Corrosion of Iron

Effect of pH and Ferrous Ion Activity

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The effect of pH and ferrous ion activity on the corrosion potential (E_c) and the corrosion rate (i_c) of iron is considered on the basis of recent data on the kinetics of the Fe/Fe^{++}aq- and the $H_2(Fe)/H^+$ aq-electrode. For solutions of negligible ferrous ion content, it is deduced that dE_c/dpH should be $-(4/5) (2.303\ RT/F)$ in acid solutions and $-(2/5) (2.303\ RT/F)$ in alkaline solutions until the corrosion potential above a certain pH-value (dependent on the hydrogen pressure) becomes nearly equal to the reversible hydrogen potential. It is further deduced that $d\log i_c/dpH$ in these three pH-ranges should be $-3/5$, $+1/5$, and -1, respectively. For solutions of appreciable ferrous ion content, it is shown that the corrosion potential in a certain pH-range (dependent on the ferrous ion activity) should be nearly equal to the reversible iron potential. It is also shown how this will affect the corrosion rate.

The effect of dissolved oxygen and of the ferrous hydroxide precipitation is somewhat discussed, and all the deductions are compared with experimental data.

1.0 INTRODUCTION

It has long been known that the corrosion potential of iron in many acid solutions varies with pH almost (but not quite) parallel to the reversible potential of the hydrogen electrode [1-4]. Some earlier workers apparently believed that the parallelism should be exact, and that the observed deviations were due to experimental faults. However, through the development of *the theory of mixed potentials* [5,6] for corrosion processes, it has become clear that this relationship cannot be more than an accidental one, whereby the observations very well may be correct.

The theory of mixed potentials allows the relationships between corrosion potential (E_c) and corrosion rate (i_c) and pH to be derived from a knowledge of the kinetics of the electrode reactions simultaneously occurring on the corroding metal surface. Such derivations have been attempted by Thomashov[7], Audubert[8], Uhlig[9], Bockris[10], Stern[11], Stern and Geary[12], and Ammar

and Riad [13], but all these derivations suffer from a poor knowledge of the anodic dissolution reaction.

The kinetics of the iron dissolution reaction has recently been studied by the author and others (see Ref.[14]), and some new data are also available on the hydrogen evolution reaction at iron electrodes. On this basis, a theoretical redetermination will here be made of the effect of pH on the corrosion potential and the corrosion rate of iron in air free solutions. The effect of ferrous ions will also be considered, and comparisons will be made with experimental data.

2.0 THEORETICAL DEDUCTIONS

The following symbols shall here be used:

i_c = rate of corrosion
i_{diss} = rate of iron dissolution
i_{dep} = rate of iron deposition
i_H = rate of hydrogen evolution
$i_o(Fe)$ = exhange current of the $Fe/Fe^{++}aq$-electrode
$i_o(H)$ = exchange current of the H_2/H^+aq-electrode
$i_o(OH)$ = exchange current of the H_2/OH^-aq-electrode
E_c = corrosion potential
$E_o(Fe)$ = standard potential of the $Fe/Fe^{++}aq$-electrode
$E_o(H)$ = standard potential of the H_2/H^+aq-electrode
$E_o(OH)$ = standard potential of the H_2/OH^-aq-electrode
V = electrode potential in general

All the rates will be expressed in equivalent units (*e.g.* as partial current densities) and will be regarded positive (regardless of the reactions being anodic or cathodic).

When iron is immersed in a solution, it acquires a corrosion potential and a corrosion rate defined by:

$$E_c = V \tag{1a}$$

$$i_c = i_{diss} - i_{dep} \tag{1b}$$

We shall here mainly consider cases in which hydrogen evolution is the only reaction occurring in addition to the $Fe/Fe^{++}aq$-electrode reactions themselves. For such cases, stationary conditions require

$$i_H = i_{diss} - i_{dep} \tag{2}$$

and the corrosion potential must obviously be that mixed potential at which this equation is satisfied.

In a previous work [14], it has been shown that:

$$\log i_{diss} = J(Fe) - pOH + (2F/2.303\ RT)\ (V - E_o(Fe)) \tag{3a}$$
$$\log i_{dep} = J(Fe) - pOH - 2pFe - (2F/2.303\ RT)\ (V - E_o(Fe)) \tag{3b}$$
$$\log i_{(H)}(a) = J(H) - pH - (F/4.606\ RT)\ (V - E_o(H)) \tag{3c}$$
$$\log i_{(H)}(b) = J(OH) - (F/4.606\ RT)\ (V - E_o(OH)) \tag{3d}$$

where (a) and (b) refer to acid and alkaline solutions, respectively, and

$J(\text{Fe})$ $= \log i_0(\text{Fe})$ at $\text{pFe} = \text{pOH} = 0$ (4a)
$J(\text{H})$ $= \log i_0(\text{H})$ at $\text{pH} = 0$ (4b)
$J(\text{OH})$ $= \log i_0(\text{OH})$ at $\text{pOH} = 0$ (4c)

Strictly, (3c) and (3d) are not always valid at and above the corrosion potential because of a promoting effect of the iron dissolution reaction on the hydrogen evolution reaction [14]. This effect will certainly affect the corrosion, but not necessarily the pH-dependence of the corrosion, and will therefore be neglected in the present treatment.

By the equations (2) and (3), both the mixed potential (V) of the corroding metal and the partial rate of the various reactions (i_{diss}, i_{dep}, i_H) at this potential are completely determined. Through the definitions (1), the corrosion potential (E_c) and the corrosion rate (i_c) are thereby also given as functions of pH, pOH, and pFe at constant temperature.

Solutions of negligible ferrous ion content

Most corrosion cases of practical importance imply aqueous solutions of relatively low ferrous ion content. This content may for the present purpose be regarded negligible when

$$i_{dep} < i_{diss}/100 \qquad (5)$$

which, according to (3a) and (3b), means:

$$E_c > E_0(\text{Fe}) - (2.303 \, RT/2F) \, (\text{pFe} - 1) \qquad (6)$$

In such cases, the corrosion rate is given within an accuracy of 1 % by:

$$i_c = i_H = i_{diss} \qquad (7)$$

Remembering $pK_w = \text{pH} + \text{pOH}$, we easily have from (1a), 3a), (3c), (3d), and (7):

$$E_c(a) = (2/5) \, (2.303 \, RT/F) \, [J(\text{H}) - J(\text{Fe}) + pK_w - 2\text{pH}] + (1/5) \, [E_0(\text{H}) + 4E_0(\text{Fe})] \qquad (8a)$$

$$E_c(b) = (2/5) \, (2.303 \, RT/F) \, [J(\text{OH}) - J(\text{Fe}) + pK_w - \text{pH}]) + (1/5) \, [E_0(\text{OH}) + 4E_0(\text{Fe})] \qquad (8b)$$

$$\log i_c(a) = (1/5) \, [4J(\text{H}) + J(\text{Fe}) - pK_w - 3\text{pH}] + (2/5) \, (F/2.303 \, RT) \, [E_0(\text{H}) - E_0(\text{Fe})] \qquad (8c)$$

$$\log i_c(b) = (1/5) \, [4J(\text{OH}) + J(\text{Fe}) - pK_w + \text{pH}] + (2/5) \, (F/2.303 \, RT) \, (E_0(\text{OH}) - E_0(\text{Fe})] \qquad (8d)$$

For cases in which pK_w, $J(\text{H})$, $J(\text{OH})$, and $J(\text{Fe})$ are independent of pH (this will usually be the case when excess indifferent electrolyte is present), these equations further show:

$dE_c(a)/d\text{pH}$ $= -(4/5)(2.303 \, RT/F)$ (9a)
$dE_c(b)/d\text{pH}$ $= -(2/5)(2.303 \, RT/F)$ (9b)
$d\log i_c(a)/d\text{pH}$ $= -3/5$ (9c)
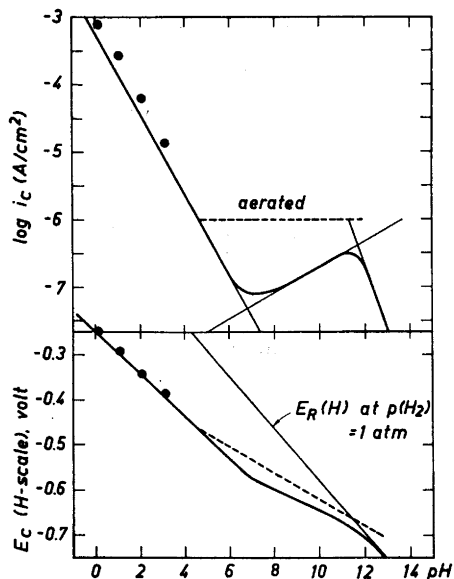$d\log i_c(b)/d\text{pH}$ $= +1/5$ (9d)

Fig. 1. Calculated effect of pH at a hydrogen pressure of 1 atm. (fully drawn lines) and of dissolved oxygen (stipulated lines) on the corrosion potential and the corrosion rate of iron. The points apply to iron in $HCl-KCl-(FeCl_2)$ solutions at 20°C (Hurlen[14]).

The deductions represented by eqns. (8) are graphically presented in Fig. 1. The following values have there been used for the various constants [14]:

$$T = 293° K \qquad pK_w = 14.17$$
$$E_o(H) = 0 \qquad E_o(OH) = -0.82 \qquad E_o(Fe) = -0.46$$
$$J(H) = -5.36 \qquad J(OH) = -5.07 \qquad J(Fe) = 3.58$$

By these values, the corrosion rate is given in A/cm^2 and the corrosion potential in Volt on the normal hydrogen scale.

In Fig. 1 is also indicated what is to be expected when the corrosion potential approaches the reversible potential of the hydrogen electrode, $E_R(H)$. The latter potential can certainly not be exceeded by the former in a completely de-aerated solution, and we have as a limit:

$$(E_c)_{lim} = E_o(H) - (2.303 \, RT/F)pH \qquad (10)$$

At this limit, when considering (1a), 3a), (7), and (10), we also have

$$(d\log i_c/dpH)_{lim} = -1 \qquad (11)$$

In all the above calculations, the solutions have been assumed to be in equilibrium with hydrogen of standard atmospheric pressure, and no account has been made of a possible formation of solid corrosion products on the metal surface. Such a formation will certainly affect the corrosion by the resistance barrier it creates for at least some of the part reactions.

The points shown in Fig. 1, represent values experimentally found by the author [14] in $HCl—KCl—(FeCl_2)$ solutions. These points lie somewhat above the calculated lines because of a promoting effect of the iron dissolution reac-

tion on the hydrogen evolution reaction (see Ref.[14]). The dashed lines in Fig. 1 indicate what is to be expected for the corrosion rate and the corrosion potential when the solution contains dissolved oxygen of an amount giving a limiting oxygen reduction current of 10^{-6} A/cm^2. Also in this case, an upper pH-limit must be reached above which the corrosion potential will be equal to the reversible potential of the oxygen electrode, and the corrosion rate will vary according to (11). This is not shown in Fig. 1. A more detailed discussion of the effect of dissolved oxygen must await further data on the kinetics of the oxygen reduction reaction.

Solutions of appreciable ferrous ion content

Also in ferrous ion containing solutions, we must expect the corrosion rate and the corrosion potential to be in accordance with the above deductions as long as the requirement (6) is obeyed. However, with increasing pH (decreasing E_c) and increasing ferrous ion activity (decreasing pFe) this requirement must subsequently be broken. Under such conditions, we are not allowed to neglect the deposition reaction, and the corrosion rate must be represented by the complete equation (1b). Considering further the equations (2), (3c), (3d), and the obvious limiting condition

$$(E_c)_{lim} = E_o(\text{Fe}) - (2.303 \, RT/2F)\text{pFe} \tag{12}$$

we easily have:

$$(\log i_c(a))_{lim} = J(\text{H}) - \text{pH} + \tfrac{1}{4}\,\text{pFe} - (F/4.606 \, RT)\,[E_o(\text{Fe}) - E_o(\text{H})] \tag{13a}$$

$$(\log i_c(b))_{lim} = J(\text{OH}) + \tfrac{1}{4}\,\text{pFe} - (F/4.606 \, RT)\,[E_o(\text{Fe}) - E_o(\text{OH})] \tag{13b}$$

These deductions are presented graphically in Fig. 2, where they are represented by the curves extending into the dashed lines. These curves represent what is to be expected for the corrosion rate and the corrosion potential if there were no ferrous hydroxide precipitation, and if the solution were in equilibrium with hydrogen of sufficiently low pressure to satisfy the requirement

$$E_R(\text{H}) > E_c + (2.303 \, RT/F) \tag{14}$$

all over the pH-range considered.

The completely drawn curves in Fig. 2 represent what is to be expected at a hydrogen pressure of one atmosphere if there were no ferrous hydroxide precipitation. In actual cases, however, precipitation will occur when [15],[16]

$$\text{pH} = 6.7 + 0.5 \, \text{pFe} \tag{15}$$

This equation also gives the minimum pFe (maximum ferrous ion activity) obtainable at any given pH, and it shows how pFe will vary with pH when precipitation occurs.

The curves in Fig. 2 have been crossed at those points at which, from (15), we have to expect the ferrous hydroxide precipitation to start. For any of these curves, that part lying to the right of such a point cannot be realized.
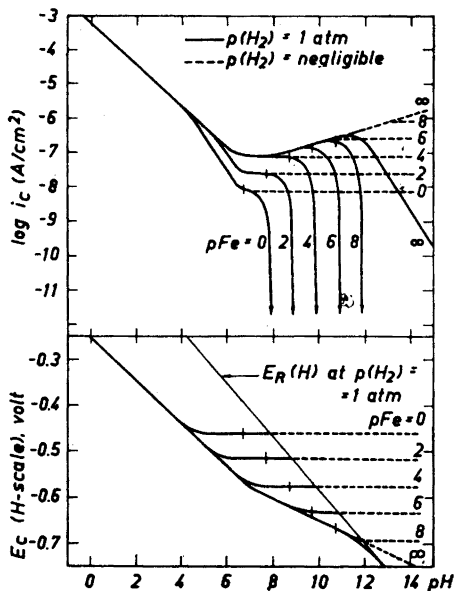
Fig. 2. Calculated effect of pH and ferrous ion activity on the corrosion potential and the corrosion rate of iron at a hydrogen pressure of 1 atm. (fully drawn lines) and at a negligibly small hydrogen pressure (stipulated lines) in the hypothetic absence of ferrous hydroxide precipitation (see the text).
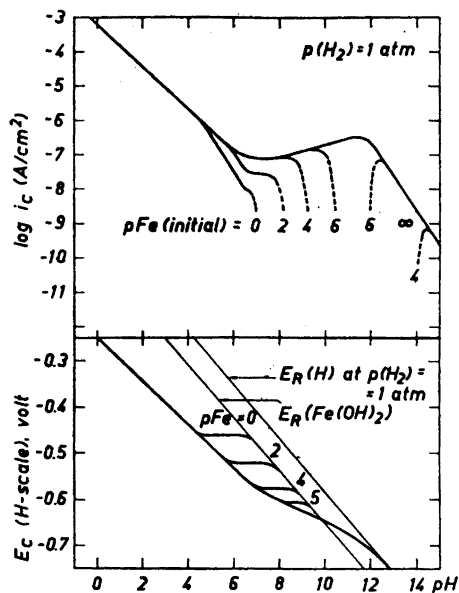
Fig. 3. Effect of pH and ferrous ion activity on the corrosion potential and the corrosion rate of iron at a hydrogen pressure of 1 atm. when regard is made of the ferrous hydroxide precipitation (see the text).

A prediction of how the corrosion potential will behave when precipitation occurs, is given in Fig. 3. It is much more difficult to predict what will happen to the corrosion rate. If the only effect of the precipitation were to decrease the ferrous ion activity, we should expect the corrosion rate to vary along a curve given by the precipitation points (crossed points in Fig. 2) for solutions of lower ferrous ion activity (higher pFe) than the one considered. It is likely, however, that a more marked effect of the precipitation is to give a protective film of ferrous hydroxide on the iron surface. The stability of such a film will probably increase with pH until the ferroate formation begins to destroy it. According to the data given by Pourbaix [15], we should expect that this starts at a pH of about 10.6, and that no precipitate should remain at pH-values above that given by:

$$pH = 18.3 - pFe \text{ (initial)} \qquad (16)$$

From (15) and (16), it appears that precipitation should not occur at all in solutions of initial pFe-values above 7.7. In such solutions, therefore, the corrosion of iron is most likely not affected by the ferrous ions whereby the corrosion rate curves should follow the one applying to pFe $= \infty$. Also in

solutions of initial pFe-values below 7.7, the corrosion must be expected to be independent of the ferrous and the ferroate ions at pH-values above that given by (16). The situation should then be somewhat as shown in Fig. 3.

In this treatment, the homogeneous hydrolysis of the ferrous ion has been ignored, and this seems justified on the basis of the low value ($10^{-9.5}$) found by Hedström [16] for the hydrolysis constant of this ion.

3.0 DISCUSSION

The above deductions have been made without considering the possible effect of impurities in the electrode material and of anions on the reactions of the $Fe/Fe^{++}aq$- and the $H_2(Fe)/H^+aq$-electrode. There are indications [14] that the impurities usually present in mild steel do not affect the iron electrode reations very much, whereas some of them strongly affect the hydrogen evolution reaction. Thereby, the corrosion behaviour will certainly also be affected. However, if the impurity effect is pH-independent, the relative relationship between corrosion and pH may still be as deduced above. There further are indications [14] that neither chloride ions nor sulphate ions do directly affect any of the above reactions. The deductions should therefore apply to both chloride and sulphate solutions. However, it may be a requirement that excess indifferent salt be present. The data used above are namely determined under such conditions, and it is further well known [6] that the effective potential drop at the electrode surface in dilute solutions may be affected by the salt content.

The literature is rich in experimental studies concerning the effect of pH on the corrosion of iron and steel (especially the latter), but only few of these seem to have been carried out under rigorous experimental conditions. Gatty and Spooner [1] have given a general summary of the data obtained up to 1938. They conclude that the variation of the corrosion potential with pH in acid solutions of several types is just that given by (9a) above. It has already been shown (Fig. 1) that this relationship also is in agreement with recent results of the author in acid chloride solutions. It is further in accordance with relatively recent results of Makrides, Komodromos, and Hackerman [17] in acid chloride solutions, of Hoar and Hurlen [18,19] in acid sulphate solutions, and of Bonhoeffer and Heusler [20,21] in acid sulphate and perchlorate solutions. Stern [22,23] and D'Ans and Breckheimer [24] report a variation more parallel to the reversible hydrogen potential.

The relationship (9b) for the corrosion potential in de-aerated alkaline solutions is also in relatively good agreement with the data gathered by Gatty and Spooner [1]. These data further show that the corrosion potential reaches the reversible hydrogen potential at a pH of about 12 and from there on follows this potential. This compares well with the deductions graphically presented in Fig. 1. As (9b) has been deduced partly on the basis of data obtained on the kinetics of the iron dissolution reaction in acid solutions, its good agreement with experimental data may be regarded a strong indication that the dissolution mechanism is the same in alkaline as in acid solutions (see Ref.[14]).

The deductions showing that the corrosion potential in ferrous ion containing solutions should be independent of the ferrous ion activity at low

pH-values and be nearly equal to the reversible potential of the $Fe/Fe^{++}aq$-electrode at somewhat higher pH-values (see eqn. (12) and Figs. 2 and 3) are excellently confirmed by the observations of D'Ans and Breckheimer [24].

The data available on the effect of pH on the corrosion rate of iron are somewhat conflicting. Thus, Stern [22,23] and Bonhoeffer and Heusler [20,21] in their recent work found a nearly pH-independent corrosion rate in solutions of low pH, whereas previous authors mostly have reported a logarithmic relationship to be obeyed under such conditions (see Refs. [1-4]). The recent work of Hoar and Hurlen [18,19] in acid sulphate solutions and of the present author [14] in acid chloride solutions (see Fig. 1) also gave a logarithmic relationship between corrosion rate and pH. Such a relationship is also reported by Novikov [25] and by Balezin and Krasovitskaya [26] as a result of comprehensive investigations on this subject with various types of iron and steel in various types of solutions. The results of the latter authors in acid sulphate solutions moreover agree with those of Hoar and Hurlen in such solutions and with those of the present author in acid chloride solutions in showing a pH-dependence quite near to that given by (9c) above.

The deductions predicting that the corrosion rate should go through a minimum in the vicinity of the neutral point and thereafter increase with pH according to (9d) until it again should fall when the corrosion potential approaches the reversible hydrogen potential (see Fig. 1), may be more difficult to test experimentally. In this pH-region, the measurements may easily be affected by dissolved oxygen (if not adequately removed) and by a possible formation of solid corrosion products on the metal surface (if the ferrous ion content in the solution is not kept low enough). In the vicinity of the neutral point, it is also difficult to have an adequate control of the pH. On this basis, the predicted corrosion-rate/pH relationship shown in Figs. 1 and 3 for iron in alkaline solutions is not in disagreement with the experimental results quoted in the well known corrosion monographs [1-4]. Some authors [27-29] have also experimentally found that the corrosion rate (especially in streaming solutions) goes through a minimum at a pH somewhat below the neutral point and through a maximum at a higher pH (cf. Figs. 1 and 3).

The electrode behaviour of corroding iron has been the subject of much study, thought, and speculation. This applies especially to the potential/pH-relationship in acid solutions, which long has been known [1] to be linear with a slope somewhat less than the 58 mV/pH of the reversible hydrogen electrode. Attempts have previously been made to explain this relationship on the assumption either of a hydride film formation on the iron surface [1,30,31] or of a formation of an ideal iron-hydrogen alloy in the surface [24,32-34]. Neither of these explanations have been accepted as satisfactory[20], however. More promising attempts have been made on the basis of the theory of mixed potentials [7-13], but also these have been unsatisfactory, mainly because of a poor knowledge of the kinetics of the iron dissolution reaction.

The present treatment represents a new attempt in solving this classical problem of corrosion science. Also this treatment is based on the theory of mixed potentials, and it applies the improved knowledge which recently has been gained on the iron dissolution reaction [14]. The reasonable fit of the theo-

retical deductions to many experimental data gives rise to the hope that we now are nearer to understand the corrosion behaviour of iron.

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