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Short Communication

Anodic protection of mild steel in sulphuric acid

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Abstract

Corrosion of mild steel in dilute sulphuric acid can be controlled to an acceptable level by anodic protection. Analysis of potentiostatic polarization curves for mild steel in sulphuric acid of different concentrations and at different temperatures reveals the parameters necessary for application of anodic protection to this system. A comparison of the corrosion rates of the unprotected and the anodically protected mild steel is made. The efficiency of anodic protection in controlling corrosion is determined; protection efficiencies in most of the cases are of a very high order (99%).

Key words: Anodic protection, corrosion of mild steel, acid environment.

1. Introduction

Corrosion of carbon and stainless steels in concentrated sulphuric acid can be controlled to a large extent by the technique of anodic protection[1] as demonstrated and reported by several workers[2-6]. In a previous communication by the present authors[8] the results of investigations on anodic protection of mild steel were reported for sulphuric acid of 1, 2 and 3 N concentrations at the temperatures 28°, 33° and 40° C. It was then found that corrosion of mild steel could be controlled to a fair degree by applying anodic protection. In the present investigation, results of further work on anodic protection of mild steel in acids of higher concentrations and higher temperatures than those reported previously are presented.

2. Experimental

Preparation of mild steel specimens for electrochemical and corrosion (weight loss) tests, electrolyte and the apparatus are similar to the procedure followed earlier[7-9]. The only addition to the apparatus is a digital potential readout (Model DR-37) accessory manufactured by Bausch and Lomb. This was connected across the potentiostat and was used as an accurate null detector for measurement of corrosion potentials. During the manual potentiostatic polarization runs, this digital readout displayed precisely the potentials being applied to the working electrode through the potentiostat. Calculations of (1) weight loss of the anodically protected specimen through numerical analysis[10] and (2) protection efficiencies reported in Table II are described in more detail elsewhere[8].

3. Results and discussion

As described earlier, potentiostatic anodic polarization curves were obtained for mild steel. The electrolytes chosen were 1, 5 and 10 N sulphuric acid and the temperatures were 25° and 75° C. These curves are illustrated in figs. 1, 2 and 3.

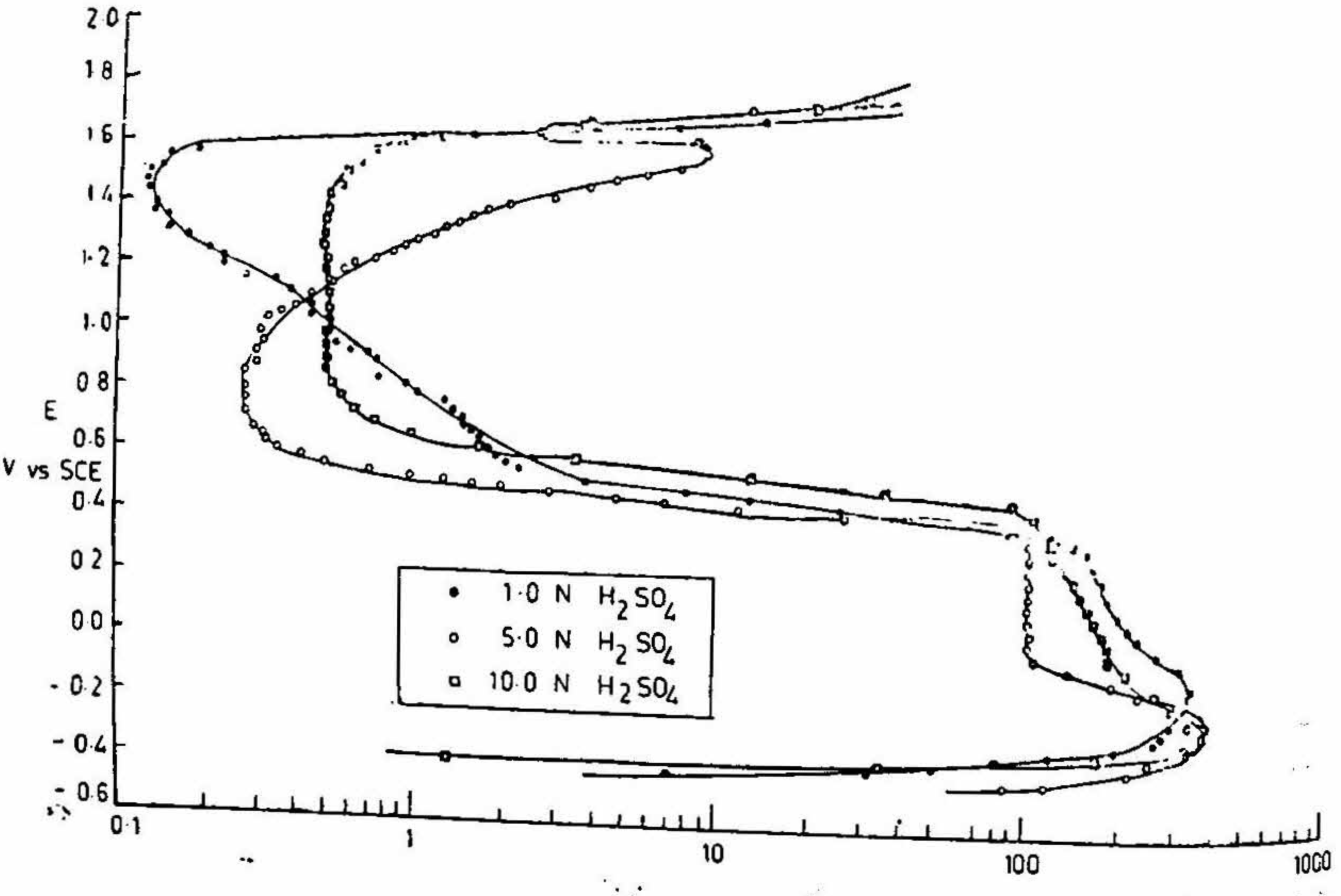

FIG. 1. Effect of concentration on potentiostatic polarization of mild steel in sulphuric acid at 25 °C.

The electrochemical parameters, *viz.*, corrosion potential, critical current density, passive current density and passive zone were obtained from the polarization curves and are summarized in Table I. For purposes of comparison, data for the case of 1 N acid at 25° C is included in the tables. These data are taken from ref. 8.

It is found that increase in acid concentration from 1 to 10 N and an increase in temperature from 25° to 75° C influence the corrosion potentials as reported in Table I. This shift presumably occurs, in the former case, due to concentratin polarization and in the latter case due to the hydrogen overvoltage effect (activation polarization).

The magnitude of the critical current density increases with increase in acid concentration from 1 to 5 N. However, when the acid concentration is increased to 10 N, the critical current density decreases instead of increasing and this behaviour is observed both at 25° and 75° C. As sulphuric acid acts as an oxidant at higher concentrations, this could be responsible for higher passivation and consequent reduction in values of critical current density.

In contrast to critical current densities, the passive current densities do not show any such reversal on increasing the concentration of acid. The passive current densities keep increasing with acid concentration and temperature.

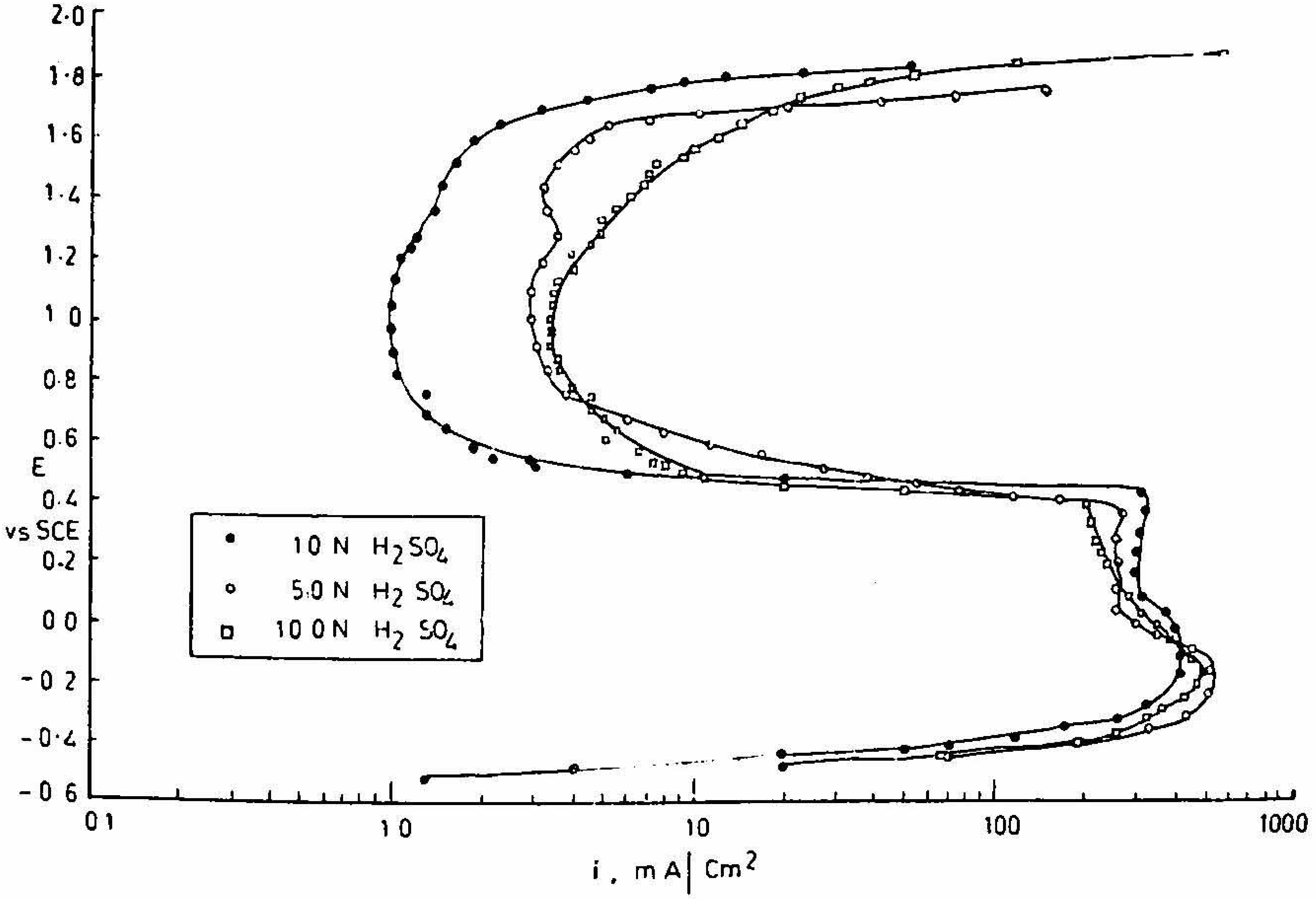

Fig. 2. Effect of concentration on potentiostatic polarization of mild steel in sulphuric acid at 75° C.

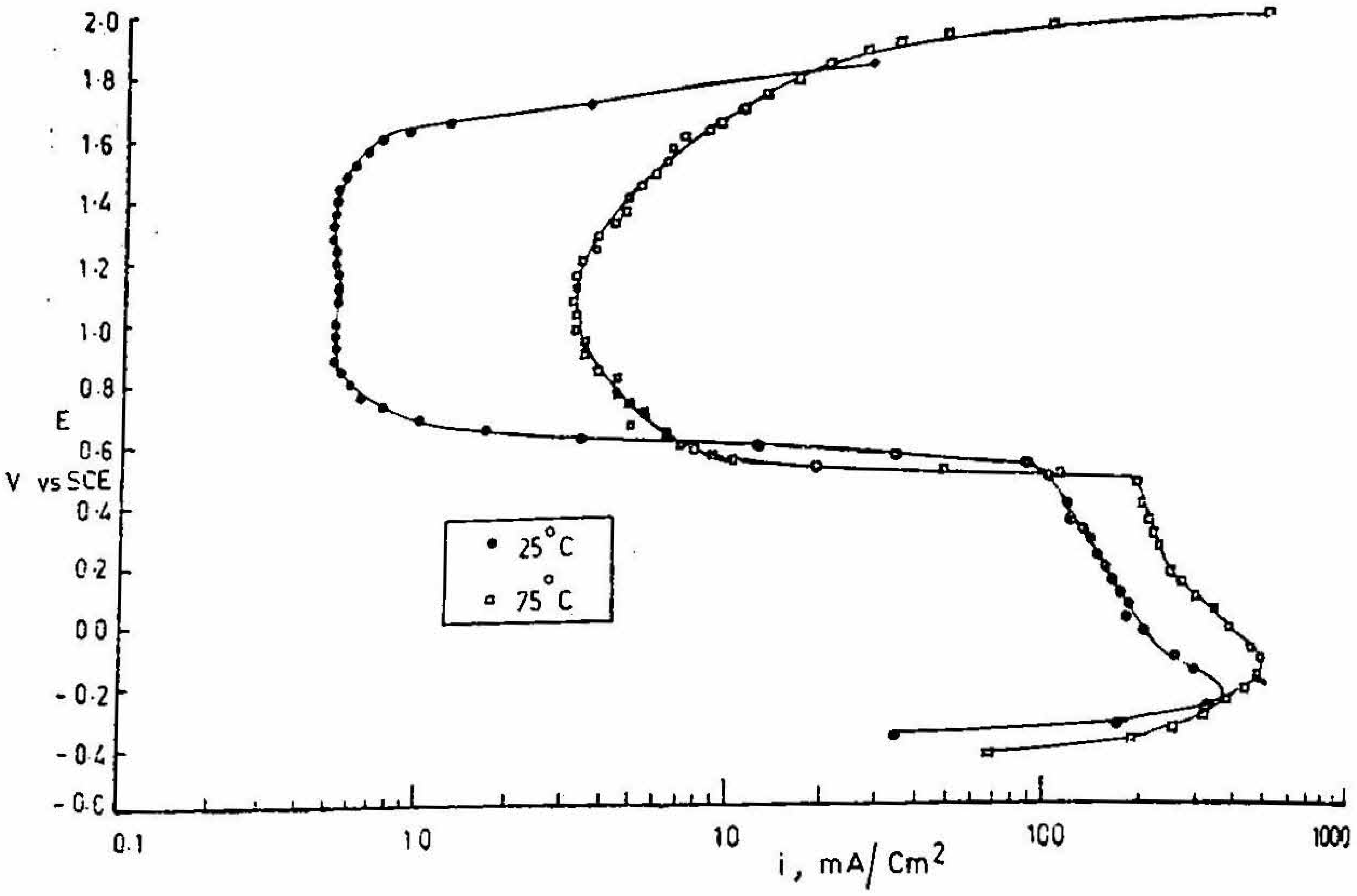

Fig. 3. Effect of temperature on potentiostatic polarization of mild steel in 10 N sulphuric acid.

The passive zone remains relatively the same for all the cases studied, with the lower limit varying between + 0·380 and + 0·455 V *vs* SCE and the upper limit between + 1·580 and + 1·635 V *vs* SCE.

Table I

Electrochemical parameters for mild steel in sulphuric acid

Acid conc. N	Temp. °C	E_{corr} V *vs* SCE	i_{crit} mA/cm²	$i_{passive}$ mA/cm²	Passive zone V *vs* SCE
1·0	25	—0·532	360	0·11	+0·393–+1·593
1·0	75	—0·560	410	1·0	+0·400–+1·610
5·0	25	—0·470	380	0·28	+0·425–+1·625
5·0	75	—0·500	522	2·9	+0·380–+1·580
10·0	25	—0·430	375	0·51	+0·455–+1·635
10·0	75	—0·485	508	3·3	+0·460–+1·600

The passivating (protection) potential chosen for anodically protecting the mild steel specimens (Table III) is that potential which exhibited the smallest current density during the polarization runs.

Table II gives a comparison of unprotected and anodically protected mild steel. It can be seen that the corrosion rates for the anodically protected specimens are very insignificant as compared with those for the unprotected ones. The protection efficiencies attained by anodic protection are of a very high order (97 to 99%). Fontana and Greene[11] have classified materials with corrosion rates between 20–50 mpy as " Fair Corrosion Resistant " and Table II reveals that for anodically protected mild steel, in the case of 1 N acid at 25° C the corrosion rate is 13·2 mpy; in the case of 5 N acid at 25° C the corrosion rate is 14·9 mpy and in the rest of the cases the rates lie between 43–66 mpy. Hence, mild steel would rate as a safe material for handling sulphuric acid up to 10 N concentration even at higher temperatures.

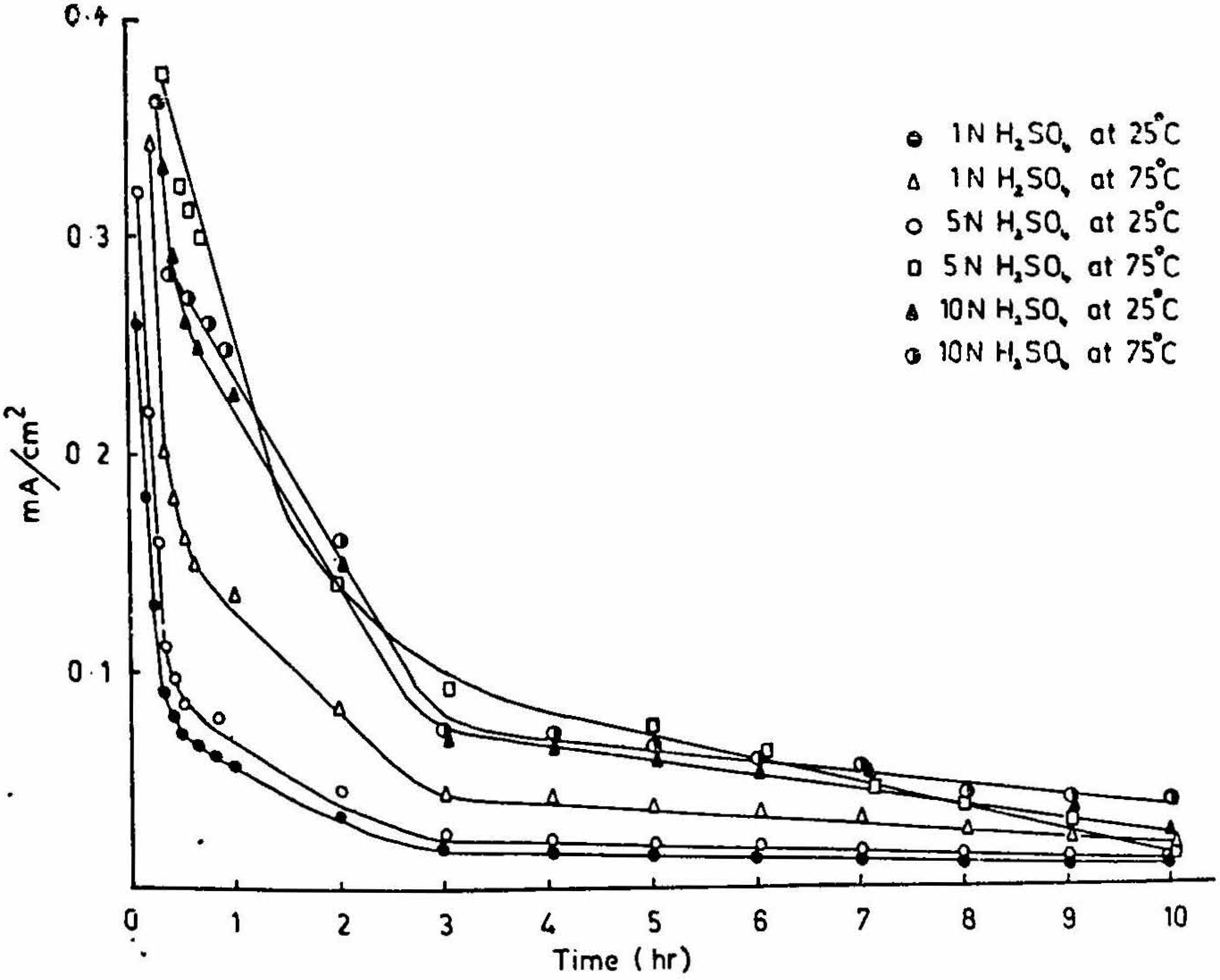

FIG. 4. Change in current density with time at applied protection potentials for mild steel in sulphuric acid.

However, the corrosion rates reported in Table II are estimated from the weight loss over the ten-hour anodic protection run. The passive current densities that are reached at the end of the ten-hour run (Table III, column 5) when converted to their corresponding corrosion rates (Table III, column 7) show that mild steel would be corroding at rates between 5–20 mpy for the cases studied in this paper. Greene[9,12] observed during a study of an 18/8 stainless steel in 1 N sulphuric acid at 25° C that the attainment of steady state current in the passive zone required nearly 100 hours or even more. Stern[13] has observed the same minimum time requirements for steady state in ferric chloride and ferric sulphate solutions. Although the corrosion behaviour of mild steel is different from that of stainless steel, it has been observed by Banks and Suddury[14] that the behaviour of current density for mild steel in sulphuric acid (93%) in the passive zone is similar to that of stainless steel. In their studies, they have observed that current densities for mild steel (when it was anodically protected) decreased rapidly during the first 24 hours. In some cases, as long as 120 hours was required before the current density was independent of time. In the present investigations, it is seen from fig. 4 that the passive current densities show a decreasing trend at the end of 10 hours. Hence, it is possible that with longer exposure, much smaller passive current densities may be reached and consequently the actual corrosion rates for anodically protected mild steel would be much smaller than those reported in Table III.

Table II

Comparison of unprotected and anodically protected mild steel in sulphuric acid (Exposure time : 10 hours)

Acid conc. N	Temp. °C	Wt. loss unprotected mg.	Wt. loss anodically protected mg.	Corrosion rates		Percentage of protection efficiency
				Unprotected mpy	Anodically protected mpy	
1·0	25	37·8	0·8	625	13·2	97·9
1·0	75	413	2·6	6823	43·0	99·4
5·0	25	398	0·9	6575	14·9	99·8
5·0	75	1532	3·2	25310	53·0	99·8
10·0	25	1313	3·3	21692	54·5	99·7
10·0	75	2544	4·0	42029	66·0	99·8

The surface of the anodically protected mild steel specimens did not reveal any localized attack or pitting corrosion. This observation is in agreement with the investigations reported by others who studied the corrosion behaviour of mild steel in sulphuric acid[15,16] and the anodic protection of steel in concentrated sulphuric acid[2-4,6,14,17]. The above investigators have observed only general or uniform corrosion of mild steel when it was anodically protected in the concentrated acids. Further, no pitting corrosion was detected as seen from the photomicrographs of the passivated steel surface reported by Locke *et al*[4]. Hence, in the presence of such conclusive evidence on the absence of pitting corrosion on passivated steel, it is assumed that the corrosion of anodically protected mild steel is of the type of uniform corrosion.

4. Conclusions

As it is corrosive, mild steel is not suitable for handling dilute sulphuric acid. However, by judicious application of anodic protection, mild steel may be considered as a safe handling material for corrosive acids even at temperatures as high as 75° C. The degree of protection offered by this technique is as high as 97 to 99% for the cases studied and reported in this paper.

Table III

Results of laboratory experiments on anodically protected mild steel in sulphuric acid (Exposure time : 10 hours)

Acid conc. N	Temp. °C	Applied passivating potential V *vs.* SCE	Wt. loss (calculated from electro-chemical data) mg	Carrent density at the end of 10-hr run mA/cm^2	Corrosion rate	
					Calculted from wt. loss of column 4 mpy	Calculated from current density of column 5 mpy
1·0	25	+1·160	0·82	0·012	13·9	6·0
1·0	75	+0·900	1·9	0·015	31·4	7·5
5·0	25	+1·000	1·0	0·010	16·5	5·0
5·0	75	+1·100	3·8	0·010	63·8	5·0
10·0	25	+1·000	3·0	0·020	49·6	10·0
10·0	75	+1·000	3·2	0·039	53·0	19·5

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References

1.	RIGGS, O. L. AND LOCKE, C. E.	*Anodic protection*, Plenum Press, 1981.
2.	SUDBURY, J. D., RIGGS, O. L. AND SHOCK, D. A.	*Corrosion*, 1960, **16**, 47t.
3.	SHOCK, D. A., RIGGS, O. L. AND SUDBURY, J. D.	*Corrosion*, 1960, **16**, 55t.
4.	LOCKE, C. E., HUTCHINSON, M. AND CONGER, N. L.	*Chem. Engng. Prog.*, 1960, **56**, 50.
5.	BANKS, W. P. AND FRENCH, E. C.	*Mater. Prot.* 1967, **6**, 48.
6.	FISHER, A. O. AND BRADY, J. F.	*Corrosion*, 1963, **19**, 37t.
7.	STERN, M. AND MAKRIDES, A. C.	*J. Electrochem. Soc.* 1957, **104**, 56.
8.	SASTRY, T. P. AND RAO, V. V.	*J. Electrochem. Soc. India*, 1981, **30**, 288.
9.	GREENE, N. D.	*Experimental electrode kinetics*, Rensselaer Polytechnic Institute, Troy, New York, 1965.
10.	SASTRY, S. S.	*Introductory methods of numerical analysis*, Prentice-Hall of India Pvt. Ltd., New Delhi, 1977.
11.	FONTANA, M. G. AND GREENE, N. D.	*Corros. Engng.* (revised edition), McGraw-Hill Inc., 1978.
12.	GREENE, N. D.	*Proc. First Inter. Congr. Metall. Corros., London*, 1961, Butterworths, 1962, p. 118.
13.	STERN, M.	*J. Electrochem. Soc.*, 1959, **106**, 376.

14. Banks, W. P. and Sudbury, J. D. *Corrosion*, 1963, **19**, 300t.

15. Taylor, R. J. and Williams, L. F. G. *Corrosion*, 1980, **36**, 41.

16. Hines, J. G. and Williamson, R. C. *Corros. Sci.*, 1964, **4**, 201 and 221.

17. Siebert, O. W. *Mater. Performance*, 1981, **20**, 38.