Anodic Protection of Mild Steel in Acid Environment : Part I.

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CORROSION of mild steel in sulphuric acid at different concentrations and different temperatures, can be controlled by application of anodic protection. Anodic polarization curves are obtained to evolve the suitable parameters for applying such anodic protection. The protection scheme is tested by holding the metal in the passive region and monitoring the passive/corrosion current density over a ten hour period. The degree of protection obtained by anodic protection technique is calculated in each case. The technique is found to be very satisfactory at lower temperatures. The weight loss suffered by the metal in these cases is very negligible. At higher temperatures however, the efficiency of protection is much less. presumably due to the poor adherence of the protective film.

While cathodic protection is extensively practised for controlling corrosion, anodic protection is comparatively a novel technique. Although the main limitation of anodic protection is that this technique can be employed only for such metals and alloys that can be passivated in the given environment, it still deserves further exploration as a reliable means of controlling corrosion because there are many metals and alloys of the active-passive type that are extensively used in various industries. It has hitherto been the practice to employ cathodic protection even in cases where the metal could be passivated, because cathodic protection is considered safe and does not require the degree of sophistication and rigid control of parameters as in anodic protection. However, anodic protection has certain unique advantage in that, it not only protects but also offers a means for monitoring the instantaneous corrosion rate because the applied current is usually equal to the corrosion rate of the protected system. Also, the operating conditions for anodic protection can be precisely established by laboratory polarization studies. In contrast, the operating limits for cathodic protection are usually established by empirical tests and the final choice is usually based on past experience. Moreover, the disadvantage of hydrogen embrittlement, which poses a major problem for cathodic protection in acid media, is completly non-existent in anodic protection.

The possibility of anodic protection by impressed currents was first visualised as early as 1954 in the papers published by Edeleanu[1,2] The first industrial application of this technique was reported by Sudbury and co-workers[3,4]. Anodic protection was also successfully applied in the paper industry by Banks, Hutchinson and Hurd[5]. Application of this technique for controlling corrosion of various metals of commercial importance in aggressive media was also reported[6-11].

Mild steel is one major material of construction extensively used in chemical and allied industries. Hence, it was considered appropriate to study the applicability of anodic protection technique for controlling its corrosion in acids which are frequently encountered in chemical industries. Nelson[12] and King[13] suggested carbon steel as an important material of construction, the latter recommending its use for storage tanks and pipe fittings in H_2SO_4 of 55°-60° Be' and 66° Be' grades. Fontana and Greene[14] have reported that concentrations of H_2SO_4 below about 65% at any temperature are dangerous, with corrosion rates for steel exceeding 200 mpy.

In the present studies are on the technique of anodic protection for mild steel in dilute acids. Anodic polarization curves were run, to evolve important and useful parameters relevant to the passivation of mild steel in such dilute acids at different temperatures. The latter half of this paper deals with the practical application of these parameters evolved for passivation, to study the degree of protection that can be imparted by this technique.

EXPERIMENTAL

The mild steel sample used, was obtained through kind courtesy of N.M.L. Jamshedpur, its chemical composition being. C = 0.13%, Mn = 0.5% P = 0.065%, S = 0.03% and Si = 0.05%.

Cylindrical specimens (5.0mm dia, and 15.0mm length) are carefully cut, machined, threaded and thoroughly polished successively with 1/0, to 4/0 grade emery papers to obtain a bright and uniform surface. The specimens are subsequently cleaned in a mild detergent solution, rinsed with acetone and double distilled water, dried and stored for further use.

For each run, the specimen is accurately weighed and its dimensions are carefully measured before it is mounted as described by Stern and Makrides[16]. The mounted specimen constituting the working electrode, is again cleaned in a mild detergent solution, thoroughly rinsed with double distilled water and quickly transferred to the polarization cell containing the electrolyte under study.

The multinecked polarization cell is similar to the one described by Greene[16] a modified version of a cell proposed by Stern[17]. Two auxilary platinum electrodes are placed on either side of the working electrode to provide a uniform current flux. The positioning of the reference electrode (Saturated Calomel Electrode) is slightly changed in the present experimental set-up because of the inconvenience with the type of reference electrode–luggin probe set-up suggested by Greene[16]. A survey of literature shows that the type of set-up used in this work (see inset in Fig. 1) appears to be fairly popular. The entire multineck flask assembly is immersed in a constant temperature bath and the electrolyte is maintained at ± 1°C of the chosen temperature.

AR grade H_2SO_4 is used to prepare the electrolyte of desired concentration. It assays the chloride content < 0.00002%. Double distilled water free of organic matter is used.

The potentiostat used is Wenking Model LB 75 M. The operator selector switch provided on the module can be set at four different positions vix., E_s, E_c, E_r and I. In the E_s position the electrochemical cell is separated from the potentiostat. In the E_c position the built in voltage suppression control comes into operation. The corrosion/rest potential of the cell is measured in the E_r position by reading the deflection on the

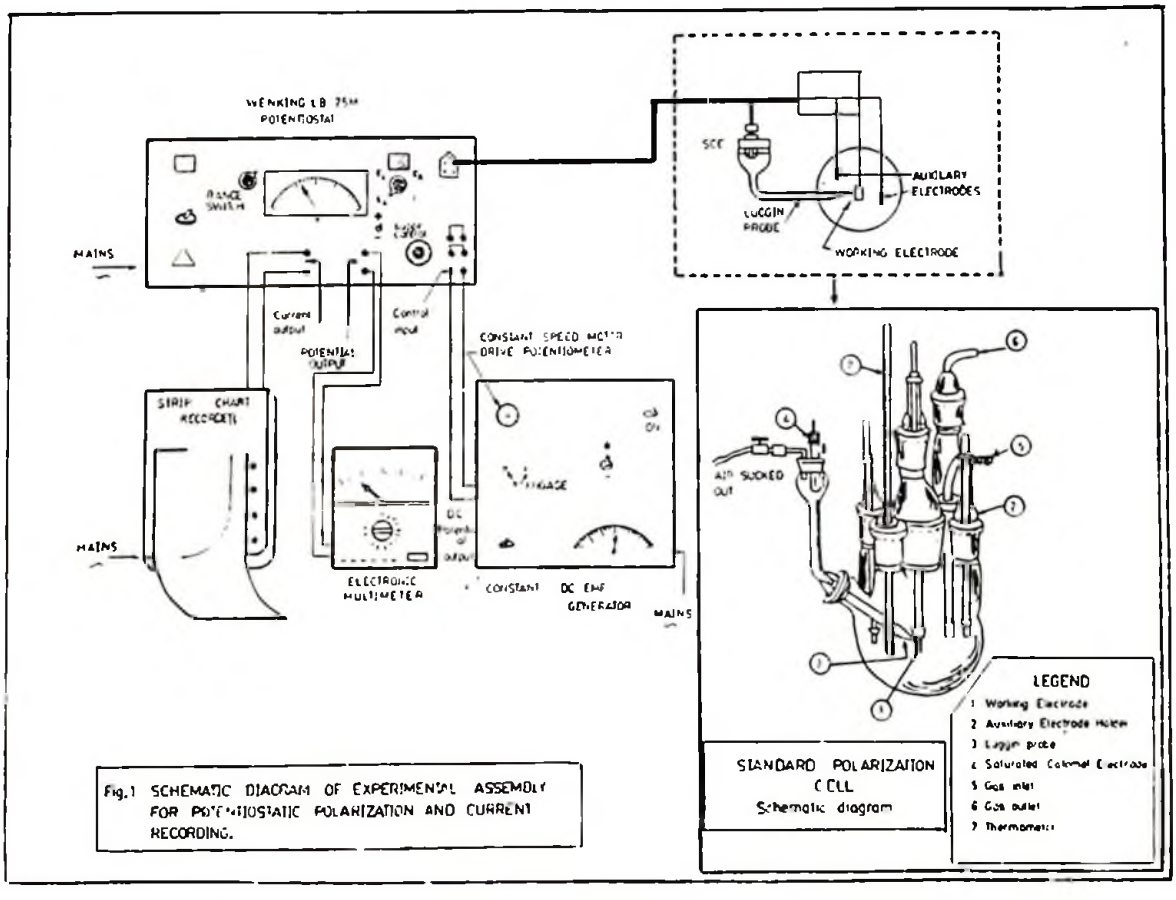


Fig.1 SCHEMATIC DIAGRAM OF EXPERIMENTAL ASSEMBLY FOR POTENTIOSTATIC POLARIZATION AND CURRENT RECORDING.

panel meter when the dial of the control voltage source is set at zero. It is also possible to measure the corrosion/rest potential by compensating it via the built in control voltage source. When the operator selector switch is flipped from the E_r to the I position, the cell is connected to the potentiostat. The instrument has a built in overload protection against operating errors. Applied potentials required for polarisation studies are superimposed by connecting an external voltage source to one of the three summing inputs provided.

The external voltage source used is the one used for polarographic studies with only one scan rate (20 minutes to cover the chosen span voltage) of the potential generated in ramp. It has been operated in the manual mode though it could be operated in the automatic mode. Non-availability of a log-converter and limitation with regard to scan rate of voltage have limited attempts for automatic record of the polarisation curves. An FET Electronic Multimeter (Model PM 2503) is used to monitor the applied potentials.

The potentiometric strip chart recorder is of ECIL Ltd. It has different input sensitivities and several chart speeds each of which is claimed to be electronically regulated.

Though the potentiostat has a built in voltage regulator to compensate for fluctuations in line voltage within $\pm$ 10%, a stabilized power source is used.

A five pin–five wire cable connects the electrochemical cell to the potentiostat. The connections to the different electrodes are made by colour coded pins. The important aspects of the experimental set-up are shown in Fig. 1.

PROCEDURE

The mild steel electrode is carefully prepared, accurately weighed and its dimensions are measured before it is mounted as already described in the experimental section. The auxilary platinum electrodes and the reference electrode with the luggin probe are introduced in the cell. The electrical connections to the potentiostat and the dc-potential generator unit are made as shown in Fig. 1.

Sufficient time is allowed for the working electrode to reach steady state condition corresponding to the corrosion potential (E_k). The value of E_k is checked directly. A more accurate value of this corrosion/rest potential is obtained by applying opposing potential from the built in voltage suppression control circuit of the potentiostat. For this purpose, the operator selector is switched to I position and the helipot dial of the suppression control is turned until the panel meter indicates null reading in the most sensitive setting of the current range switch. In the I position, the cell gets connected to the potentiostat and the imbalance in the potential of the working electrode vis a vis the reference is responsible for the current shown on the meter. The helipot potentiometer of the potentiostat supplies a potential in series opposition to the potential of the working electrode and hence a null indication is obtained when the suppression control is adjusted to the corrosion potential. Drawing sizeable currents through the working reference electrode system for long periods will polarize the electrodes and lead to erroneous results in the subsequent studies. To obviate this problem, the approximate corrosion potential is first measured by setting the operator selector switch in E_r position and the control potential from the helipot is then adjusted to this reading. The operator selector switch is flipped to the I position and finer adjustments are made in the helipot till a null indication is obtained. This precaution ensures that very little current is drawn through the circuit during the process of measuring corrosion potentials.

The anodic polarization curves for mild steel in different concentrations of acid at different temperatures, are run manually. After setting the suppression control at the corrosion potential which corresponds to zero applied current and keeping the operator selector in I position, the potential from the external source is increased to polarize the electrode in the noble direction. These applied potentials are increased in steps of 25 mV each and the corresponding current is noted directly from the panel meter, with the current range switch in the appropriate position to provide

maximum sensitivity. It is found that a stable current corresponding to steady state conditions can be obtained in one minute and hence the current is recorded exactly at intervals of 1 minute. Whenever the conditions are suitable for passivation of mild steel in the given acid, the current shows a progressive increase and at a certain critical potential the current records a sharp decrease, indicating the attainment of the passive state. Further increase in applied potentials gives rise to the passive zone, followed by an increase in current once again corresponding to the transpassive region.

Such anodic polarisation curves are run for different concentrations of the acid at different temperatures. The current-potential values plotted are illustrated in Fig. 2, 3 and 4 and the relevant important parameteres pertaing to the different conditions are summarized in Table 1. The concentrations of H_2SO_4 are 1.0 N, 2.0 N and 3.0 N and the polarization curves are at temperatures of 28°, 33° and 40°C. The critical current densities for passivation, the passivating potentials, the passive current densities and the safe passive zones for each set of acid concentration and temperature are shown in table 1.

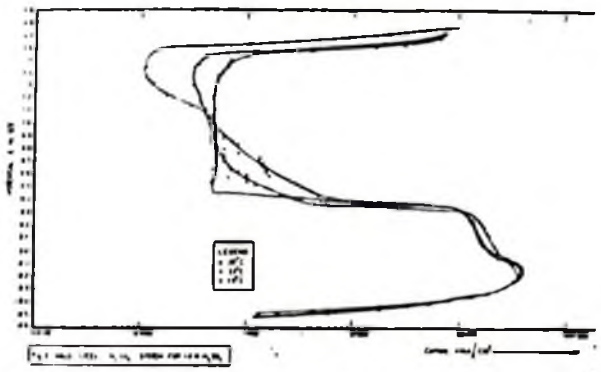


Fig. 2 Mild Steel-H_2SO_4 System For 1.0 N H_2SO_4

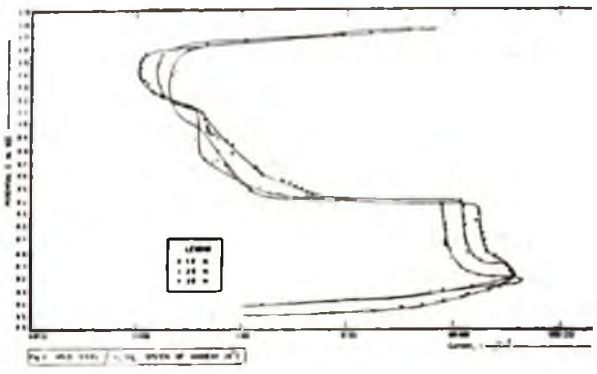


Fig. 3 Mild Steel/H_2SO_4 System of Ambient 28°C

TABLE 1

Anodic polarization parameters for mild steel in sulphuric acid

Run No.	Acid Concn. (N)	Temp. (°C)	Polarization parameters: Corrosion potential V vs SCE	Critical current density mA/cm²	Passivating potential V vs SCE	Passive current density mA/cm²	Passive zone V vs SCE
1	1.0	28	−0.532	360	0.393	0.11	0.393 – 1.593
2	1.0	33	−0.500	379	0.450	0.30	0.450 – 1.550
3	1.0	40	−0.482	400	0.418	0.46	0.418 – 1.618
4	2.0	28	−0.450	380	0.460	0.16	0.460 – 1.635
5	2.0	33	−0.438	389	0.439	0.38	0.439 – 1.589
6	2.0	40	−0.430	415	0.465	0.52	0.465 – 1.615
7	3.0	28	−0.440	450	0.445	0.22	0.445 – 1.620
8	3.0	33	−0.433	470	0.447	0.81	0.447 – 1.622
9	3.0	40	−0.428	540	0.460	2.40	0.460 – 1.635

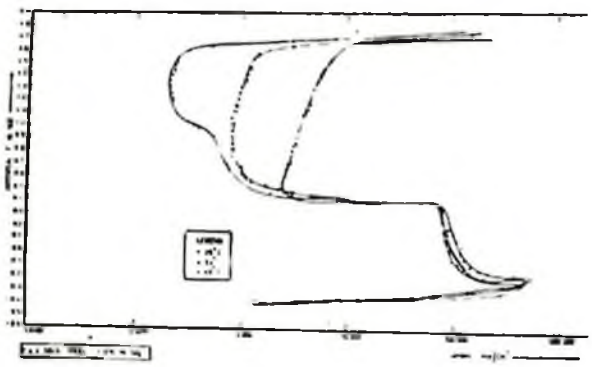


Fig. 4 Mild Steel–3.0 N H_2SO_4

The parameters evolved above are used to investigate the efficiency of anodic protection, in controlling the corrosion rate of mild steel in such dilute acids. The clean and dry electrode is initially weighed and its dimensions are measured before it is mounted and exposed to the chosen acid medium at the chosen temperature. This working electrode is held, for ten hours, at a safe passivating potential, as worked out from the anodic polarization curves studied earlier. The change in passive/corrosion current density over this period is monitored by connecting the strip chart recorder to the current output terminals of the potentiostat. The current displayed on the panel meter of the potentiostat is available at the current output terminals. Within the potentiostat, circuitry exists to convert this current into the corresponding proportionate potential, by passing it through appropriate precision resistors introduced in the circuit. The magnitude of these resistors is such that at any current setting of the range selector, the maximum output voltage at the current output terminals is constant at 200 mV. Thus, maximum sensitivity for the strip chart recorder is obtained by calibrating its input sensitivity to 200 mV full scale deflection (fsd) of the recorder pen with the help of the uncalibrated potentiometer available on it. By so calibrating the recorder, the fsd of the recorder pen corresponds to the current range set at the range selector of the potentiostat. Though the maximum output at the current output terminals is 200 mV irrespective of the position of the range selector, the potential recorded by the strip chart recorder is proportional to the cell current, e.g., if the range selector is set to the position corresponding to 3.0 mA fsd and if the recorder reads 30 divisions on a 100 division chart paper, this corresponds to a current of (30/100) × 3 mA = 0.9 mA. This can also be checked from the panel meter. The chart speed in all cases, is set at 20 cm/hr. To be sure that the applied passivating potential is held at the safe potential, the voltage reading on the Electronic multimeter connected across the potential output terminals of the potentiostat, is checked from time to time and minor adjustments are made as and when necessary, as the poteniostat is capable of hunting and rectifying such variations in applied potential. This experimental procedure is repeated for the concentrations and temperatures chosen. The current density values over this ten hour period as read from the chart records are presented in Table 2. At the end of the ten hour period, the recorder is switched off, the working electrode is disconnected, removed from its mount, freed from its mount, freed from any corrosion products adhering to it by mechanically scrubbing it with a rubber stopper under running water, cleaned, dried and weighed. Blank runs, for the same conditions of acid concentration and temperature as selected above, are made with the mild steel specimens, without any impressed currents.

The experimental conditions are given in Table 3. The last column of this table shows weight loss of the metal as calculated by Faraday's law using the data of Table 2.

Treatment of Results

The degree of protection offerered by anodic protection is calculated directly from weight loss measurements and also from Faraday's law using the data of Table 2. For comparison of this degree of protection, a term "protection efficiency" is defined as the factor

$$\text{protection efficiency } (\%) = \frac{W-W'}{W} \times 100 \qquad (1)$$

where W and W' are the losses in the weight of the metal, without and with anodic protection, respectively, illustrated below, for mild steel in 1.0 N acid at 28°C.

A. By direct weight loss method

From Table 4, W and W' are 37.8 and 0.8, respectively. Substituting these values in Eq. (1)

$$\text{protection efficiency } (\%) = \frac{37.8-0.8}{37.8} \times 100 = 97.88\ \%$$

TABLE 2

Effect of time on the passive current density of anodically protected mild steel in sulphuric acid.

Time mins.	hrs.	Passive current density mA/cm² for 1.0 N/28°C	1.0 N/40°C	3.0 N/28°C	3.0 N/40°C
Start		0.74	0.81	1.46	3.88
5		0.26	0.29	0.61	1.76
10		0.18	0.29	0.54	1.76
15		0.13	0.31	0.49	1.80
20		0.09	0.32	0.48	1.82
25		0.08	0.32	0.47	1.83
30		0.07	0.33	0.46	1.84
35		0.069	0.35	0.40	1.85
40		0.068	0.38	0 35	1 86
45		0.067	0 42	0.32	1.87
50		0.066	0.45	0 31	1.88
55		0.065	0.49	0.30	1.88
60		0.064	0 58	0.29	1 88
—	2	0.038	0 58	0 22	2.04
—	3	0.017	0.58	0 20	2.31
—	4	0.016	0 58	0 19	2.47
—	5	0.015	0.58	0.18	2.71
—	6	0.014	0.59	0.17	2.90
—	7	0.012	0.59	0.16	3.06
—	8	0 012	0.59	0.15	3.22
—	9	0.012	0.59	0.13	3.41
—	10	0.012	0 59	0.12	3.57

B. From Electrochemical Measurements

As already stated the change in passive/corrosion current density with time is monitored on a strip chart recorder. The current decreases fairly rapidly during the first one hour and comparatively slowly during the next nine hours. To apply Faraday's law, the corrosion current is obtained by analysis of the current-time curve. Table 2 summarises the change in passive/corrosion current density with time. The area under the curve is obtained by using the trapezoidal rule of numerical integration, by using the equation[10].

Area under the current-time curve

$$= \frac{h}{2}\left[y_o + 2(y_1 + y_2 \ldots\ldots + y_{t-1}) + y_t\right]$$

where, h is a small time-cell selected ; y_o to y_t are the values of the passive/corrosion current density from start to the t^{th} interval of observations ; t is 1 hour for the first part and 9 hours for the second part of the calculations as described below :

It is observed that the change in the passive/corrosion current density in the first one hour is fairly rapid as compared to the change in the next nine hours. Hence, calculations for the area under the curve, for the first hour and next nine hours are made separately. Subsequently, these two areas are added up to give the total area under the curve.

For the first hour, the time-cell h is taken as 1/12 hour (5 minutes). Then, the values of $y_o, y_1, y_2, \ldots\ldots, y_t$ will be the values of the current density recorded in column 2 of Table 2, at 5 minute intervals. Taking these values, we obtain from Eq. (2),

I_1t (area under the curve for the first hour) $= 0.1289$ mA. hr. cm^{-2}

For the next nine hours, the time-cell h is taken as 1 hour. The values of $y_o, y_1, y_2, \ldots\ldots, y_t$ for these nine hours will then be the values of the current density recorded in column 2 of Table 2, at 1 hour intervals. Substituting these values in Eq. (2) we obtain,

I_2t (area under the curve for remaining nine hours) $= 0.174$ mA. hr. cm^{-2}

The total I t for the ten hours of observation then works out to

$$I\,t = I_1t + I_2t = 0.1289 + 0.174 = 0.3029 \text{ mA. hr.cm}^{-2}.$$

This value is reported in column 7 of Table 3. The weight loss of the metal, for the ten hours is now calculated from Faraday's law as follows :

$$W' = I\,t\,A\,e \qquad (3)$$

where W' is the weight loss of the metal, in mg.

I is the current density, in mA/cm²

t is the time of exposure, in secs.

A is the area of the electrode, in cm²

e is the electrochemical equivalent
= 0.000289 for Fe.

The value of I t as already calculated
= 0.3029 mA. hr. cm^{-2}
= 0.3029 × 3600 mA. sec. cm^{-2}

The value of A as reported in Table 3 = 2.6 cm²

Substituting these values of I t, A and e in Eq. 3, we obtain,

$W' = 0.3029 \times 3600 \times 2.6 \times 0.000289 = 0.82$ mg.

This weight loss is tabulated in the last column of Table 3.

The protection efficiency is now calculated as

$$\text{protection efficiency (\%)} = \frac{37.8 - 0.82}{37.8} \times 100$$
$$= 97.83\%$$

Similar calculations as described above, for mild steel in 1.0 N acid at 28°C, are made for the other cases also. These calculated values are also recorded in Table 4.

RESULTS AND DISCUSSION

The first part of the work, summarized in Table 1, is for determination of the important parameters relevant to passivation and anodic protection of mild steei. It is found that mild steel is passivated at the three concentrations and temperatures chosen, by polarizing it to sufficiently noble potentials. The corrosion potentials tend to

TABLE 3

Results of laboratory tests for anodically protected mild steel in sulphuric acid; test period : 10 hours.

Run No.	Acid concn. (N)	Temp. (°C)	Applied passivating potential V vs SCE	Electrode Surface area cm^2	Total area under the currrent time curve mA.hr.cm^{-2}	Weight loss by Faraday's l aw mg.
1	1.0	28	1.168	2.6	0.3029	0.82
2	1.0	40	1.218	2.6	5.6521	15.30
3	3.0	28	1.160	2.56	2 0721	5.52
4	3.0	40	1.172	2.55	26.766	71.01

TABLE 4

Efficiency of anodic protection applied to mild steel corroding in sulphuric acid; test period : 10 hours

Run No.	Acid concn. (N)	Temp. (°C)	Blank run : Wt loss of metal without anodic protection, W, mg.	Wt loss with anodic protection W', mg. by Faraday's law.	Wt loss with anodic protection W', mg. by Direct weight	Protection effy (%) from Faraday's law,	Protection effy (%) from Direct weight
1	1.0	28	37.8	0.82	0.80	97.83	97.88
2	1.0	40	68.2	15.3	14.0	77.57	79.47
3	3.0	28	83.1	5.5	5.2	93.38	93.74
4	3.0	40	145.4	71.0	69.6	51.17	52.13

drift in in the cathodic direction with an increase in acid concentration and also with an increase in temperature. For example, the corrosion potentials in 1.0N acid are −0.532, −0.500, and −0.482V vs SCE at 28°, 33°, and 40°C respectively. Similarly, at a constant temperature of 28°C, the corrosion potentials in 1.0, 2 0 and 3.0 N acids are −0.532, −0.450 and −0.440V vs SCE respectively.

The magnitudes of the critical current densities required for the transition of the metal from active to passive state at 28°C are 360, 380, and 450 mA/cm² when the acid concentrations are 1.0, 2.0 and 3.0 N respectively, while at constant acid concentration of 3.0 N, these are 450 mA/cm² at 28°, 33° and 40°C respectively. These changes in the magnitudes of the critical current density, with changes in acid concentration and temperature are in conformity with the expected pattern, as corrosion of mild steel increases both with increase in acid concentration and temperature.

The passive zone for each set of acid concentrations and temperatures is seen in the last column of Table 1. The lower limit varies roughly between 0.393 and 0.465V vs SCE, with upper limit between 1.550 and 1.635V vs SCE.

Higher acid concentrations and higher temperatures could not be studied at present since the maximum current limit of the potentiostat is 1 ampere.

The passivating potential as reported in Table 3 is a safe potential selected from the passive zone for each case studied. On impressing the appropriate passivating potential, the mild steel electrode gets passivated as seen from the rapid decrease in current.

The results of short term laboratory experiments on anodic protection of mild steel are tabulated in Tables 3 and 4. It will be seen from the results that the protection efficiency (%) as calculated are in reasonably good agreement. Regarding the degree of protection offered, the effect of temperature appears to be more predominant than of acid concentration. In 1.0 N acid the protection efficiency is as high as 97.88% at 28°C while it is only 79.47% at 40°C. Similarly, in 3.0 N acid they are 93.74% and S2.13% at 28° and 40°C respectively. At the lower temperature of 28°C there is only a marginal fall in the degree of protection from 97.88% to 93.74% when the acid concentration is increased from 1.0 N to 3.0 N. The behaviour is markedly different at the higher temperature of 40°C. The protection efficiency in this case, falls from 79.47% to 52.13% when the acid concentration is increased from 1.0 N to 3.0 N. The smaller degree of protection observed at the higher temperature of 40°C is due to the fact that the passive/corrosion current density is much higher at the elevated temperatures. It is further observed that at the higher temperature of 40°C, the change of current density with time shows a peculiar pattern. It falls with time as in the other cases during the first few minutes of passivation and then increases gradually during the remaining time. The effect is specially marked in 3.0 N acid at 40°C. The initial passive current density in this case is 3.88 mA/cm² which falls to 1.76 mA/cm² within ten minutes and then progressively increases to assume a final value of 3.17 mA/cm². It is possible that at these higher temperatures, the protective passive film is not as adherent as at the lower temperature.

CONCLUSION

Corrosion of mild steel in sulphuric acid can be controlled by applying anodic ptotection. The degree of protection offered, as judged from protection efficiency calculations, varies with the concentration and temperature of the acid. Comparatively safe and reliable protection is obtained at lower temperatures for different concentrations of sulphuric acid to which the mild steel is exposed.

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