THE CORROSION OF MILD STEEL IN SULPHURIC ACID SOLUTIONS.
EFFECT OF pH AND SOLUTION AGITATION

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ABSTRACT

The corrosion of mild steel in de-aerated sulphuric acid solutions has been studied in the pH range 0.3-1.2 at two different levels of solution agitation.

Potentiodynamic polarization in the pre-Tafel region was employed throughout at various exposure times and the resistante polarization,R_p, calculated.
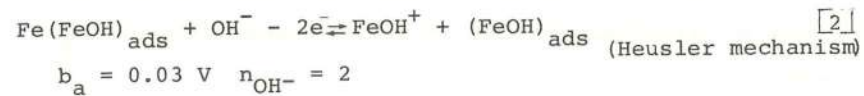
R_p varies with pH pointing towards a maximum at pH = 1 irrespective of agitation. Agitation did not interfere with R_p vs pH curve shape but displaced it towards lower values, with a more marked effect for pH < 1.

Voltamograms run after 24 hours exposure were found to be shifted towards lower current densities for rapid agitation at all pH's indicating an "inhibiting effect"due to an increase in agitation. Two anodic Tafel regions were evident, the first showing slight dependency on pH and the second with values in the range of 0.020-0.040 V, often found in acid solutions. Calculated b_a values found by curve fitting of the plot E vs i, using different combinations of b_a and b_c, gave values of the order of 0.080 V which agree with experimental values. Calculated and experimental b_c values were found to be 0.110 V.

It is demonstrated that the corrosion of mild steel in sulphuric acid solutions depends on solution agitation, effect that has been observed by other authors. The mechanistic implications of this experimental fact in relation to the role of sulphate and hydroxyl ions in the anodic process are discussed.

INTRODUCTION

A large amount of research has been dedicated to the study of the corrosion phenomena of iron and steel in acid solutions. The mechanism put forward for the anodic process assumes the participation of hydroxyl ions with some authors differing in what should be considered as the rds:

$$(FeOH)_{ads} - e^- \rightleftarrows FeOH^+ \qquad \boxed{1}$$
$$(Bockris\ mechanism)$$
$$b_a = 0.04\ V \quad n_{OH^-} = 1$$

$$Fe(FeOH)_{ads} + OH^- - 2e^- \rightleftarrows FeOH^+ + (FeOH)_{ads} \qquad \boxed{2}$$
$$(Heusler\ mechanism)$$
$$b_a = 0.03\ V \quad n_{OH^-} = 2$$

The number of factors that affect the corrosion of mild steel in sulphuric acid is reflected in a way by the different values of the kinetic parameters found in the literature (1,2,3) (for b_a varies between 0.020 to 0.100 V with n_{OH^-} from 0 to 2).

The differences, sometimes, can be accounted for in terms of the techniques used as in the case of steady and transient (4) or in terms of the argument that the several reaction paths susceptible to occur do not differ greatly in their energies bringing as a consequence different mechanism triggered by changes in situ or by the experimental conditions (5).

The surface activity of the metal by degradation brought about by hydrogen evolution as well as by high density of crystal imperfections produced by cold work is also invoked (6,7).

This work is concerned with the corrosion behaviour of mild steel in sulphuric acid solutions at low pH at two different levels of agitation. The tendency of the system to corrode is evaluated using the polarization resistance method and unidireccional voltametry.

EXPERIMENTAL

A mild steel rod was used as working electrode with the following composition: 0.10% C, 0.35% Mn, 0.017% P, 0.021% S, Fe balance. The material was heat treated in vacuum to give grain size 7 (8).

The rod was mounted in epoxy resin leaving as exposed area the cilinder base with 19.6 mm^2.

Before every experiment the electrodes were polished with emery paper up to 600 grit, washed with distilled water, degreased in acetone, dryed in cool air and immersed in the test solution.

Solutions were prepared with de-ionized distilled water and analar grade reagents and the pH adjustments were made with a concentrated NaOH solution. Deaeration of the solution was made by purging with free oxygen nitrogen overnight prior to immersion of the electrode.

Potentiodynamic polarization curves were run using a PAR 173 and a Tacussel Corrovit Potentiostats coupled to a sweep generator unit and an X-Y recorder. A scan rate of 1 mV/sec was used in both cases. The electrochemical cell

was a typical Greene cell (recommendation G5 ASTM) and all potentials were measured against a saturated calomel electrode (SCE).

RESULTS

Effect of pH

The analysis of the linear portion of the plot E $\underline{vs}$ i when polarization is limited to $\pm$ 25 mV from the corrosion potential revealed changes in R_p within a factor of 5 for changes of 0.3 pH units before giving place to a maximum near pH 1. Afterwards a rapid decreased in R_p values was observed, as seen in figure 1, where data for exposure time of 6 hours are shown.
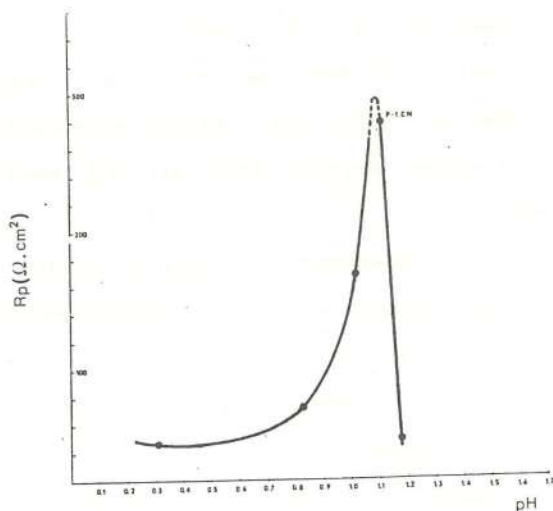

Figure 1. The dependence of R_p on pH for mild steel in 1.0 N H_2SO_4 solutions. Exposure time: 6 hours.

Other variables such as concentration, level of solution agitation, exposure time do not affect the general shape of the curve R_p $\underline{vs}$ pH: assimetric in relation to the maximum followed by a rapid decay which appear to be non-dependent on experimental conditions, in turn the position of the maximum and the absolute values of R_p before the maximum seemed to be a function of the above mentioned variables as will be shown later on.

Effect of agitation and exposure time

The effect of agitation was studied at two different concentrations and followed up to 24 hours exposure time for all pH values pointed out in the proceeding section (0.3-1.2).

Figure 2 shows the effect of agitation slow (P) and rapid (G) on the E,i characteristics for the system mild steel / / 1.0 N H_2SO_4 in the neighbourhood of the corrosion potential.
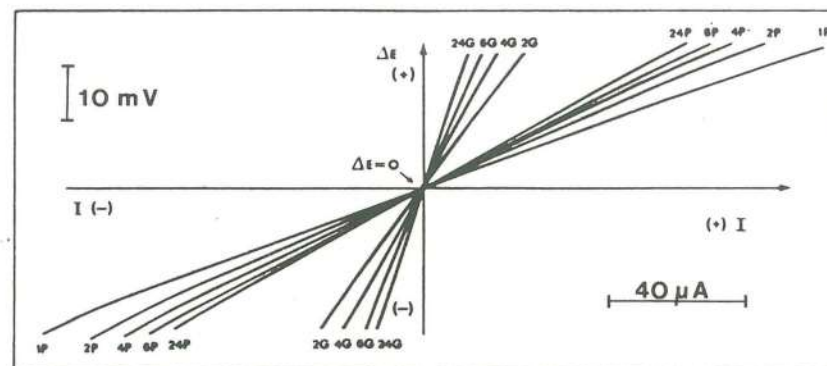

Fig. 2. Polarization behaviour in the pre-Tafel region for mild steel in 1.0 N H_2SO_4 solution with agitation at two levels: slow (P) and rapid (G) at various exposure times (1,2,4,6,24 hours). Sweep rate 1mV s^{-1}.

An increase in the slope $(\frac{dE}{dI})_{\Delta E = 0}$ with time and agitation is evident. This increase is associated to a decrease in corrosion current density.

Presented in figure 3 are the values of $R_p (\Omega.cm^2)$, calculated from plots such as those presented in figure 2, as a function of exposure time and for different pHs.
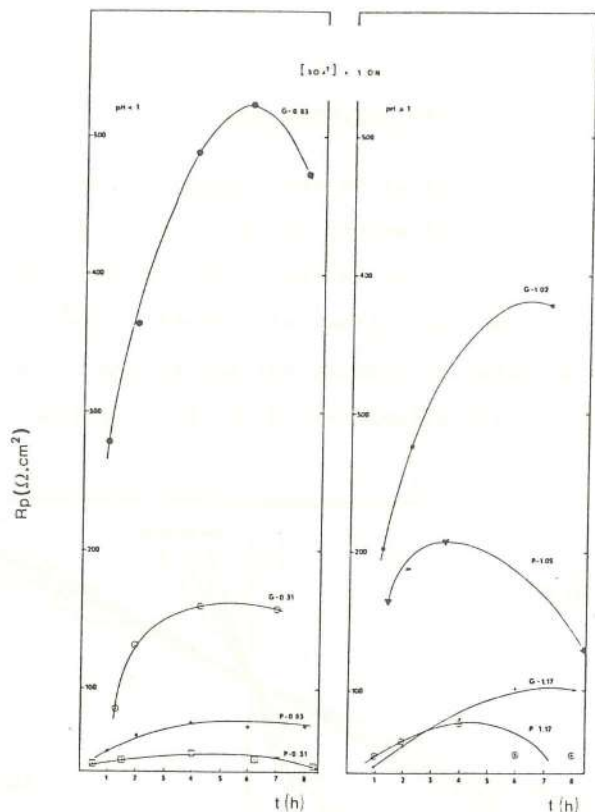

Fig. 3. The dependence of R_p on exposure time up to 8 hours at various pH's and for slow (P) and rapid (G) agitation.

The general tendency as far as exposure time is concerned is one of increase in the first 4 hours followed by a slight

decrease in R_p. Similiar tendencies are found for 0.5 N H_2SO_4. A general increase in R_p is noticeable when agitation is increased, this being valid for all values of pH studied.

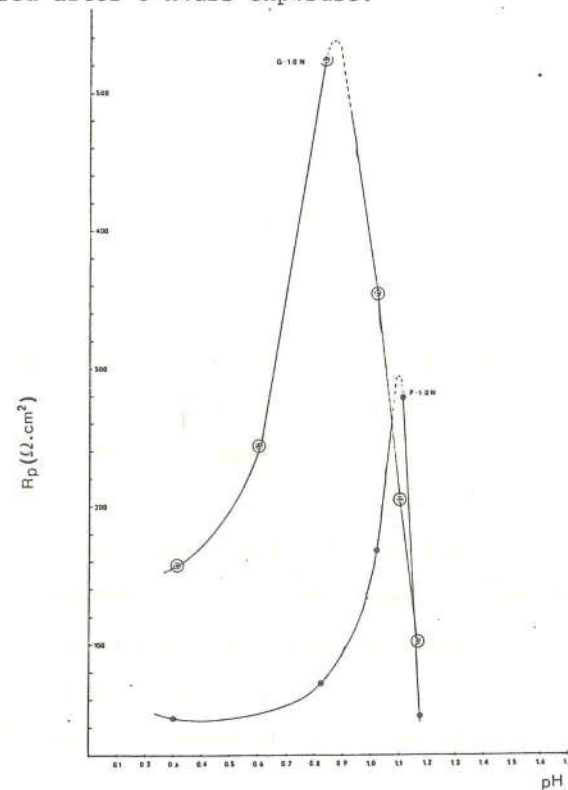Figure 4 summarizes the effect of agitation for 1.0 N H_2SO_4 registered after 6 hours exposure.

Fig. 4. The effect of agitation on the R_p, pH plane characteristic of mild steel in 1.0 N H_2SO_4. The data presented correspond to 6 hours exposure time .

The effect is characterized by:

- a striking increase in R_p values for pH values < 1
- a change in the position of the maximum towards slightly more acidic pH

- an abrupt change in R_p after the maximum is reached where R_p appear to be independent of agitation.

A similar situation is encountered when using 0.5 N H_2SO_4 eventhough the values of R_p are found to be smaller.

The Tafel region and the acid corrosion of mild steel

Results obtained for the anodic branch when polarization is extended to +200 mV from the corrosion potential are represented in Table 1.

The presence of two well defined linear regions in the Tafel domain gave two different values for the anodic Tafel constant ba. At lower overpotentials ba values (b_{a_1}) vary from 0.020-0.046 V according to pH, whislt for higher overpotentials (b_{a_2}) the variation is between 0.070 and 0.093 V (values reported for slow (P) agitation). As it is noticeable in Table 1 agitation does not introduce variation in the values of the Tafel constants when compared at a fixed pH value, eventhough the current was shifted to lower values in the presence of rapid agitation. This experimental fact confirms the results obtained in the pre-Tafel region where an increase in agitation was associated to an increase in R_p (decrease in the corrosion current density).

The results concerning the cathodic branch of the polarization curves seems to be much more straightforward than those of the anodic branch. The Tafel region was clearly defined with an average slope of $b_c = -0.110$ V (SCE).

The cathodic current density is also found to decrease with an increase in solution agitation. The curves for slow and rapid agitation approach each other very distinctly as

the pH of the solution increases. This observation was also reported by Bala (11).

TABLE 1. Experimental values for the Tafel slopes b_{a_1} and b_{a_2} according to pH and solution agitation P(slow) and G(rapid) for mild steel in 1.0 N H_2SO_4.

b_{a_1} (V/dec)			b_{a_2} (V/dec)	
pH	P	G	P	G
0.30	0.076	0.089	0.034	0.030
0.60	0.093	0.113	0.045	0.040
0.83	0.092	0.130	0.021	0.021
1.11	0.067	0.076	0.023	0.017
1.17	0.070	0.067	0.046	0.050

Considering that - the classical b_a values for the anodic process of iron and steel in acidic solutions are reported to b_a of the order of 0.030-0.040 V, nearer to the values for the second Tafel region found in this work and also - the need to relate R_p values to values of the corrosion current density, then the question of the determination of the Tafel constants b_a and b_c by an independent method arises.

The method used in this work is one that includes the curve fitting of the polarization curve in the pre-Tafel region and combines the equation of a corroding electrode [3] and the Stern and Geary equation [4] that relates $I_{corr.}$ to R_p (10).

$$I = I_{corr} \left[\exp. (\frac{E-E_{corr}}{b_a}) - \exp(-\frac{E-E_{corr}}{b_c}) \right] \qquad [3]$$

$$I_{corr} = \frac{b_a \cdot b_c}{2.303(b_a+b_c)} \cdot \frac{1}{R_p} \qquad [4]$$

$$2.303 \; R_p I = \frac{b_a \cdot b_c}{(b_a+b_c)} \left[\exp_{(\frac{E}{b_a}')} - \exp \frac{-E}{(b_c}') \right] \qquad [5]$$

$$b_a' = b_a/2.303 \qquad [6]$$

In this way IR_p vs E available experimentally depend only on b_a and b_c, and departing from classical values of b_a and b_c (10) the theoretical curves are generated and compared with those obtained experimentally.

Classical values of b_a and b_c such as 0.030-0.120 V or 0.040-0.120 V did not give a good fit of the E vs i experimental curve. An acceptable fitting was produced when combinations of b_a (20 to 120 mV) and b_c values (-70 to -150 mV) were introduced in equation [5] and the procedure used for the classical values repeated. For the systems studied b_a values of 80-85 mV were, after corrections introduced in R_p calculations. Results were in agreement with values in the first Tafel region obtained when polarization was extended to +200 mV from corrosion potential.

The values of b_c found together with a b_a of 0.080 - - 0.085 V, to give a satisfactory curve fitting were 0.100 - - 0.110 V .

DISCUSSION

Changes in mechanisms of the anodic dissolution of mild steel in acidic solutions due to alterations in the solution pH have been reported by some research workers (11,12). It is generally associated to pH values from 1.2 to 1.5 and to the presence of chloride ions.

In this research and within the range of pH studied and judging by the values of the parameters b_a and b_c one can not anticipate changes in mechanisms due to pH effects especially when taking into account the first Tafel region (eventhough a small dependency on pH is observed), but there is a definite effect of pH on the polarization resistance of the system i.e., on the net corrosion current density.

A decrease in corrosion current density found when agitation is introduced has been also reported by other authors (13) eventhough cases reporting an increase are also encountered (14).

It should be stressed that factors such as composition of the electrode and agitation of solution could influence the system's behaviour and to make comparisons could in some cases be of no significance at all.

Invoked in the literature is the idea that a superficial catalytic agent, this being a hydroxyl complex or one formed by the reduction of a sulphate containing ion, may interfere in the acceleration of the corrosion process. Eventhough the possibility of the ion reduction is considered of little significance when taking into account the rate at which hydrogen ions are reduced in strongly acidic solutions. But the question

is now put in terms of the concentration of the catalytic agent formed by ion reduction, so that acceleration of the corrosion process can be considered significant. The effect of SO_3^{2-}, $S_2O_4^{2-}$ and $S_2O_3^{2-}$ concentration, which are final products of the cathodic reduction of HSO_4^- ions, on the corrosion rate of iron has been recently studied (11) in order to elucidate their role as catalyst in the corrosion process. Apparently very small concentrations, of the order of $10^{-7}M$, are needed for a substancial increase which is found to be more severe the lower the pH of the solution.

The existance of two Tafel slopes for the systems under study indicate the possibility of parallel reactions that dependent on potential take part preferentially at lower or higher overpotential giving place to a change in mechanism .

The second Tafel region can be considered as one representing an anodic process tipo Heusler, judging by the b_a values encountered and the activity of the metal surface (6). In the present experimental conditions the mechanism is kept invariant with the introduction of solution agitation, the reactions ocurring only at a slower rate.

The first Tafel region with an average value of b_a of 0.080 V may well indicate the participation of SO_4^{2-} products.

Again, when agitation is imposed, corrosion reactions occur giving lower current densities.

This might be indicative that in either case the role of agitation is limited to blow away substances that somehow contribute to the acceleration of the corrosion process.

As far as the nature of the catalytic agent is concerned

there is no possibility of further discussion since experimentally there are no data to elucidate whether this agent is the product of the reduction of sulphate ions or other substances generated as a result of other constituents in the electrode (such as sulphur or phosphorous).

The dependence of the corrosion current density on pH as demonstrated by polarization resistance measurements is critical and is object of research in progress. The extension of the pH range within the acid domain will be subject of further publications.

CONCLUSIONS

- The corrosion of mild steel in 0.5 and 1.0N H_2SO_4 is very sensitive to changes in pH in the range of 0.3 to 1.2.

- The sharp increase and decrease in the values of R_p provoked by variations in pH especially around 1 reinforces the idea put through in the literature about the presence of a catalytic substance probably generated in situ on the metal surface, triggered by a change in local pH.

- A competitive effect between a catalytic complex and the traditional adsorbed hydroxyl complexes could be on the bases for the explanation of the sudden changes around the maximum of the R_p vs pH curves.

- The increase in R_p values brought about by the introduction of agitation without affecting the way R_p depends on pH confirms that agitation interferes only in "inhibiting" to a certain extent the global rate of the reactions without changing its mechanism.

- Reduction of the hydrogen evolution reaction and as a consequence a decrease in the degradation of the metal surface also helps to explain the tendencies encountered by the introduction of solution agitation.

- The b_a values to be used in order to calculate corrosion currents are those produced by the 1st Tafel region which are of the order of 0.080 V, value considered non-classical for mild steel in sulphuric acid solutions.

- Summarizing, the analysis of the pre-Tafel polarization behaviour gave indications not only of changes in the corrosion current density due to pH, agitation of the solution, concentration and exposure time but also contributed successfully to the calculations of b_a and b_c, producing values in agrement with those found experimentally, without further polarization of the electrode.

RESUMO

O efeito do pH no intervalo 0,3 a 1,2 e o efeito da agitação da solução sobre a corrosão de aço de baixo teor em carbono foi estudado em soluções desarejadas de ácido sulfúrico.

A polarização potenciodinâmica na região pre-Tafel foi usada com o objectivo de determinar a resistência de polarização, R_p, para vários tempos de exposição.

As variações de R_p com o pH caracterizam-se pela existência de um máximo a pH $\approx$ 1 para os níveis de agitação estudados. A agitação da solução não afecta a forma da curva R_p vs pH traduzindo-se numa diminuição dos valores de R_p associada a um decréscimo na agitação, efeito mais pronuncia-

para pH < 1.

Voltamogramas ao fim de 24 horas de exposição revelaram para o caso da grande agitação e para todos os valores de pH estudados uma diminuição de densidade de corrente e ainda a presença de duas zonas lineares com comportamento de Tafel, a primeira mostrando uma ligeira dependência do pH e a segunda com valores de b_a no intervalo de 0,020 - 0,040 V.

Os valores de b_a e b_c calculados por ajustamento dos valores E,i na região pre-Tafel, produziram valores da ordem dos 0,080 e 0,110 V respectivamente que concordam com os valores experimentais obtidos na região de Tafel.

Demonstra-se que a corrosão do aço em soluções de ácido sulfúrico entre outros factores é função da agitação do meio, o que também tem sido observado por outros investigadores. As implicações mecanísticas deste facto experimental, no processo anódico bem como o efeito dos iões sulfato e hidróxido são objecto de discussão.

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ELECTROCHEMICAL BEHAVIOUR OF
1-(o-NITROBENZYLIDENE)AMINO-4,6-DIPHENYL-2-PYRIDONE

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ABSTRACT.

The electrochemical behaviour of 1(o-nitrobenzylidene)amino--4,6-diphenyl-2-pyridone, in ethanolic Britton-Robinson buffer, has been studied using polarographic, voltammetric and controlled-potential electrolysis methods.

Reduction of $-NO_2$ group to -NHOH is first observed in acidic and neutral media, while reduction of the aldiminic bond (similarly as it takes place in analogous compounds), accompanied by hydroxylamine reduction, occurs later. In basic medium, reduction of hydroxylamine is easier than that of the aldiminic bond.

The hydroxylamine stability is pH dependent, it is stable in neutral medium and unstable in acidic and basic media. As a consequence, the appearance of an ECE mechanism --in the reduction of $-NO_2$ group-- is observed in basic medium.

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