ON CORROSION OF FERROUS METALS IN TYPICAL INDIAN SOILS—PART III WROUGHT IRON

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Corrosion of wrought iron in ten Indian soils, employing Schwerdtfeger's soil corrosion cell procedure has been studied. The corrosion of wrought iron in non-acidic soils proceeds through electrochemical mechamism. Usually the rate of corrosion is maximum at the beginning and with the development of the film of the common products, the rate gradually decreases with time until it becomes more or less constant. In most of the cases 'uneven' general or local corrosion with pittings is observed. The maximum penetration is directly proportional to the corrodibility. Soils having moisture equivalent in the range 25—30% are most corrosive. The corrosivity of soil increases with increase in the concentration of soluble electrolytes. Ferric oxide present in laterite soil functions as a cathodic depolariser and hence increases the corrosivity. The corrodibility (M) increases with maximum cell current (I) or average cell current ($\bar{I}$) as $M^2 \propto I$ an $M^2 \propto \bar{I}$. In and acidic soil the corrosion mainly proceeds through the mechanism of direct chemical reaction. The results have also been analysed and correlated with various factors.

Plain wrought iron has been one of the commonly used forms of ferrous metal for the construction of materials for underground service[1]. It has been considered to be better corrosion resistant than other forms of iron in various environments including soil[2]. Hence it was preferred for underground service. Field investigations have, however, revealed that there is no significant difference in the corrosion behaviour of the different forms of plain iron in soils[3,4]. Consequently the demand for wrought iron has decreased in recent years, but steel, in its various forms and qualities, has not been able to replace it completely. Wrought iron has some qualities, collectively designated as toughness, which highly commend it for various applications[5]. It has, therefore, been widely used as one of the materials for the construction of distribution and transmission pipelines[6,7]. Considering the importance of wrought iron in the underground structures, its corrosion in ten typical Indian soils has been studied using Schwerdtfeger's soil corrosion cell procedure[8—10] and the results are presented in this paper.

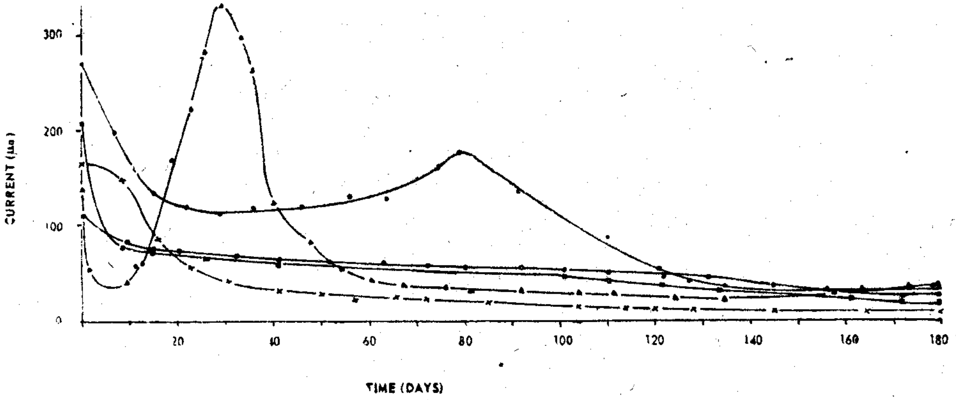

FIG. 1—Time-cell current curves for wrought iron [●— Nagpur; □—Delhi; ×—Trivandrum; ○—Banglore and △—Ratnagiri]

EXPERIMENT

The physico-chemical properties of each soil pertaining to its corrosivity, were reported in an earlier communication[10]. The details regarding the preparation of wrought iron electrodes, setting up of the soil corrosion cells, periodic determinations of short circuit currents, dismantling of cells, cleaning and pickling of electrodes, determination of corrosion loss, its penetration and the statistical analysis of the results were given in the earlier communication[10]. The pickling weight loss of 0·0035 gm was deducted from the weight loss of each electrode in order to ascertain the net loss due to corrosion.

Mean cell current—Time curves for all the sets are given in Figs. 1 and 2 and the data on the corrosion loss, corrosion penetration and quantity of electricity flowing through the cell is given in Table 1.

RESULTS AND DISCUSSION

Order of corrosivity—The statistical test based on Student's *t* function has been employed to ascertain whether the difference between the corrosivities of two different soils is significant or not. The results are given in Table 2.

Hence as regards the corrosivity towards the particular sample of wrought iron, the order of the soil is : Jodhpur desert $\leqslant$ Sambalpur laterite $<$ Bangalore red Delh alluvial $<$ Nagpur black Coimbatore black $\leqslant$ Trivandrum forest Ratnagiri laterite Delhi saline $<$ Alleppey peaty soil.

The corroded surface—Wrought iron is essentially a ferrite matrix, consisting of almost pure iron, through which the slag or iron silicate is disseminated in the form of several millions of filaments per square decimeter[11]. Pearlite areas formed because of very small amount of carbon, are also distributed. Generally it is presumed that ferritic areas function as anodes and the slag inclusions as cathodes in active corrosion cells[3]. The differential nature of the film of corrosion products on wrought iron surface is another important cause of surface inhomogenity to create anodic and cathodic areas.

TABLE I

DATA ON CORROSION OF WROUGHT IRON IN SOILS

Soil	Mean corrosion rate (g/dm². ½year). (decamicrons).	Standard Deviation	Coefficient of variation	Penetration (decamirons).		Quantity of electricity delivered by the cell in six months. (milliamp. days)
				Maximum	Ave. Max.	
Delhia lluvial	3·101	0·129	3·3	42	33	8·4
Bangalore red	3·031	0·202	6·7	40	30	9·4
Ratnagiri laterite	5·169	0·249	4·8	88	72	11·3
Nagpur black	4·180	0·206	4·9	88	58	17·6
Trivandrum forest	4·623	0·438	9·3	79	75	5·2
Sambalpur laterite	1·985	0·112	5·6	36	34	2·4
Coimbatore black	4·514	0·357	7·9	102	60	29·0
Delhi saline	5·257	0·370	7·0	92	72	31·4
Jodhpur dessert	1·203	0·036	3·0	25	20	0·9
Alleppey peaty	7·047	0·366	5·2	46	43	5·4

In order to give a standard surface finish to all the electrodes, they were abraded mechanically with the help of emery paper No. O. Hence the surface of the electrodes prior to their function in the cells, was either covered with a Bielby film[12] or according to latest views has undergone plastic deformation[13,14] During abrasion the abrasive particles are also embedded in the surface. These particles constitute a major electrochemical inhomogenity in the surface[15]. The surface conditions of the metal do not have much practical effect on the corrodibility parameters in these experiments as the surface layer of either Bielby film or plastic deformation is comparatively easily removed in the initial stages and then the rate of further corrosion would depend on the structure of the interior metal[16].

The electrodes of wrought iron corrode in soils mostly in the form of uneven general or local corrosion with pittings. The cathodes in Trivandrum forest and Sambalpur laterite soils and unperforated electrodes in Jodhpur desert soil corrode in highly localised or pitting form. Even general corrosion has been observed in the anodes in Sambalpur laterite and perforated electrodes in Jodhpur desert soil. It is important to note that cast iron and mild steel electrodes in Alleppey peaty soil ($pH = 2 \cdot 5$) corrode in the form of even general corrosion because of the direct chemical corrosion reaction[10,17]. But wrought iron in such environment corrodes in the form of uneven general corrosion.

The slag inclusions and the corrosion products of wrought iron are comparatively more protective in nature so that the anodic points formed by spontaneous breaking of

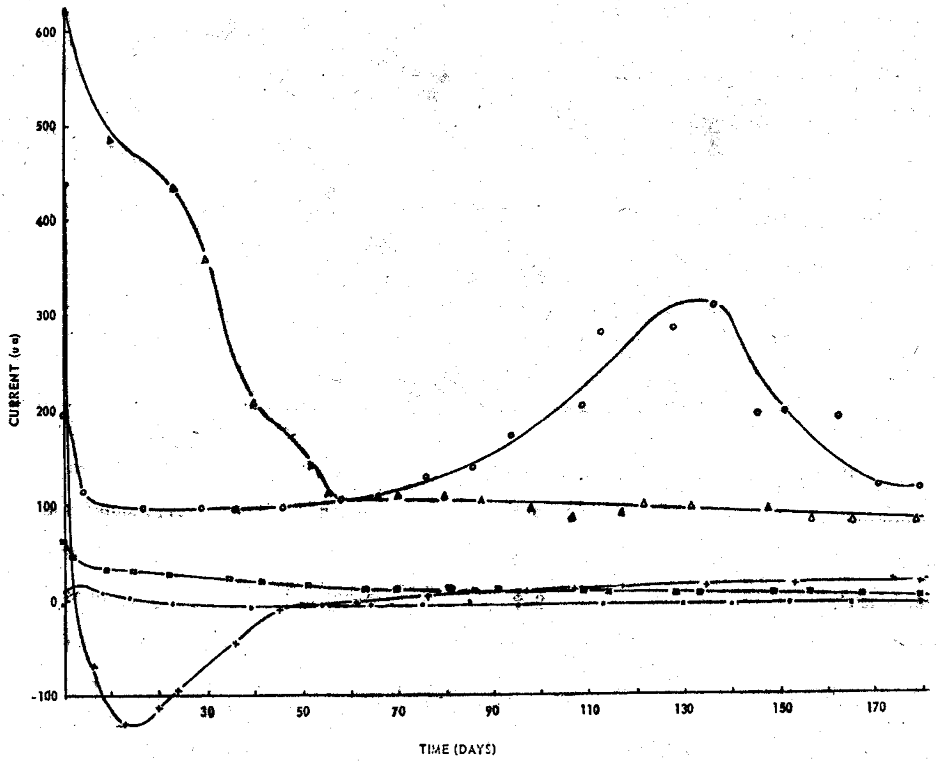

FIG. 2—Time-cell current curves for wrought iron. [△—Delhi saline; ○—Coimbatore; □—Sambalpur. ●—Jodhpvr and ×—Alleppey]

the film do not spread out uniformly all over the surface. Hence uneven general or loca corrosion with pittings is usually observed on wrought iron in soils.

Average maximum penetration, as against maximum penetration, has a better correlation with the corrodibility of the metal. The scatter diagram of the two variables is give in Fig. 3. This indicates a linear relationship. The regression equation has been calculate to be

$$\bar{P}=14\cdot3M$$

where $\bar{P}$ = the average maximum penetration in terms of decamicrons.

and M=Mean corrosion loss in terms of g/dm^2. $\frac{1}{2}$ year.

The point of the Alleppey peaty soil is an exception because of its acidic nature.

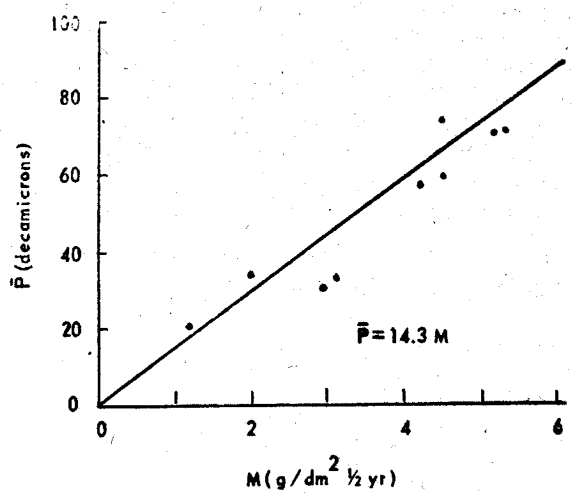

FIG. 3—Average maximum penetration corrodibility curve.

Mean short circuit current—The prominent features of Mean Cell Current—Time curves are

(*a*) The initial short circuit currents are different for different soils. In most of the cases the initial currents are maximum. The cell having Jodhpur desert soil takes about five days to stabilise when its current is maximum. The cell currents generally decrease with time and in several cases the decrement, after a period ranging from 10—60 days, is much less though a slight change persists up to the end of the total period.

TABLE 2

SIGNIFICANCE TEST ON CORROSIVITY OF SOILS FOR WROUGHT IRON

Name of soil	't' with respect to the previous soil	Significance value	Remarks
Jodhpur desert			
Sambalpur laterite	1·3	0·30	Not significant
Bangalore red	9·0	<0·005	Very significant
Delhi alluvial	0·6	0·56	Not significant
Nagpur black	8·8	<0·005	Very significant
Coimbatore black	1·6	0·16	Not significant
Trivandrum forest	0·8	0·44	—do—
Ratnagiri laterite	2·2	0·085	—do—
Delhi saline	0·4	0·70	—do—
Alleppey peaty	6·9	<0·005	Very significant

The rate of corrosion in such cells is maximum at the beginning. As corrosion proceeds a partly protective film of the products of corrosion reactions covers the electrodes. Initially the polarisation of electrodes increases with the thickness of the film of corrosion products, but beyond a certain thickness of the film, the polarisation is not appreciably enhanced further by the increment of the film thickness.

(*b*) Abrupt enhancements in the cell current of several individual cells have been observed at different intervals. This is because of the spontaneous breaking of the film of corrosion products[18].

(*c*) In the cell containing Ratnagiri laterite soil, the cell current rapidly falls, reaches a minimum and again increases to a maximum value, much greater than the initial value, and then again decreases gradually. In all probabilities this is due to the chemicals exerting depolarisation action at the electrodes. It is considered that free ferric oxide present in the laterite soil[19], because of its desilication, may be the depolarizing agent as rust or oxide of iron is found to act as depolarizing agent in the corrosion of iron[20].

(*d*) The behaviour of the cell current in Alleppey peaty soil is very peculiar. The current is comparatively of a high order at the time of setting, but this current rapidly falls and within two days the polarity is reversed. Then the current with reversed polarity increases, reaches a maximum value in 15 days, again falls and becomes zero in about 65 days. Next the original cell polarity is obtained and the current increases for sometime and then its magnitude remains almost constant upto the end. Before the setting of the corrosion cells, both the electrodes are covered with a film of atmospheric oxidation products which is significantly more protective and resistant against the corrosive action of the environment as compared to the films on other plain ferrous metals. Hence initially the cell can be represented as

Fe : Iron oxide/soil, more air/soil, less air/iron oxide: *Fe*
(perforated). (Non-perforated)

The perforated electrode functions as cathode and the non-perforated one as anode.

After setting of the cell, hydrogen ions in the soil ($pH = 2\cdot5$) migrate towards the cathode and away from the anode. Hence the film at the cathode dissolves at a greater rate than the film at the anode. Consequently the potential of the perforated electrode decreases as free iron surface is gradually exposed more to the soil electrolytes. Simultaneously E.M.F. and the cell current decrease.

As the soil is acidic, the direct chemical corrosion of iron proceeds in the following two ways :

(*i*) By displacement of hydrogen.

$$Fe + 2H^{+} \rightarrow Fe^{++} + H_2 \uparrow$$

(*ii*) By oxidative reaction[17]

$$Fe + H_2S\,O_4 \text{ (adsorbed)} + \tfrac{1}{2}O_2 \rightarrow Fe\,SO_4 + H_2O$$

$$\text{or } Fe \rightarrow Fe^{++} + 2_e$$

followed by the following series of reactions:

$$2\,Fe\,SO_4 + H_2SO_4 + \tfrac{1}{2}\,O_2 \rightarrow Fe_2\,(SO_4)_3 + H_2O$$

$$Fe_2\,(SO_4)_3 + 3\,H_2O \rightarrow Fe_2\,O_3 + 3\,H_2\,SO_4$$

$$\text{or } 2\,Fe\,SO_4 + 2\,H_2O + \tfrac{1}{2}\,O_2 \rightarrow Fe_2\,O_3 + 2H_2\,SO_4$$

The rate of oxidative anodic reaction is proportional to the oxygen concentration, hence it proceeds with greater rate at the perforated electrode, causing a decrease in its potential.

As a net effect of the above factors, the E.M.F. and the cell current decrease, become zero and then negative. Finally all oxide film is dissolved and then the cell can be represented by

Fe / soil, more air/soil, less air / *Fe*
(Perforated) (Non-perforated)

At about this stage maximum negative E.M.F. and the corresponding cell current is obtained.

As the electrochemical reaction proceeds, the relative concentration of Fe^{++} and Fe^{+++} ions increase in the vicinity of perforated electrode. Consequently its potential also rises. After the intervening equipotential point, the E.M.F. again becomes positive and the cell current passes through the zero value, increases to a maximum and becomes approximately constant for the rest of the period.

(*e*) The E.M.F. of the cell constituted by Jodhpur desert soil reverses within 18 days and remains so up to the remaining period. Such a behaviour is also shown by the cells containing cast iron and mild steel in this soil. The reason for this has been given in an earlier communication[21].

The scatter diagram of maximum mean cell current is given in Fig. 4. The regression equation for the two parameters has been calculated to be

$$M^2 = 0{\cdot}061\, I$$

where M = Mean corrosion loss in terms of gms/dm^2. $\frac{1}{2}$ year.

I = Maximum mean cell current in terms of microamperes.

The scatter diagram of the corrodibility and the amount of electricity passing through the short circuit for a period of six months, represented by the area between the Mean Short Circuit Current--Time curves and Time axis is in Fig. 5. The relationship between the two parameters is given by the regression equation $M^2 = 0{\cdot}96\ Q$.

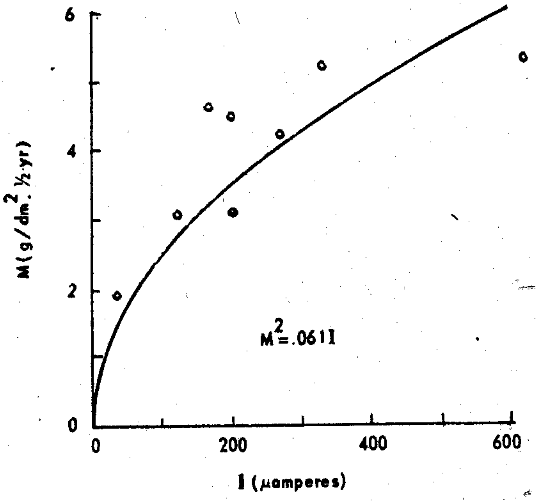

FIG. 4—Maximum mean cell current-corrodibility curve.

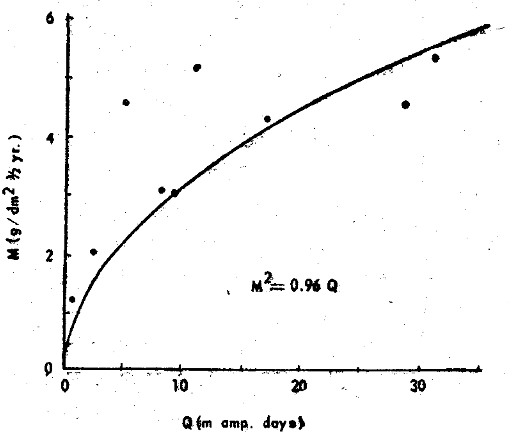

FIG. 5—Relationship between corrodibility and amount of electricity passing through the cell.

where Q = amount of electricity in milliampere days.

The point for Alleppey peaty soil has been excluded from the calculation of this curve as in this case heavy direct chemical corrosion occurs.

Soil properties and corrosivity—The effect of soil properties on its corrosivity towards wrought iron is similar to that towards cast iron and mild steel.

Some correlation of the soil corrosivity towards wrought iron, expressed as corrodibility of the metal in soils, with certain individual soil properties have been obtained in the case of non-acidic soils. Alleppey peaty soil, because of its highly acidic nature, is very highly corrosive. The scatter diagram of corrodibility in relation to moisture present in a soil is given in Fig. 6. The corrodibility increases with increase in the moisture content and is maximum when the moisture content is between 25—30%. This is in accordance with the observation of Mamedov[22] for steel. With enhancement of moisture content the corrodibility again decreases. This qualitatively supports the conclusions of Markovic[23] [24] that the soils low in water and high in air or *vice-versa* are less corrosive, but the soil at the optimum level of both are most corrosive. This region is 25—30%. Hence for the soils *in situ* the moisture equivalent, which is an index of field capacity, should be regarded as the concentration of water controlling the corrosivity of the soil.

The amount of clay present in a soil is a fairly good index of its moisture equivalent. Hence the corrodibility of soil will depend on its clay percentage in a manner qualitatively similar to water content.

As regards the dependence of soil corrosivity towards wrought iron as a function of its resistivity, observations similar to that towards cast iron[10] and mild steel[21] can be made namely that the soil corrosivity decreases qualitatively with increase in soil resistivity.

The effect of soil *pH* on its corrosivity towards wrought iron is the same as for cast iron and mild steel as evidenced by the Pourbaix diagram[25] according to which the soils having *pH* below 9·5 will be corrosive. Soil corrosivity is not a function of its *pH* when *pH* is in the range of 4-10. Soils having *pH* below 4 will exert direct chemical corrosion alongwith the electrochemical corrosion. Hence the corrosivity of Alleppey peaty soil is significantly high.

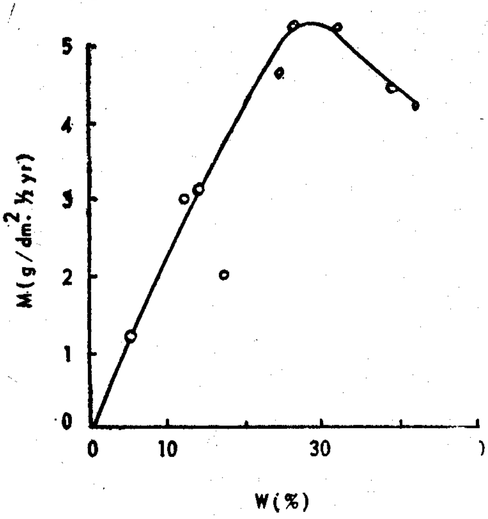

FIG. 6—Moisture-corrodibility curve.

The laterite soils like Ratnagiri laterite soil, containing free ferric oxide due to desilication will be comparatively more corrosive because ferric oxide exerts a depolarising influence[20]. The nature and concentration of soluble salts present in the soil will exert multiple influences viz, resistivity, electrode potentials, film properties, adsorption etc. on the corrosion of wrought iron in soils. The effect will be similar to the corrosion of other plain ferrous metals[10,21].

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