Electrodissolution and Corrosion of Metals by Alternating Currents

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IT is well known that in the electrodissolution of metals unidirectional currents are involved. However under certain conditions, alternating currents can also cause dissolution although it may be at a lower rate than direct currents. Such a method of electrodissolution by a.c. would be proffered industrially for those metals where chemical dissolution is tedious. The dissolution of powdered metals of the platinum group and nickel under the influence of alternating currents have been discussed. Investigations carried out on the a.c. electrolytic corrosion of Fe, Pb, Cu, Al and other metals have also been reviewed. The effect of frequency of a.c. and also the influence of superimposition of a.c. on d.c. have been discussed.

One of the major undesirable effects of corrosion caused by a.c. is the corrosion of underground structures like water and gas supply pipe lines due to stray alternating currents. The phenomenon of stray current, access of a c. to the underground structure and rectifitation by corrosion products are discussed. Corrosion by a.c. is a complex phenomenon and a complete understanding will require a large amount of systematic work in this direction.

THE investigations covered in this review fall into two categories : i) studies relating to deliberate dissolution of metals by alternating current (a.c) and superimposition of a c. on d.c. ; ii) undesirable corrosion mainly of underground structures caused by stray alternating currents.

The results presented in the first part dealing with the deliberate dissolution of metals by a.c. would be useful for those metals where chemical dissolution is tedious. The influence of frequency of a.c. as well as the effect of superimposition of a.c. on d.c. on the dissolution of metals have been dealt with in detail. In the second part, the undesirable corrosion of buried structures by stray alternating currents is presented. The phnomenon of stray current, access of a.c. to underground structures and rectification of a.c. by corrosion products are discussed briefly.

A large number of investigations have been undertaken on corrosion by a.c. The works published before 1960, have been discussed by Kulman[1]. Venkatesh and Chin[2] have recently reviewed the fundamentals of the alternating current electrochemical processes.

Electrodissolution of metals by alternating current : It is well known that direct currents are associated with electrorefining of metals. The anodic dissolution of metals by d.c. does not proceed smoothly in a number of cases where polarization sets in and leads to passivation. It was never thought that a.c. superimposed on d.c. would bring about any elect ochemical transformation. A survey of the literature, however, reveals that such a technique of using either a.c. alone or superimposed a.c. on d.c. in electrochemical work has resulted in success and in some cases it may have useful applications. Use of a.c. alone for dissolution has the further advantage of avoiding the rectification of a.c. into d.c. Moreover, normal 50 or 60 Hz a.c. is conveniently available.

It would be appropriate at this stage to see how the use of a.c. alone can bring about the dissolution of metals. When alternating current (50 H,) is passed between two electrodes in an electrolytic cell, they act as anode and cathode alternately 50 times per second. There can more than one anodic as well as cathodic reactions. The probable reactions are as follos :

When it is anode,

$$\underset{1}{M \rightarrow M^{++} + 2e} \quad \underset{2}{2OH^- \rightarrow H_2O + O + 2e} \quad \underset{3}{2Cl^- \rightarrow Cl_2 + 2e}$$

(# may take place in the chloride bath) and when it is cathode,

$$\underset{4}{M^+ + 2e \rightarrow M} \quad \underset{5}{H^+ + e \rightarrow \tfrac{1}{2} H_2}$$

The ideal condition for successful dissolution of the metal would be when reaction (1) takes place preferentially in the anodic half cycle and reaction (5) takes place preferentially in the cathodic half cycle. This will depend upon the rates of these reactions. The rates of these electrochemical reactions may be expressed in general, in terms of current density, i, by use of the Tafel relationship as follows :

$$i^M = i_o^M . \exp(-\alpha^M \eta^M F/RT)$$
$$i^c = i_o^a . \exp(-\alpha^c \eta^c F/RT)$$

where M is the metal under consideration and G is the gas. (may be H_2, O_2 or Cl_2 as the case may be)

i = actual current density, i_o is the exchange current density, α is the exchange coefficient, T is the temperature, F and R are constants and η is the overvoltage required for anodic and cathodic reaction.

The total current density, $I_{avg} = i^M + i^o$. In anodic cycle, i^M is the current utilised for metal dissolution and i^o is for gas evolution (O_2 or Cl_2 as the case may be). Depending upon potential considerations for the dissolution of metal under study, the part of Iavg, would be consumed for metal dissolution. In cathodic cycles, i^M is the current for metal deposition and i^o, for H_2 evolution. Here also depending upon the deposition potential of the metal under consideration the I_{avg} would get divided between metal deposition and H_2 evolution.

If the quantity of electricity expended for dissolution of metal in anodic cycle is greater than the quantity of electricity expended for metal deposition in cathodic cycle, then only there would be effective dissolution of metal by a. c.

The current efficiency, for a. c. conditions can be calculated by weight loss method. The part of the alternating current which is actually utilised in the electrolysis is the average value or d. c. equivlent denoted as I_{avg}. This can be calculated from the relation.

$$I_{avg} = \frac{2\sqrt{2}}{\pi} I_{r.m.s.}$$

where I r. m. s. is the current indicated by a. c. ammeter.

If Q is the quantity of electricity (where $Q = I_{avg} \times t$ and t is the time of electrolysis) then the weight of the metal (m') that would dissolve theoretically at 100% efficiency is

$$m' = \frac{Q}{F} \times \frac{Aw}{n}$$

where, F = Faraday., Aw = Atomic wt of metal, n = valency. Hence

$$m' = \frac{I_{avg} \times t \times Av}{n \times F} = \frac{2\sqrt{2} \times I_{r.m.s.} \times t \times Aw}{\pi \times n \times F}$$

If m is the actual loss in weight of metal during the the electrolysis, the current efficiency is calculated as

$$C.E.\ (\%) = \frac{m}{m'} \times 100.$$

In general, let us examine the current (I) versus potential (ϕ) curve for the anodic dissolution of a metal. The typical curve is shown in Fig. 1.

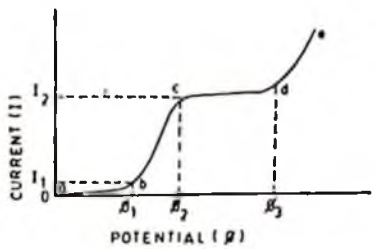


FIG.1. CURRENT (I) VERSUS POTENTIAL (ϕ) CURVE

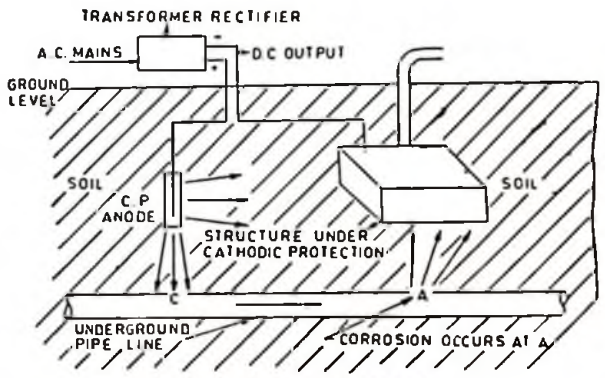


FIG. 2. STRAY CURRENT CORROSION

The branch abc of the curve corresponds to anodic dissolution of the metal, the branch cd indicates sharp change of the electrode potential (under conditions of diffusional control) which is usually interpreted as the point at which the concentration polarisation begins. This is due to the fact that the rate of diffusion of cations from the electrode becomes considerably lower than the rate of electrode reaction whereby metal cations pass into solution. Under these conditions another electrode process becomes possible in the branch de, i. e. electrolytic evolution of gases. Thus if the electrolytic dissolution of the metal is effected by alternating current value below I_2 (i. e. if the process is conducted in the linear region of curve bc) there is virtually no evolution of the gas due to next reaction. during the anodic half cycle. Under these conditions the entire current will be utilised for metal dissolution only.

In the cathodic cycle two reactions are possible — i) Evolution of hydrogen. ii) Deposition of metal. Which reaction takes place depends upon potential consideration. If only H_2 evolution takes place there will be net dissolution of the metal.

The dissolution of powdered metal of platinum group involves a number of laborious operations involving high temperature and pressure. Further, the use of concentrated acids for dissolution at high temperatures pollutes the atmosphere by acid fumes These metals can be dissolved by the use of alternating currents. The dissolution of platinum and rhodium with a.c. of industrial frequency (50 Hz) in different acids like HCl and HBr has been studied[1].

In the case of nickel dissolution in HCl by a.c.[4] it has been found that the efficiencies for nickel dissolution is maximum between 4 and 6 N of HCl solution. The low rate of nickel dissolution in dilute HCl solution is probably due to the formation of insoluble oxide film. The passivating effect diminishes with increasing concentration of HCl in the solution and hence the rate of nickel dissolution increases with increasing acid concentrations. However. at high HCl concentrations the dissolution decreases owing to the low solubility of nickel chloride in concentrated HCl solutions. The electrochemical dissolution of nickel in H_2SO_4[5] by sine wave a.c. (50 Hz) has shown that the dissolution efficiency increases with increase in concentration of H_2SO_4 as well as current density. With increeses in concentration of H_2SO_4 the passivating effect due to oxide formation diminishes as the oxide dissolves in concentrated acid and hence dissolution efficiency with increase in current density is probably due to the reduction of higher oxides of nickel into lower oxides during the cathodic half cycle and their subsequent dissolution tn acid.

The dissolution of nickel has also been studied by using square wave type a.c. of lower frequency (0.5 Hz). However, the dissolution efficiency in this case increases with increase in acid concentration, but decreases with increase in current density. At higher current densities the evolution of oxygen and hence the formation of nickel oxide is enhanced during the anodic half cycle and this thick oxide layer is not reduced in the cathodic half cycle. At higher frequency the dissolution efficiency increases as the passivation cannot take place during the short anodic pulse.

The dissolution of mild steel in HCl and H_2SO_4 by sine wave a.c. (50 H_z) has been studied[6]. The dissolution efficiency has been found to increase with increase in concentration of acids but decrease with the progress of electrolysis. With increase in current density there is an initial increase but subsequently the efficiency falls. The dissolution of mild steel with square wave a.c. of low frequency (0.5 H_z) has also been studied. Increase in concentration of acids and frequency leads to increase in dissolution efficiency. However, the dissolution decreases with increasing current density and time of electrolysis.

Influence of Frequency : Although a number of factors are responsible for the results obtained in electrolytic studies by a.c., it has been observed in a number of cases that frequency of a.c. plays a very important role.

Kortum[7] reports that copper electrodes in KCN solution are completely dissolved when a.c. of 16 H_z is applied but they cease to dissolve completely at higher frequencies, say 1000 H_z. A possible explanation put forward is that copper cyanide formation can take place with in $\frac{1}{10}$th of a second and all the copper ions that are dissolved in anodic half cycle from the cyanide complex and no copper ions are available for deposition during the cathodic half cycle when current of 16 H_z is applied. Consequently copper keeps on disolving continuously. On the other hand, at the frequency of 1000 H_z the copper ions dissolved in the anodic half cycle cannot form copper cyanide complex within $\frac{1}{1000}$th of a second, but during this small time interval, copper can redeposit during the cathodic half cycle. Thus, there is no net dissolution of copper at the higher frequency.

Influence of frequency of a.c. on the passivation of titanium metal has been reported by Tomashov[8]. The investigation was carried out in 10 NH_2SO_4 and frequency of 10-10,000 H_z was used. A.C. shifts the potential to more positive values and increases the corrosion rate contary to the case with d.c., for which passivation takes place due to anodic polorisation and corrosion ceases. With increase of frequency at a given potential the corrosion rate also increases. It is established that the time needed to adsorb a monolayer of oxygen is approximately 10^{-4} sec. Since the the time required to form a subsequent chemical bond between oxygen

and titanium is considerably longer, no oxide can be formed during the period when higher frequencies are employed.

Influence of frequency on the rate of iron dissolution by a.c. has also been reported by Tomashov[9]. Low carbon steel wire electrodes were polarised in N-HCl solutions with sinusoidal a.c. at frequencies upto 1 KHz. The anodic and cathodic polarisation curves were traced in the respective half periods by using the amplitude current density. The phase shift between the polarising current and the potential of the electrode was determined. Corrosion was detected by weight loss method. The polarisability of the electrode both in the anodic and cathodic half periods decreased with increase in frequency, (0.02-1 KHz), suggesting that the respective reactions are enhanced at higher frequencies. This effect is attributed to the presence of a concurrent reaction, the ionisation of H absorbed during the cathodic half period, proceeding simultaneously with the iron dissolution during the anodic half period. When the frequency increased, the total amount of electricity consumed during the anodic half period decreased, while the H ionisation component remained constant ; hence it can be assumed that the metal dissolution is restricted and corrosion is decreased. Experimental data for the total and partial amounts of electricity consumed by metal dissolution of H adsorption and ionisation at various frequencies confirm this assumption.

The corrosion behaviour of mild steel in 1 N sulphuric acid subjected to alternating currents in the range of 250μ A to 100 mA/cm^{-2} at frequencies varying from 30 to 1000 Hz has been studied by Yamuna and Subramanyan[10] also. It has been found that at low current values, the corrosion rate increases with frequencies upto 200 Hz but diminishes with frequencies above this value. At relatively high current values the corrosion rate decreases with increasing frequencies. The explanation put forward for the increase in corrosion rate with frequency upto 200 Hz for low currents is as follows :

The slow step in the hydrogen evolution reaction on iron can be removal of adsorbed hydrogen At low frequencies most of the hydrogen atoms have sufficient time to form molecules and escape from the metal surface. As a.c. frequency increases lesser and lesser amounts of hydrogen atoms are produced during the half cycle, thus fewer are available for the ionisation reaction. This condition rules the reaction until the frequencies reach 200 Hz and so metal dissolution rate increases up to this stage.

Above 200 Hz, however, hydrogen atoms adsorbed on the surface have insufficient time to recombine with the result that increased amounts are available for ionisation reaction. Ionisation becems appreciable in the anodic cycle as frequencies exceed 200 Hz. At higher current values, relatively larger amounts of hydrogen atoms are available on the metal surface and hence as frequency increases, hydrogen ionisation increases at acorresponding rate, As a result the dissolution of metal during the anodic cycle is diminished.

The electrochemical dissolution of mild-steel and nickel in hydrochloric acid and sulphuric acid has been studied recently[11] with alternating current of varying frequencies (from 25 Hz to 2000 Hz) For both, mild steel and nickel, with increasing frequency, the current efficiency decreases exponentialy. With increasing current density (32-100 ma/cm^2) and increasing acid concentration (0.5-2.0 N), the current efficiency increases. Mild steel is dissolved more efficiently in sulphuric acid than hydrochloric acid but reverse is true for nickel.

Superimposition of A. C. on D. C. : Many workers have studied the effect of superimposition of a.c. on d.c. in electrolysis. The amounts of electrochemical effects of superimopsed a.c. depend on the ratio of a.c to d.c. component of the current as well as on frequency. Superimposition of a.c. on d.c. reduces any irreversibility in the electrode process. The superimposed a.c. acts as depolariser and reduces anode and cathode polarisation. Superimposition results in reduction of oxygen overvoltage and electrochemical passivity of anodes.

Superimposed a.c. in electrolysis is employed in the modified Wohlwill gold refining process[12] and converted it from laboratory curiosity to commercial success. This process is used for the treatment of gold anodes of high silver content. The use of a.c. allows the employment of higher current density. It causes the adherent film of AgCl to flake off readily and prevents passivation.

Juchniewicz[13] studied the superimposition of a.c. on d.c. with platinum electrodes. He points out that when the r.m.s. value of a.c. exceeds 70.7

percent of the d.c., conditions will become bipolar. This means that during part of the cycle, the platinum will be actually cathodic. It is believed that this interferes with the normal passive film on the platinum and leaves sufficient hydrogen to prevent effective repair during the parts of the time when platinum is anodic.

Vijayavalli et. al.[14] studied the anodic oxidation of lead in sulphuric acid with superimposed a.c. on d.c. The use of a.c. tends to boost the formation of lead dioxide. The porous nature of the passiva-film, indicated by the resistance measurements, explained the continued formation of lead dioxide.

A study of corrosion of lead in tap water with a.c. and with superimposed a.c. has been reported by Galimberete[15]. Corrosion with constant a.c. was found to increase with time. The rate of corrosion was also found to increase with a,c. density. With superimposed a.c. on d.c. the corrosion was found to increase than that with mere d. c.

In contrast to the above studies Rao et al.,[16] reported that superimpositiom of a.c. on d.c. lowers the passivation time as well as passivation potential in the case of cadmium in KOH solution. This is due to uniform cadmium hydroxide layer formation when a.c. plus d.c. is used which quickly passivates the anode and prevents further dissolution.

Chin, Fu and Venkatesh[17],[18] have used sinusoidal current and voltage modulations to study the effect of a.c. on the passivity of mild steel using 0.5 M aqueous sodium sulphate solution. They measured the anodic polarization of mild steel when a.c. was superimposed on to laboratory cell. AC shifted the polarization curves towards the negative direction. In the passive region a.c. destroyed the passivity and caused an increase in the passivity current density. At 200 mA/cm^2 metal dissolved at a rate equal to that in the active region. This phenomenon was similar to addition of chloride ions to sulphate solutions. Chin and Venkatesh further used a simple charge transfer model to simulate the polarization curves with a digital computer. The calculated curves showed the qualitative agreement with the experimental curves.

Corrosion of Metals by Alternating Currents: In this section of the review, the undesireble effects of a.c. on metals is considered. Particularly the corrosion of underground structures by stray alternating currents is covered. At the outset it would be appropriate to see what is stray current corrosion and how d.c./a.c. gains access to the underground metalic structures.

There are many sources of stray currents underground. The most dangerous from the stand point of corrosion are high power direct currents that pass into the grounds from electrified railroads: If the individual lengths of rail are connected badly, a fraction of the current passes to the ground. This will join pipe or sheath below the rails and rejoin the rails closer to the negative feed point. The setting up of the following cell,

Pipe (anode) / soil/rail (cathode)

will lead to corrsion of the pipe. Such an attack on pipes by stray currents has been nicely illustrated by Evans[19]. The methods of preventing such a type of attack have also been dealt with by him.

Another good iliustration of 'stray current' corrosion can be given by considering a cathodic protection system. A major risk associated with the application of cathodic protection is that the protection current can be picked up at one location on a nearby structure in the electrolyte (or conducting soil) and discharged at another location. This is illustrated in Fig. 2. (page:232) At C the metalic structure will give up electrons and cathodic reaction results: At the point, A, the anodic reaction of metal inisation (corrosion) occurs. Such stray current corrosion is also referred to as interference: Interference is often difficult to detect because the pick up and discharge location may be very widely separted.

The above two examples have shown clearly how d.c. gains access to the underground metalic structures and stray current corrosion results. In a similar, way, when a.c. gains access to the underground structure,corrosion by stray a.c.results, since several metal/metal oxide junctions have rectifying effect on alternating currents. Hence it must be pointed out that not only stray d.c. but stray a.c. can cause interference damage. Stray a.c. may be selectively picked up as rectified current by a metal having some slightly adherent corrosion product on it and wherever this current is discharged the corrosion will be severe. The magnitude and polarity of the current are important. Anodic currents would, of course, be of most direct concern. However

cathodic currents also would be of interest because of their indirect effect on neighbouring structures which would become anodic.

Haring [20] discussed the mechanism of electrolytic rectification and presented a theory for Al and Ta electrodes. Tantalum like aluminium forms oxide film which blocks the flow of current, whenever the electrode is anode, and passess current (electrons) when the electrode is cathode. Recently Nobel and Shine[21] have examined the possibility of using a.c. in electrochemical machining and found that Ti and Al were suitable tool materials because they passivated readily on the anodic cycle causing rectification. Any and Mounios[22] found lead to become more anodic with respect to iron when a.c. was applied and measured the d.c. component of the current. Williams[23] studied the corrosion of metals, (iron, copper, aluminium and lead) under the influence of a.c. It was observed that the corrosion rate of Al was 40 % of like value of d.c., whereas Cu, Pb and Fe corrode only at a level of less than 1 percent of like d.c. value. The corrosion products have been detected and it was confirmed that the rectification of a.c. by natural rectifiers is responsible for the attack. The work of Galimberte[15] on the corrosion of lead by a.c. showed that when Mg was made counter electrode and a.c. was passed, corrosion was found to increase due to rectifying effect. Raine[24] has also shown that the effect of a.c. is most serious on metals prone to act as rectifiers. He states that lead is not seriously affected by a.c. upto 12 volts, whereas Al suffers at small voltages unless the current density is very low.

Aluminium appears to be more susceptible to a.c. corrosion than ferrous materials. That a.c. causes additional corrosion equal to only one 1 percent of that caused by d.c. may be true for steel but not true for aluminium where the figure can be as high as 50 percent.[25] Caution should therefore be exercised in the use of aluminium pipes underground. It may also be noted here that the effect of a.c. will vary with conditions.[26] Under stagnant conditions where the removal of cation is slow, redeposition during cathodic half cycle may nearly compensate for corrosion during the anodic half cycle. Though this may be true for some metal, as far as aluminium is concerned there will be no redeposition.

Waters[27] carried out laboratory and field investigations to determine the corrosive effects of alternating currents on metals. The tests included specimens of iron and also various couples such as copper/steel or brass/galvanised steel. It was shown that a.c. was capable of increasing the corrosion rates especially where there are bimetallic couples. Of the salts examined, chlorides had the greatest effect on corrosion, sulphates were only slightly less corrosive and bicarbonates had the least effect.

Certain other undesirable effects of corrosion by a.c. have also been reported. It has been found by Shipely[28] that iron and copper electrodes used in wate heaters corroded when 60 Hz a.c. exceed a certain critical current density. Yet another undesirable effect of a.c. corrosion is the unsuitability of metals like stainless steel, gold and platinum when used as electrodes in conductivity measurements of concentrated acids. In this connection, Bentley and Prentice[29] studied the corrosion of these metals in concentrated acids of H_2SO_4, HNO_3 and their mixtures. They have observed corrosion of all these metals with low frequency. a.c. There was significant corrosion at 50 Hz whereas the corrosion was not evident at frequencies greater than a few KHz. The corrosion observed at low frequencies is attributed to the transfer process occuring in a time of the order of 10^{-3} seconds. At frequencies greater than a few KHz the transfer does not occur.

There are many reports of the corrosion of underground cables[30]. The failure generally occurs at the bare concentric neutral wires in contact with soil and at the locations where corrossion is expected to be least likely to occur. In the USSR, corrosion is estimated to be responsible for 6.7% of the under ground cable failures[31]. In the United States, the failure rate has reached such an alarming level that the IEEE has formed a special committee to look into the problem. Some preliminary investigations indicate that the corrosion of bare neutral wires is caused by stray currents and differential aerations in soil[32-34] The flow of a. c. between the bare neutral and the soil accelerates the corrosion.

A theoretical analysis of the influence of alternating potential or a. c. on the corrosion of metals was made by Gellings[35] who showed that only the systems with non-linear polarization curves were slightly influenced by a. c. and the systems with linear polarization curves exhibited no influence at all. His analysis was valid tor a. c. frequencies below 100 Hz. Devay et al[36-38] performed more

rigorous analysis. They examined the cathodic and the anodic, processes which follow the Tafel relation on the metal surface and obtained expressions for the calculation of the corrosion potentials and corrosion current densities when a. c. was super imposed on the metal surface. M khailovskii et al[19] classified metals into two groups according to the values of the reversible potentials. The first group was composed of Cu, Fe, Pb, Sn and Zn which corroded primarily by oxygen depolarization in soils. The second group included electronegative metals such as Mg. Al-Ti and Ta. They found that the second group was subjected to intensive corrosion when exposed to a. c. in soils.

Pookote and Chin[10] have used the oxygen diffusion cell to study the effect of a. c. on the corrosion of metals in the soil. From the weight loss data for aluminium, copper, mild steel and 50–50% tin–lead alloy it was observed that aluminium suffered the most severe attack by a. c. whereas copper was least affected.

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