ON POTENTIALS OF FERROUS ELECTRODES IN SOIL CORROSION CELLS

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Open circuit potentials of electrodes and short circuit currents of soil corrosion cells constituted by cast iron, mild steel and wrought iron electrodes in the typical Indian soils have been determined and the voltages and the internal resistances of the cells have been calculated. The electrode potentials do not have a simple correlation with any of the soil properties. In non-acidic soils, the cell voltage at first increases abruptly with moisture equivalent, reaches maximum at about 15 and then decreases gradually. Based on this an interpretation has been offered for the maximum corrosivity of soils, having moisture equivalent, 30, as observed for mild steel and wrought iron. In an acidic soil electrode potentials of all the ferrous metals are indentical and cell voltages, very small. Hence most of the corrosion proceeds through direct chemical reaction. Cast iron is slightly less corrodible than mild steel and wrought iron because of additional protective influence of liberated carbon deposited over the metal.

The soil corrosion cell procedure, devised by Denison[1] and modified by Schwerdt-feger[2], is the best form of the accelerated test for the evaluation of soil corrosivity or metal corrodibility and the electrochemical study of the corrosion phenomena[3]. Such a cell is represented by Fe | soil (saturated) || soil (water up to moisture equivalent level) | Fe. The assembling of such a cell has been described earlier in detail[4]. The electrodes in such a cell corrode by differential aeration cell action, local electrochemical action and direct chemical action. Therefore the cell is a close resemblance of the actual phenomena of subterranean corrosion. The corrosion of cast iron[4], mild steel[5] and wrought iron[6] in ten different typical Indian soils, in terms of corrosion loss per unit area per half year and the chronological behaviour of the short circuit current, have been studied in detail by adopting the above proedure.

The short circuit current of a cell is usually maximum at the beignning, decreases gradually with time and after a certain period, the change is much less significant. This behaviour is represented by asymptotic nature of cell current—time curves[4-6].

Certain cells deviate from this general pattern of the chronological behaviour of cell current. Some require a small period for stabilisation after which the cell current becomes maximum. The cells constituted by a soil having some depolarising agent register increment in the cell current at some stage, but after attaining the maximum, the behaviour becomes as usual. The cells containing a sandy soil exhibit reversal of polarity after a short time. There are some other types of deviation from the general behaviour. But in all such cases the current usually stabilizes within a period much earlier than 180 days and then the change in the cell current with time becomes much less significant. Therefore the electrode potentials measured at the end of 180 days are the indices of the potentials of the electrodes after the initial covering of the rapidly forming corrosion products, whose protective action becomes fairly constant and does not significantly increase with further increment in the film thickness.
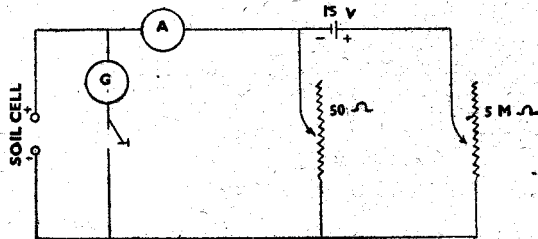
Fig. 1—Zero-resistance ammeter.

The electrode potentials and the corresponding cell current, lead to some important informations regarding the behaviour of the plain ferrous metals in soils viz, the cell voltage, internal cell resistance and the properties of the film of the products of corrosion reactions. Therefore, before dismantling of the cells set up for the determination of the corrodibility data [4—6], the electrode potentials and the cell current of each cell were determined.

EXPERIMENTAL

Cell Current—The short ciruit current of each cell was determined with the help of a zero resistance ammeter. The circuit diagram of the ammeter is given in Fig. 1.

Electrode Potential—The stainless steel screen and the filter paper at the bottom of the cell was removed and a plug of a saturated calomel electrode (-0.24 V with respect to the normal hydrogen electrode) was connected with the soil there. The potentials of anode and cathode were determined with the help of a modified Interrupter-Potentiometer.[7] The connections were made in such a way that at the time of determination, current did not flow through the cell.

RESULTS

As the corrosion cells for each metal-soil set were assembled in quadruplicate, the potential and current determinations were also made in quadruplicate. The results are reported as mean of four values. The voltage and the internal resistance of each cell were calculated from the above data. The physico-chemical properties, pertaining to soil corrosivity and the cell dimensions have been reported in an earlier communication[4]. Accordingly, it has been calculated that the part of the internal resistance in a cell due to the soil is 0.16ρ, where ρ is the soil resistivity.

The data have been recorded in Table 1. The potentials are with reference to normal hydrogen electrode.

DISCUSSION

The anode and cathode potentials of each ferrous metal in different soils are different. There appears to be no simple correlation between electrode potentials with any of the soil properties. This absence of correlation is due to the multiplicity of factors responsible for the corrosion reactions. It can be qualitatively stated that the electrode potentials of less corrosive soils are usually higher than that of more corrosive ones.

Cathode potentials of all the metals in Trivandrum forest and Sambalpur laterite soils and a few other stray cases are higher than the null point[8] for iron (-0.02 V). Therefore under certain soil conditions, the potential of a ferrous metal surface can be more

TABLE I

ELECTROCHEMICAL DATA OF SOIL CORROSION CELLS

Soil	Resistance due to soil in the cell ($\times 10^2$ ohms)	Metal	Anode Potential (V)	Cathode potential (V)	Cell voltage (V)	Cell current (μ amp)	Internal cell resistance ($\times 10^3$ ohms)	Remarks
Delhi alluvial	5·8	C.I.	−0·25	−0·08	0·17	16	10	
		M.S.	−0·30	−0·18	0·12	18	6·6	
		W.I.	−0·34	−0·16	0·18	13	14	
Bangalore red	1·9	C.I.	−0·17	+0·02	0·19	16	12	
		M.S.	−0·25	−0·04	0·21	18	12	
		W.I.	−0·31	−0·08	0·23	22	10	
Ratnagiri laterite	4·6	C.I.	−0·26	−0·07	0·19	26	7·3	C.I.=Cast Iron
		M.S.	−0·30	−0·17	0·07	6	12	M.S.=Mild Steel
		W.I.	−0·30	−0·20	0·10	33	3·0	W.I.=Wrought iron
Nagpur black	1·2	C.I.	−0·16	−0·11	0·05	42	1·2	
		M.S.	−0·10	−0·07	0·03	25	1·2	
		W.I.	−0·25	−0·15	0·10	30	3·3	
Trivandrum Forest	14	C.I.	−0·07	+0·04	0·11	6	18	
		M.S.	−0·05	+0·09	0·14	12	12	
		W.I.	−0·09	+0·01	1·10	6	17	
Sambalpur laterite	35	C.I.	−0·05	+0·15	0·20	3	70	
		M.S.	−0·00	+0·16	0·16	2	80	
		W.I.	−0·10	+0·10	0·20	5	40	
Coimbatore black	1·0	C.I.	−0·13	−0·04	0·09	101	0·9	
		M.S.	−0·19	−0·16	0·03	84	0·3	
		W.I.	−0·20	−0·14	0·06	118	0·4	
Delhi saline	0·5	C.I.	−0·12	−0·04	0·08	60	1·3	
		M.S.	−0·18	−0·05	0·13	104	1·2	
		W.I.	−0·18	−0·01	0·17	88	1·9	
Jodhpur desert	14	C.I.	−0·04	−0·07	−0·03	2	15 ⎫	The cells are with
		M.S.	−0·13	−0·18	−0·05	4	13 ⎬	reversed polarity.
		W.I.	−0·14	−0·17	−0·03	2	15 ⎭	
Alleppey peaty	1·8	C.I.	−0·41	−0·40	0·01	5	2·0	
		M.S.	−0·41	−0·40	0·01	38	0·3	
		W.I.	−0·41	−0·40	0·01	20	0·5	

positive than its natural potential. The cathode potentials of the metals in Bangalore red and Delhi saline soils are also comparatively high.

The potential of cast iron electrodes in non-acidic soils are higher than the corresponding potentials of wrought iron, except the cathode potential in Delhi saline soil. The general observation may be due to the difference in the form of corrosion of two metals. Cast iron has generally corroded in the form of general[9] and wrought iron, local corrosion. Hence a
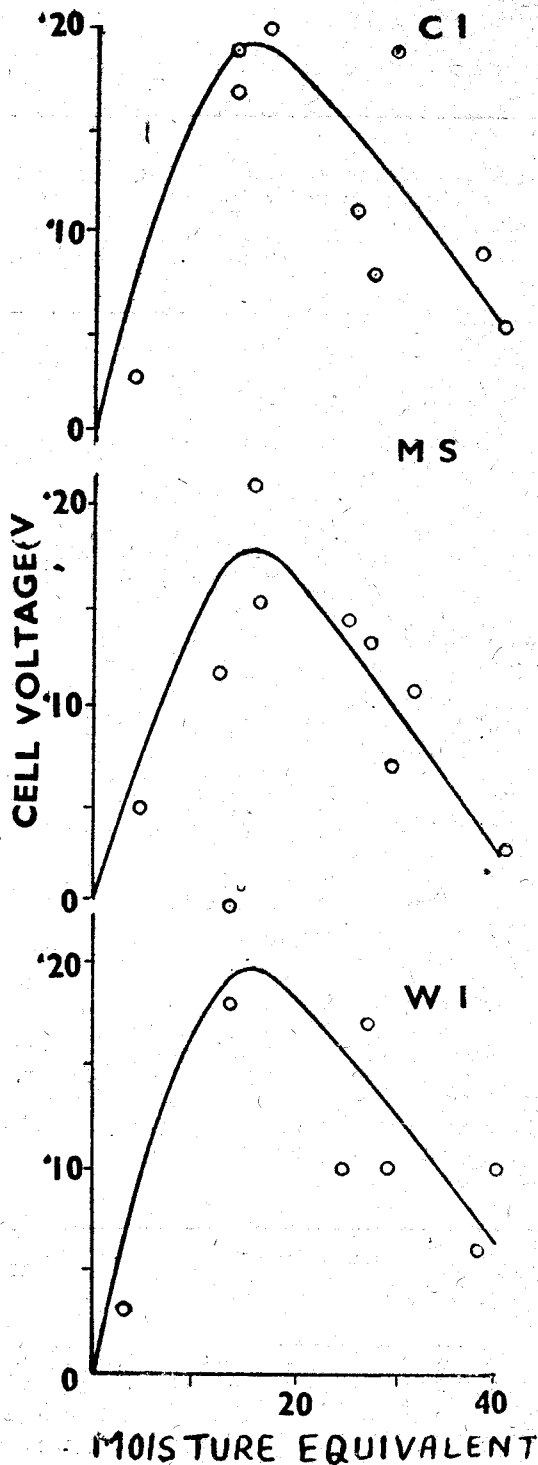
Fig. 2—Cell voltage—Moisture Equivalent curves.

thick layer of corrosion products has deposited all over the surface of cast iron and the potential of each electrode is given by the half cell Fe (corrosion products) | soil whereas in the case of wrought iron part of the surface is covered by a thick layer and the rest by a superficial layer of corrosion products. Hence its overall potential is lower than that of cast iron.

The anode potentials of mild steel electrodes are higher than or equal to those of corresponding anode potentials of wrought iron. However, generalisation is not possible in the cases of the electrode potentials of cast iron and mild steel and cathode potentials of mild steel and wrought iron.

The electrode potentials of all the three ferrous metals in Alleppey peaty soil (pH $2 \cdot 5$) are identical. These potentials are significantly lower than that in non-acidic soils. This ie due to the acidic nature of the soil. The electrode potentials are constituted mainly by the half cell Fe/H^+ without any effective intervening film over the metal surface. Hence the values are identical and much lower as compared with the values in the non-acidic soils. The voltages of these cells are of low order. Hence the electrodes corrode mainly by direct chemical action and corrosion due to the differential aeration is relatively very small.

The cell voltage has a definite correlation with the moisture equivalent of the soil. Regression curves exhibiting the relationships between the two variables are given in Fig. 2. Though some of the points are quite away from the regression curves, due to some other important factors influencing the cell voltage, but the trend is quite clear.

As moisture equivalent is quite a consistent index of soil texture, the curves indicate that the voltage is much dependent on the soil texture. The maximum voltage is obtained with the

soils having the moisture equivalent of about 15. As the moisture equivalent increases, the voltage decreases gradually. But with decrease in the moisture equivalent, the same change occurs abruptly. Consequently the voltages of the cells containing sand or clay are significantly lower than those containing loam. The reason for such a behaviour is the permeability of the soil-water system for air, which functions as cathodic depolariser in the corrosion process. The permeability of sand for air is high. Hence the voltage of the differential aeration cell containing the sand is low. As the texture becomes progressively finer and moisture equivalent increases, the permeability of air decreases. So the difference between the rates of replenishment of oxygen at the two electrodes increases with the voltage. On the other hand, the permeability of a saturated soil for air is very little. Hence the rates of replenishment of oxygen at the two electrodes are very slow. Consequently the voltage is small in magnitude. As the texture becomes coarser and the moisture equivalent decreases and the permeability of the soil for air increases, the difference in the rates of replenishment of oxygen at the two electrodes and voltage increases gradually. At the optimum value of moisture equivalent the voltage is maximum.

The initial internal resistance of such a cell is primarily due to the resistance offered by the soil intervening the two electrodes. As the corrosion proceeds the internal resistance increases due to the polarising influence of the film of the products of the corrosion reactions. The internal resistances due to the soil at initial period are fairly of the order of 10% of the internal resistances at the end of 180 days. In the corrosion process physico-chemical changes occur in the soil mass. Consequently the resistances by the soil goes on changing. For simplicity, if it is assumed that the resistance of a soil mass remains approximately constant, the internal resistance of a cell at the end of the period can be considered to give the order of the resistance due to the film of the products of the corrosion reactions.
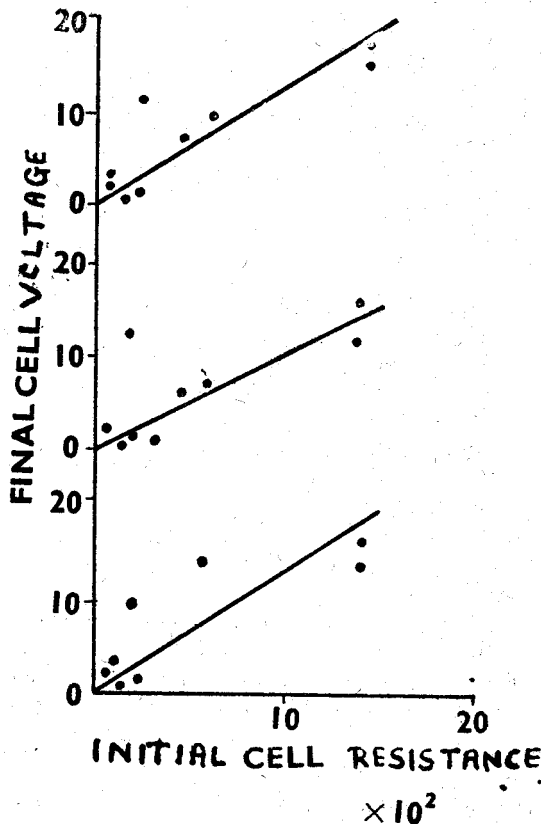
In most of the cases, internal resistance of the cell has a linear correlation with initial resistance of the cell. Regression curves showing the correlations between the two variables are given in Fig 3. The points for Bangalore red soil deviate considerably from the regression curves for all the three metals. As the initial resistance of the cells containing Sambalpur laterite soil is too high, its points have not been given in the figures. In both the cases final resistances are too high.

On the basis of the correlation it is concluded that the internal resistance, which is the sum of the resistances due

Fig. 3—Final vs initial cell resistance curves.

to the intervening soil mass and the film of the products of the corrosion reactions is primarily a function of the concentration of water and soluble electrolytes present in soil. The order of the internal resistances of the cells constituted by a soil and three ferrous metals as electrodes is the same for all the soils. The polarising nature of the film of the products of the corrosion reactions is controlled by the water and the soluble electrolytes. The film becomes more conducting with increase in their concentrations.

The internal resistances of the cells having mild steel and wrought iron electrodes in Alleppey peaty soil are of a small order. This is due to the fact that in these cases the products of corrosion reactions are formed mostly as-soluble salts which are not deposited on the iron surface as polarising films. The internal resistance of the cell having cast iron electrode in the same soil is comparatively high. Therefore it is concluded that carbon deposits remaining after the dissolution of iron exert some protective action. It is futher confirmed by the differences in the corrodibilities of the ferrous metals in the soil. The data is given in Table 2. Students 't' test [10] has been performed to determine the significant values for the differences in the corrodibilities of the three metals. 't' has been calculated by the following expression.

$$t = \triangle \left/ \left[\frac{(\Sigma\ x^2_1 + \Sigma\ x^2_2)}{(N_1 + N_2 - 2)} \left\{ \frac{1}{N_1} + \frac{1}{N_2} \right\} \right]^{\frac{1}{2}} \right.$$

where $\triangle$ is the difference between two means of two sets, x, the difference between the mean and individual corrodibilities and N, the number of experiments in a set. The suffixes 1 and 2 indicate the first and second sets of the experiment.

TABLE 2

DATA ON CORRODIBILITIES OF FERROUS METALS IN ALLEPPEY PEATY SOIL

Metal	Mean corrodibility	Standard Variation	't' with respect to previous metal	Significant value
Mild Steel	7·204	0·202		
Wrought Iron	7·047	0·366	0·75	0·48
Cast iron	6·566	0·419	2·07	0·08

The order of corrodibility is mild steel< wrought iron< cast iron. The significant value for the difference in corrodibilities of mild steel and wrought iron is very high as compared with that of wrought iron and cast iron. 48 per cent of the corrodibility results of first two metals are expected to overlap, whilst in the next two only 8 per cent.

The electrolytic current causing the corrosion is proportional to the cell voltage and the soil conductivity. The conductivity of a soil increases continually up to the water

saturation level and the cell voltage is maximum at water level of 15 per cent. Hence there should be an optimum value of water content at which the current will be maximum and the soil will exhibit maximum corrosivity. For mild steel [5,11] and wrought iron[6], the value has been found to be near about 30 per cent.

Such a maximum value of soil corrosivity has not been observed for cast iron. The corrosivity of soils towards the metal continually increases with moisture equivalent. This is due to the fact that cast iron has a considerable surface inhomogenity in the form of ferrite and graphite units[12], which leads to greater amount of local action corrosion as compared with the local action corrosion in mild steel and wrought iron which possess much less surface inhomogenity of such nature. Therefore for cast iron the corrosivity of soils of moisture equivalent more than 30 is augmented because of the local action corrosion.

The internal resistances of the cells having the three different ferrous metal electrodes, but the same soil, have been found to be of the same order. Cast iron corroded mostly in the form of general and mild steel and wrought iron in local corrosion. Therefore at the time of measurements, cast iron electrodes are covered all over by a thick film of the products of corrosion reactions and mild steel and wrought iron partly by thick and partly by superficial films. But the order of the film resistance is the same. Hence various layers of the film of the corrosion products are not equally protective. As the distance of the layer from the free metal surface increases, its protective influence decreases and finally vanishes off completely. This conclusion is supported by the hyperbolic decrease in the value of most of the cell currents. This effect is due to development of greater number and wider dimensions of cracks in the layer of the film as its distance from the metal surface increases.

ACKNOWLEDGEMENT

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