dissolution of such oxide films will expose fresh nickel surface for subsequent reactions.

The decrease of dissolution efficiency with current density while employing the square wave type of current may be explained as follows. At higher current densities, the formation of oxygen and hence nickel oxide is enhanced during the anodic half cycle. In the cathodic half cycle, this oxide layer is not completely removed because of
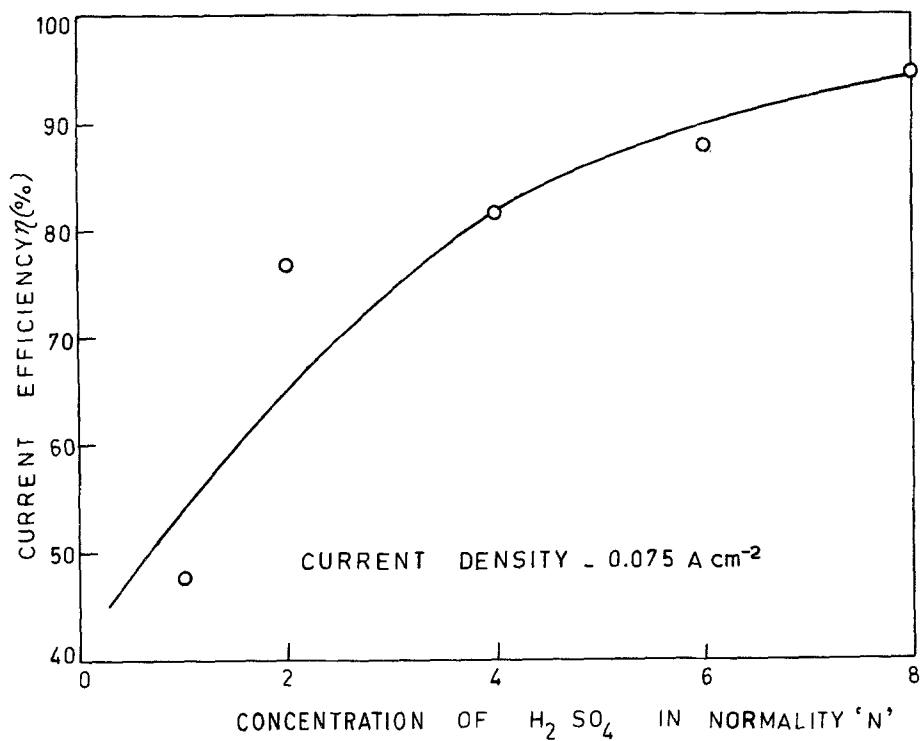
Fig. 5. Influence of concentration of H_2SO_4 on dissolution of Ni by square wave.
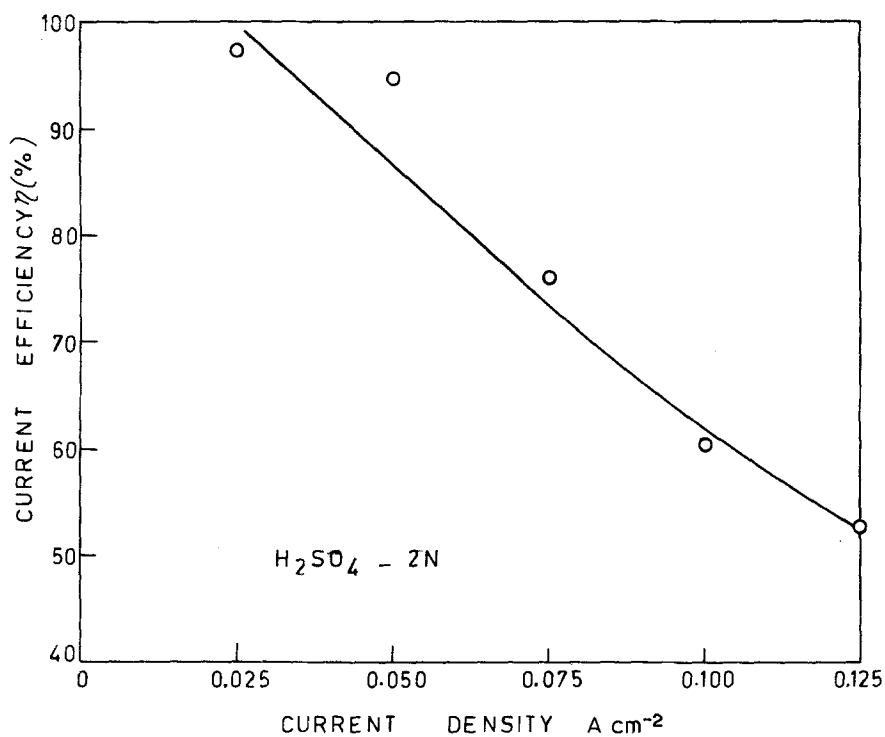

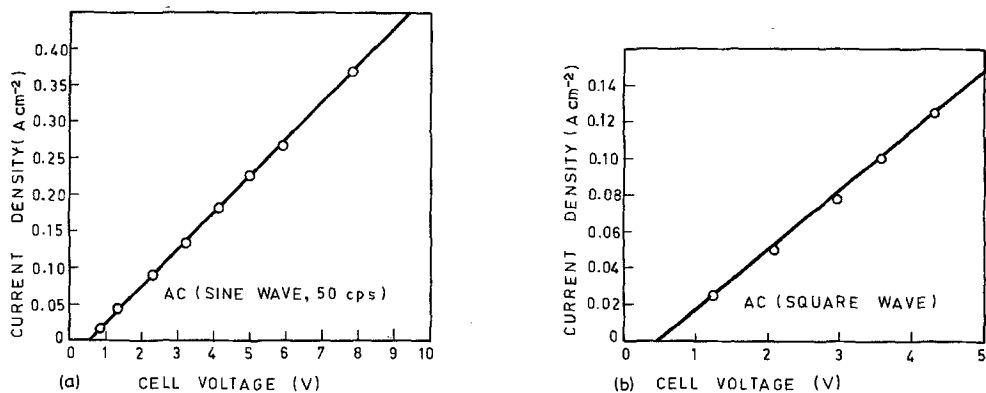Fig. 6. Influence of current density on dissolution of Ni in H_2SO_4 by square wave.

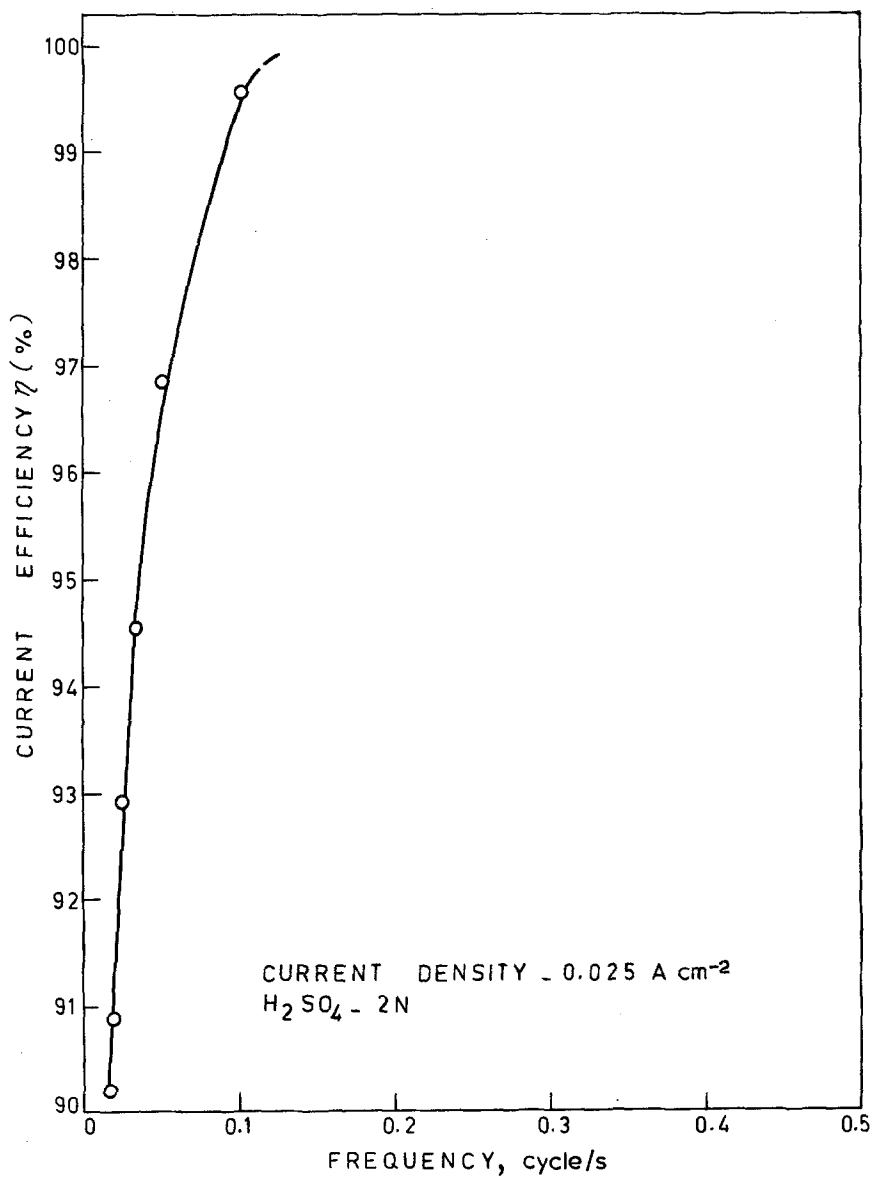Fig. 7. (a) and (b) Variation of cell voltage with current density.

CURRENT   DENSITY _ 0.025 A cm^{-2}
H_2SO_4 _ 2N

Fig. 8. Influence of frequency on dissolution of Ni in H_2SO_4 by square wave.

its thickness. The increased thickness is due to the duration of the positive half cycle, which in this case is one second. With increase in frequency of the square wave, the thickness of the oxide layer is less because of reduction in anode cycle time. Hence the increase in dissolution efficiency.

References

[1]   A.I. Ryazanov, G.D. Petrenko and E.G. Domanova, *J. Appl. Chem. U.S.S.R.* **43** (1970) 840.
[2]   A.D. Styrkas and O.N. Efimov, *ibid* 170.