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# The electrochemistry of corrosion beneath corrosion deposits

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Based on the uniform corrosion mechanisms beneath corrosion deposits described in a preceding theoretical study, the present paper shows that certain deposits attain a steady state only at the free corrosion potential. Except for the natural corrosion potential, electrochemical investigation techniques can therefore only be used to study quasi-stationary states, where the electrochemical reactions and transport phenomena are in dynamic equilibrium with the instantaneous thickness of the deposit. The electrochemistry of a metal covered by soluble or anionic insoluble deposits is very close to that on bare metal (deposits "transparent" to the imposed polarization). Conversely, deposits of the insoluble cationic type compensate nearly integrally the effects of polarization, thus behaving as veritable passive layers. It is also shown that irreversibility effects are present in the growth regime control of deposits under imposed polarization. This may lead to multiple quasi-stationary states. For example, anodic or cathodic pulses can cause an insoluble deposit to change from cationic to anionic, or vice versa. A particular consequence is the existence of a pitting or general anodic depassivation potential for insoluble cationic deposits. Similarly, there is a protection or cathodic passivation potential for insoluble anionic deposits. Altogether, electrochemical methods shall be used, not only to measure corrosion rates, but also to study the intrinsic stability of the feature of observed deposits. This should enable us really to predict long-term corrosion rates.

## 1. Introduction

While the prediction of the rate of uniform corrosion beneath a corrosion deposit is currently of great practical interest, this phenomenon occurs, by definition, in the absence of any external polarization of the metal. This would not, of course, be true for localized attack, such as that observed for steels in $CO_2$-containing media. In effect, in this case, zones of high and low corrosion on the same metal create conditions of mutual external polarization [1]. However, the latter remains extremely limited, in terms of millivolts [2, 3], even though the practical consequences, in terms of damage, can be quite serious.

In contrast, the artificial polarization of specimens is a method traditionally employed for the study of electrochemical corrosion, and has been extensively used for bare metals and for stainless steels. In both cases, it has enabled tremendous strides to be made in the understanding of corrosion, and tends, perhaps somewhat hastily, to be considered as an intrinsically modern, high-performance technique.

In the case of passivatable metals with thick passivation layers [4], a breach is already perceivable in this general agreement concerning electrochemical methods. Thus, it is already recognized that a polarization curve plotted at a "reasonable" speed usually characterizes only transient and unstable surface states, with no direct relationship to the stable regimes observed in service. For instance, in many problems concerning aluminium alloys, while polarization curves can be used to understand corrosion mechanisms, they do not always yield quantitatively significant practical data. In the case of inhibition phenomena, plotting a polarization curve can even lead to destruction of the surface conditions it is wished to study.

With uniform corrosion under corrosion deposits, it has been found [5] that diffusion, solubility and hydrolysis phenomena within the deposit itself are at least as, if not more, important than the purely electrochemical aspects of the Faraday reaction (e.g. $Fe^0 \rightarrow Fe^{2+}$) or the associated reduction reaction (e.g. $H^+ \rightarrow H_2$). Nevertheless, the polarization of a specimen remains by far the most accessible experimental technique, so that, for reasons of facility and the force of habit, it is used in this case also [2].

In contrast, it would be extremely hazardous to transpose the usual interpretations without a more detailed examination of the situation. Indeed, it is highly probable that the working mechanisms of a deposit do not react to external polarization in the same way as elementary electrochemical kinetics.

The aim of the present work was, therefore, to extend the preceding analysis of the role and control of corrosion deposits to the case of an imposed external polarization, and to determine to what extent this experimental technique can be useful for predicting the behaviour of deposits and hence the rate of uniform corrosion beneath them.

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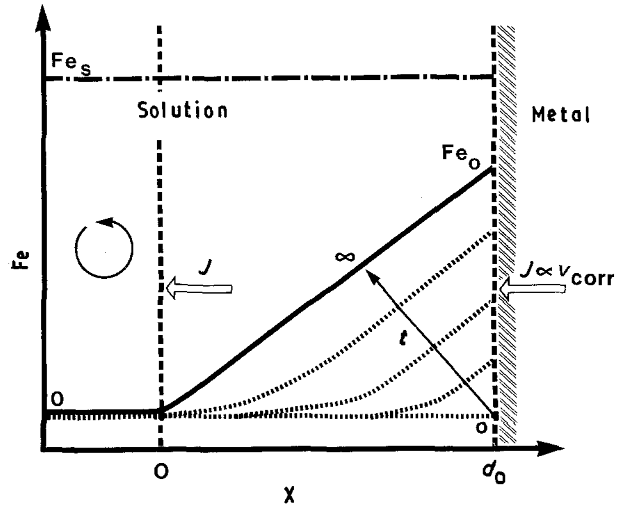

*Figure 1* Build-up of an iron concentration gradient perpendicular to the surface of a corroding bare metal.

However, before treating imposed polarization, it will probably be useful to recall current understanding of natural corrosion at the free potential.

## 2. Natural corrosion beneath a corrosion deposit

### 2.1. Build up and stabilization of deposits

A steel undergoing corrosion can only remain bare if diffusion in the liquid phase is sufficient to evacuate the flux of $Fe^{2+}$ ions injected from the metal surface (Fig. 1), taking into account the local iron solubility $Fe_s$ [5] and the thickness, $d_0$, of the limiting diffusion layer. If the driving force defined by this maximum concentration gradient is insufficient to remove the $Fe^{2+}$ ions as they are produced, local accumulation will occur, with precipitation of solid corrosion products on the metal. On a normal timescale, such precipitation begins practically instantaneously. However, growth of the deposit and the stabilization of its thickness can be quite slow. The time required is essentially that necessary for the corrosion to produce the $Fe^{2+}$ ions incorporated in the deposit. During this transient stage, the loss of iron to the corrosive medium remains negligible compared to the amount involved in the build up and growth of the deposit. The time taken to stabilize a deposit therefore increases when the potential corrosivity, i.e. the initial corrosion rate [5], decreases, and when the thickness of the stabilized deposit becomes greater. Thus, for a potential corrosivity of 1 mm/year, to cover an initially polished specimen with a fairly thick deposit of $FeCO_3$, e.g. 0.1 mm, would require about 17 days.

Therefore, in order to study uniform corrosion beneath a deposit, sufficient time must be allowed for its build up and stabilization. In comparison, the time to establish a steady state diffusion regime in the liquid phase within the deposit is much shorter, although not necessarily negligible. In effect, from previous work [5], its value is $\sim d^2/D_{Fe}$, corresponding to 2 min for a mean deposit thickness of 0.1 mm, or 3 h for a 1 mm thick scale.

In contrast to the electrochemical reactions at the metal surface, the transport mechanisms through the deposit therefore react much more slowly to external parameters, because the interstitial liquid takes several minutes to reach a new quasi steady state. Nevertheless, for both the transport phenomena and the electrochemical reactions, a stationary state always exists.

In contrast, this is not necessarily the case for the solid deposit.

### 2.2. Thickness control and protective nature of deposits

Deposit growth is traditionally held to be controlled by two opposite types of mechanism:

(i) permanent precipitation and redissolution, with no iron transport in the liquid phase;

(ii) direct formation, once and for all, with no iron transport in the solid phase.

In the preceding study [5], it was shown that neither type of mechanism is possible in a pure form. Iron transport must necessarily occur in both phases, one of them generally being predominant. This leads to a first distinction between "soluble" and "insoluble" deposits, depending on whether the majority of the iron transport takes place in either the solid or liquid phase, respectively.

In this context, a soluble deposit is necessarily protective (Fig. 2), because it limits the real corrosivity to a level solely defined by the degree of stirring in the corrosive medium and by the kinetics of the purely physical redissolution of the deposit in the external liquid. The natural corrosion rate is then totally insensitive to the electrochemical potential, and on the contrary, the combination (metal potential–deposit thickness) adapts itself to the steady state corrosion rate imposed by the speed of deposit redissolution. For a soluble deposit, the protective nature and the thickness therefore represent two perfectly independent properties.

In contrast, the protective nature of an insoluble deposit directly depends on its thickness, via its rate-controlling mechanism. In an "insoluble cationic" deposit, the corrosion rate is limited by the diffusion of the $Fe^{2+}$ cation. Because it is the slowest process in

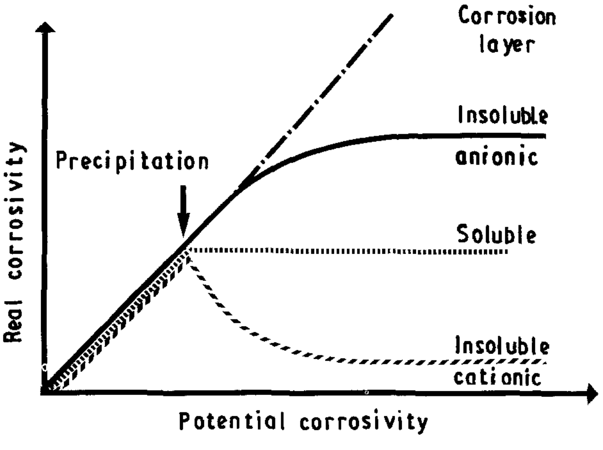

*Figure 2* Various possible forms of relationship between real and potential corrosivity.

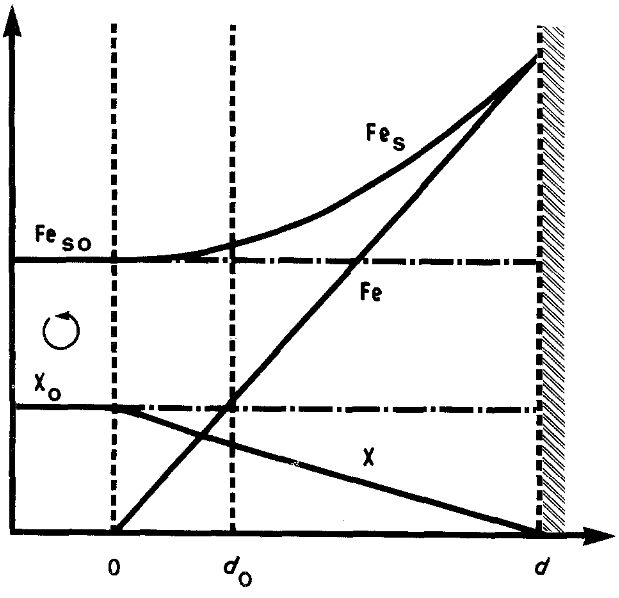

*Figure 3* Corrosion beneath an "insoluble anionic" deposit: $Fe^{2+}$ and $X^{n-}$ concentration profiles, and spatial variation of the saturating iron concentration $Fe_s$.

the system, such a deposit is the most protective possible type.

Conversely, an "insoluble anionic" deposit is controlled by the diffusion of the precipitatable anion and by its depletion in contact with the metal (Fig. 3). Consequently, the local concentration of iron increases considerably in the vicinity of the metal: the driving force for iron diffusion can therefore be much higher than in the absence of a deposit. This type of deposit can thus be completely unprotective or only very weakly protective, even for large thicknesses. In extreme cases, such a deposit will continue to grow in thickness. All the iron then accumulates and the deposit becomes profuse.

In all cases, the key to the control of deposit growth is not only the instantaneous equality between the anodic and cathodic electrochemical reactions, as for bare metal, but also the average equality, both in time and space, between the "outward" flux of species produced by the anodic reactions and the "inward" flux of the species feeding the cathodic reactions. This is the fundamental reason why the real corrosivity in the presence of corrosion deposits is different from the initial potential corrosivity of the bare metal.

In conclusion, the basic principal of growth control in a corrosion deposit is shown schematically in Fig. 4. In the steady state regime, the electrochemical kinetics and the corresponding transport kinetics are equal. For natural corrosion, the anodic and cathodic kinetics are also equal, ensuring a continuous chain of control between the supply of reacting species $H^+$ and the removal of the reaction products, $Fe^{2+}$ in the liquid phase or $FeX_{2/n}$ in the solid phase. The two available degrees of freedom are the deposit thickness, $d$, and the metal potential, $U$.

In a soluble deposit, the final redissolution rate independently fixes the free corrosion potential, $U$, via $i_A$ (Fig. 4), and the deposit thickness, $d$, via $J_H$ (Fig. 5).

In an insoluble deposit, the control chain is a complete loop. In a cationic deposit (Fig. 6), the

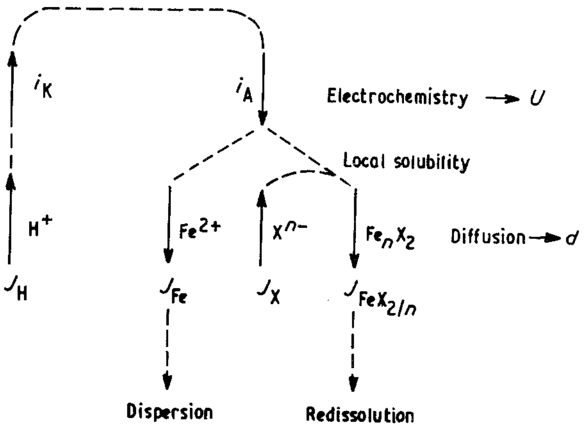

*Figure 4* Schematic representation of growth control in a corrosion deposit. Stationary regime: $J = i$. Natural corrosion: $i_A = i_K$. Soluble deposit: $J_H = J_X = J_{FeX_{2/n}}$. Insoluble deposit: $J_H = J_{Fe} \gg J_X$.

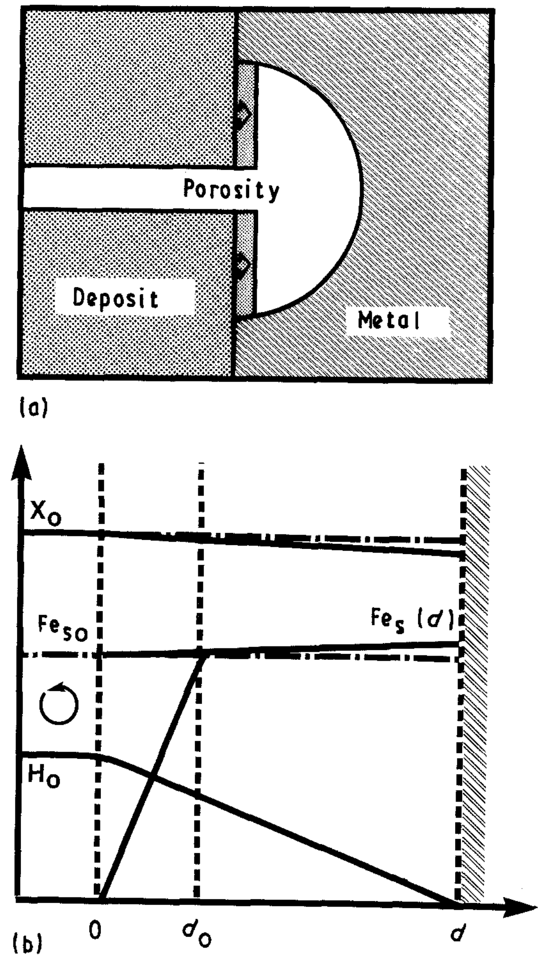

*Figure 5* Corrosion beneath a "soluble" deposit. (a) Precipitation on the rear face of the deposit. (b) $Fe^{2+}$ and $H^+$ concentration profiles, and spatial variation of the saturating iron concentration $Fe_s$.

deposit thickness must be sufficient to slow down the electrochemical kinetics, via a partial diffusion polarization, thus bringing the iron concentrations to levels close to saturation. However, the deposit must not be too thick, because complete diffusion polarization would no longer allow the transport of $H^+$ to be selectively impeded compared to that of $Fe^{2+}$ [5]. For an insoluble cationic deposit, the natural corrosion

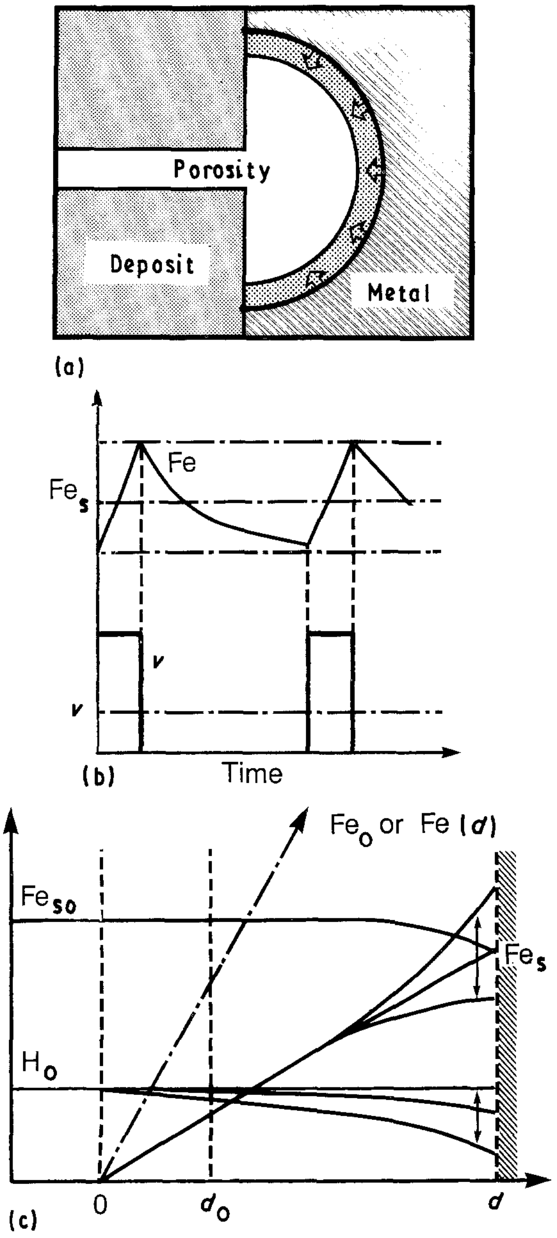

*Figure 6* Corrosion beneath an "insoluble cationic" deposit. (a) Inhibition of corrosion by precipitation of solid products on the metal. (b) Intermittent corrosion regime. (c) Fluctuations in the $Fe^{2+}$ and $H^+$ concentration profiles.

rate and the deposit thickness are therefore closely interdependent, although in a very complex manner.

In an insoluble anionic deposit, the electrochemical potential is fixed, as for bare metal, by the equality between the dominant anodic and cathodic reaction kinetics, the level of diffusion polarization being determined by the thickness of the deposit. On the contrary, the latter is determined only by the equality between the minority kinetics, corresponding to the residual deposit redissolution and the maximum precipitatable anion flux. For an insoluble anionic deposit, the corrosion rate therefore depends on the deposit thickness, but the deposit thickness does not depend on the corrosion rate.

Despite the considerable differences between the respective deposit growth control mechanisms, in all three cases, there exists theoretically only one stationary state under conditions of free corrosion, even though the equilibrium thickness may be unattainable in practice, as in the case of profuse anionic deposits. Beyond this condition, because the control chain often involves a thickness–potential interaction, it is highly probable that any direct external modification of the electrochemical potential will prevent a deposit from reaching steady states other than that already known for the free corrosion potential.

## 3. Effect of external polarization on the control of a corrosion deposit

### 3.1. Basic data

### *3.1.1. Conservation of the notion of polarization*

The previous study [5] showed both the existence of a "diffusion potential" within the deposit and its negligible character. This potential is a variant of the junction potential well known to electrochemists. It ensures both the electrical neutrality of the solution permeating the deposit, in spite of the gradients in the concentration of the diffusing species, and the stability of the fluxless concentration gradients of the ionic species which do not take part in the overall corrosion reaction. Compared to the polarizations usually used in corrosion studies, these diffusion potentials are quite negligible (a few millivolts). Their effect is simply to complete pure chemical diffusion by an electromigration component, particularly in solutions of high ionic strength, and hence to modify the stationary concentration profiles which govern transport in the solution (Fig. 7).

In contrast, the diffusion potentials have no influence on the deposit growth-controlling processes. The simple models of pure chemical diffusion thus remain good approximations for these processes. In the treatment which follows, these differences in potential within the deposit will be neglected compared to the imposed external polarizations.

In these conditions, a polarization applied between the metal and the external corrosive medium results in

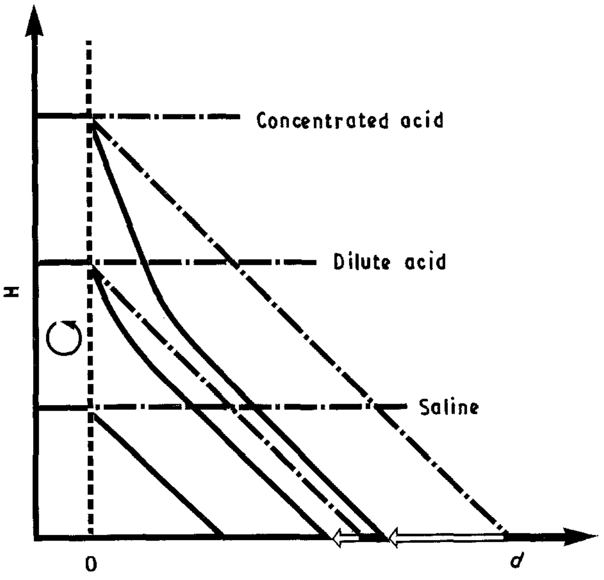

*Figure 7* $H^+$ concentration profile in a corrosion deposit. Influence of electromigration in dilute or concentrated acid media. (—·—) Pure chemical diffusion, (——) electromigration.

an almost equal polarization between the metal and the liquid in contact with it. The electrochemical response is therefore identical on bare metal and on metal covered by a corrosion deposit, and the polarization applied to the overall system is fully transmitted to the metal/solution interface beneath the deposit.

### *3.1.2. New deposit growth-control mechanism*

If an external polarization is applied to a metal, which may or may not already be covered by a corrosion deposit, the electrochemical reactions adjust to the imposed potential in a fraction of a second. The diffusion regimes then adapt themselves to the fluxes imposed by the electrochemical reactions, in a few seconds or a few minutes, depending on the thickness of the deposit when the polarization was applied. Depending on the resulting local iron or precipitatable anion concentrations, the deposit will either shrink or grow. The only difference compared to the free corrosion situation is that there is no longer an overall balance between the inward flux, $J_H$, and the outward flux of iron, but rather two independent balances between each of the electrochemical kinetics and the corresponding diffusional flow. In the steady state, the following two systems will therefore occur, at least on the assumption that the precipitation is independent of pH

$$\text{anodic system} \quad \left|\begin{array}{l} U \\ i_A = J_{Fe} \end{array}\right\} \rightarrow \text{deposit thickness } d$$

$$\text{cathodic system} \quad \left|\begin{array}{l} U \\ d \end{array}\right\} \rightarrow i_c \begin{array}{l}\text{depending on whether} \\ \text{activation or diffusion} \\ \text{polarization}\end{array}$$

With imposed polarization, the process is governed by the anodic system, the cathodic system adjusting itself to the resulting deposit thickness.

If deposit precipitation is sensitive to pH, the cathodic system may also have a return effect on the anodic system, in the case of diffusion polarization. This additional interaction naturally already existed in the free corrosion situation. However, it was so tied up in other complex interactions that its direct quantitative determination was abandoned [5]. The difference in the present case is that it becomes the only interaction between the anodic and cathodic systems, and therefore facilitates modelling of $CO_2$, $H_2S$ or calcium-rich media.

## 3.2. Effect of polarization on corrosion deposits

### *3.2.1. Soluble deposits*

The existence of this type of deposit is not related to the polarization mode, but to the physical chemistry of the precipitation beneath the deposit, involving high anion fluxes, low supersaturations, and a seeding effect favouring precipitation on the deposit already formed. Soluble deposits therefore exist both for imposed polarization and free corrosion.

In free corrosion conditions, soluble deposits always attain the stationary state, due to the control loop between the anodic reaction and the deposit thickness (Fig. 4)

$$d \rightarrow J_H \rightarrow i_C \rightarrow i_A \rightarrow J_{FeX_{2/n}} \rightarrow d$$

Under imposed polarization, if $i_A$ is greater than the dissolution rate, $J_{FeX_{2/n}}$, the deposit grows indefinitely, at a constant rate, proportional to the difference. Conversely, if $i_A$ is less than $J_{FeX_{2/n}}$, the deposit cannot form, or if it existed initially, it redissolves, with a shrinkage rate proportional to the difference. In practice, given the extremely high activation of the anodic dissolution of iron in acidic media (only 40–60 mV per decade of current), the difference between $i_A$ and $J_{FeX_{2/n}}$ quickly becomes equal to $i_A$ under anodic polarization, and equal to $J_{FeX_{2/n}}$ under cathodic polarization.

In other terms, if the steady state for natural corrosion is taken as a reference, with its corrosion potential, $U_{corr}$, an imposed polarization which is anodic with respect to $U_{corr}$ will convert a soluble deposit to a profuse deposit, with a growth rate proportional to the measured anodic current. Conversely, a cathodic polarization leads to complete redissolution of the deposit, at a rate proportional to the natural corrosion rate, $v$.

However, it will be noted that the complete redissolution of a stabilized protective deposit takes much longer than its formation from the bare metal. In effect, the time for redissolution is inversely proportional to the real corrosivity, $v$, whereas the time for deposit formation results from an average between $v$ and the initial potential corrosivity $v_0$: if the deposit is highly protective ($v \ll v_0$), the formation times, $t_f$, and redissolution times, $t_r$, are very different

$$t_r/t_f \approx (v_0 + v)/v \gg 1 \qquad (1)$$

Finally, it will be noted that the profuse deposit growth under anodic polarization renders anion transport more and more difficult. This can eventually lead to local anion depletion and may therefore transform the profuse soluble deposit to a profuse insoluble anionic deposit. This simply signifies that the production of iron by forced corrosion is so high that the two modes of transport, in both the liquid and solid phases, must be combined in order to remove the flux imposed by the anodic polarization.

In conclusion, a soluble deposit attains a steady state only under conditions of free corrosion. Under imposed polarization, it is either unstable below $U_{corr}$, or profuse above this value. Moreover, while a soluble deposit is always protective in free corrosion, it confers no protection against an external anodic polarization. This aspect has important consequences in the case of both galvanic and localized corrosion.

### *3.2.2. Insoluble anionic deposits*

As with soluble deposits, the existence of an insoluble anionic deposit is not related to the mode of polarization, but only to its effects on the matter and transport balances. As long as the precipitation of corrosion products does not completely isolate the metal, and provided that the production of iron due to the corrosion remains greater than the supply of precipitatable anions, the iron will be locally soluble and, however high the flux, will be able to be removed by liquid-phase diffusion.

The rate of deposit growth is initially governed by precipitation kinetics, and therefore by anion transport (Fig. 3). Initial growth is thus of the parabolic type ($d \times \partial d/\partial t$ = constant). This growth stops when the precipitation rate eventually becomes as low as the rate of residual dissolution at the outer surface of the deposit, i.e. when anion transport falls to a level where it can only compensate external losses from the deposit.

In free corrosion, an insoluble anionic deposit can therefore continue to grow slowly, while remaining protective, or in the other extreme, may stop growing before having become protective. In fact, its thickness is totally independent of the metal corrosion rate.

The same is true under conditions of imposed polarization. In effect, polarization of the metal does not alter the conditions of precipitatable anion transport. As long as the production of iron remains greater than the maximum transportable flux, determined by the solubility of iron in the outside medium (Figs 1 and 3), the anion remains locally depleted, and the iron becomes soluble. The insoluble anionic deposit thus has no impeding effect on the anic reaction. However, in the case of the cathodic reaction, it naturally defines the level of diffusion polarization.

Consequently, in order to study corrosion beneath an insoluble anionic deposit, it is possible to use polarization curves in the same manner as for bare metal. The only limitation is that the rate of iron dissolution must remain greater than that for anion transport.

The use of electrochemical techniques is, therefore, limited on the cathodic side. Beyond this limit, the residual precipitation of corrosion product becomes the slowest process, and the precipitatable anion concentration can be equalized throughout the deposit. The steady state regime within the deposit is thus destabilized.

It should be noted, however, that this cathodic limit is not an intrinsic property of the particular metal–corrosive medium combination. In fact, it depends on the thickness of the pre-existing deposit when the polarization is applied. For a thick deposit, the anion flux is very low ($\propto d^{-1}$). Very high levels of cathodic protection will therefore be necessary to destabilize the anionic regime. If the stationary state has been attained, the cathodic limit even corresponds to total destabilization of the deposit. In effect, the level of cathodic protection required is such that the production of iron is no longer sufficient to compensate even for residual deposit redissolution.

On the contrary, on bare metal, initial anion transport is much easier. The required level of cathodic protection is therefore considerably lower. In the limiting case, if the potential corrosivity is only slightly greater than the maximum anion flux, only a weak cathodic polarization is necessary to change the nature of the deposit formed.

In conclusion, insoluble anionic deposits are totally insensitive to polarization, at least as long as the latter remains above a certain cathodic threshold. The critical level is lower for thicker deposits and for higher natural corrosivities. Below the threshold, the deposit changes in type, or disappears altogether. Above it, the deposit is completely transparent to electrochemical effects, and it is possible to plot and interpret polarization curves in the same way as for bare metal.

### *3.2.3. Insoluble cationic deposits*

A common feature of the two preceding types of deposit is that they do not counteract the effects of anodic polarization. This is quite natural, because the production of iron does not intervene directly in the growth-controlling process. The situation is evidently completely opposite in the case of insoluble cationic deposits, where the precipitation of corrosion products occurs directly on the metal. It temporarily interrupts the dissolution process, until diffusion has time to remove the iron produced (Fig. 6). Although anodic polarization increases the rate of iron production during the active phases, the duration of the latter is proportionally decreased. The corrosion rate therefore still depends only on the iron transport kinetics, and is thus totally insensitive to the imposed polarization, be it anodic or cathodic.

As previously, the only limit is on the cathodic side, when the degree of protectivity attained prevents all precipitation, eventually leading to very slow, but complete redissolution of the deposit.

In conclusion, insoluble cationic deposits behave exactly like passive layers. Any variation in the anodic metal dissolution kinetics is automatically and integrally compensated by an opposite change in the protective nature of the deposit.

## 3.3. Effect of path and rate of polarization

### *3.3.1. Existence of irreversibilities*

Throughout the preceding discussion, the imposed polarization has been considered to be constant, or to vary only very slowly. For example, it has been seen that cathodic polarization can lead to complete redissolution of a deposit, albeit for extremely variable cathodic protection levels, depending on the type of deposit:

(a) for soluble deposits, redissolution is immediate, and occurs as soon as the rate of metal dissolution becomes lower than the real corrosivity of the medium under free corrosion conditions;

(b) for insoluble cationic deposits, it begins when the rate of metal dissolution falls below the corrosivity threshold required for initial deposit formation;

(c) for insoluble anionic deposits, redissolution takes place at highly variable polarization levels, which may be either as low as for soluble deposits or even considerably higher than for insoluble cationic deposits.

Deposit redissolution by cathodic polarization is, therefore, basically irreversible, although highly variable. It will be seen below that the same is true for deposit formation.

### 3.3.2. *Existence of multiple quasi-stationary states*

During free corrosion, the rate of anodic dissolution always has the order of magnitude of a transport rate, and more specifically of that for $H^+$ (Fig. 4). Even if the transport of $H^+$ is easier than that of $Fe^{2+}$ or $X^{n-}$, the difference is necessarily limited. The initial formation of corrosion products in solution and their removal by precipitation will therefore always have similar kinetics, so that extreme levels of supersaturation can never be attained.

On the contrary, for imposed polarization, the anodic dissolution rate can suddenly become considerably faster than all other kinetics in the system, including those for precipitation. An intense and rapid anodic pulse can thus entrain an enormous supersaturation in iron, before any precipitation has had the time to occur. When the latter does begin, the amount immediately available can then be sufficiently high to exhaust completely the local anion concentration. If a final polarization, $U$, is applied at that instant, such that the anodic current, $i_A$, is greater than the anion flux, then a perfectly stable regime of anionic control will be set up.

However, if the polarization had been increased slowly up to $U$, for an initial insoluble cationic deposit, it would have been perfectly possible to conserve the initial cationic control regime (Section 3.2.3). Conversely, with the anionic regime at the potential $U$, temporary cathodic protection could be applied, preventing the production of iron for a time sufficiently long to allow equalization of the anion concentration. On returning to $U$, cationic control would then be reestablished.

In this example, it is not possible to say that one of the control regimes is stable and the other metastable. In the absence of any external modification, each is as stable as the other at the same potential. It is equally impossible to maintain that one is more "natural" or more "artificial" than the other. In effect, it could perfectly well be envisaged that, depending on the initial immersion conditions (stirring, previously established surface layers, etc.), free corrosion might lead to either one or the other.

In conclusion, for imposed polarization as for free corrosion, ranges of potential may exist where an insoluble deposit may be either cationic or anionic, depending on the path followed to reach a given potential. For the same applied potential, a temporary anodic pulse can convert a cationic deposit to an anionic one, and vice versa.

Such effects have already been observed experimentally in $CO_2$ media [6]. To obtain stable galvanic coupling between two portions of the same metal, it was found necessary artificially to apply a cathodic flash to the future cathode. In these conditions, for practically identical potentials, it is quite possible, in certain media, to maintain a stable active couple between two electrodes of the same metal in the same corrosive medium.

## 3.4. Existence of a pitting potential for insoluble cationic deposits

It is known that insoluble cationic deposits correspond to intermittent corrosion regimes (Fig. 6). Also, it has been seen (Section 3.2.3) that the higher the potential, the stronger and shorter are the dissolution transients. The above analysis of the influence of polarization rate therefore equally applies to the effect of potential on the stability of cationic control.

In effect, the intermittent metal dissolution takes place between a threshold of undersaturation of the local medium, controlling the exposure of bare metal at the tip of a pore, and a threshold of supersaturation, governing local precipitation and repassivation. The first of these thresholds depends only on the kinetics of dissolution of the corrosion product. It therefore remains the same whatever the metal potential. On the contrary, the second threshold can vary with potential. Thus, at low values, when anodic dissolution kinetics are only slightly faster than the average corrosion rate, the rise in local iron concentration is slow. The effective supersaturation threshold for the precipitation of corrosion products is then defined only by the precipitation kinetics. When the potential increases, the dissolution transients become shorter and shorter, but also more intense. As in Section 3.3.2, a potential is attained where the production of iron is so fast that its concentration greatly exceeds the normal supersaturation level when precipitation begins, and precipitation can then entrain local anion exhaustion, leading to a change in the control mechanism, with the establishment of a stable anionic regime.

However, for a given thickness, an anionic deposit is less protective than a cathodic one. The free corrosion potential for the anionic form is thus lower than for its cationic counterpart. For a galvanic couple at the same potential, the anionic deposit will therefore be the anode and the cationic deposit, the cathode.

As a consequence, in conditions of free corrosion, if the potential of a metal covered by an insoluble cationic deposit attains the threshold corresponding to conversion to the anionic regime, the first zones transformed will ensure cathodic protection of the unconverted regions. The same surface will therefore comprise areas with a cationic deposit, which is both protective itself and under cathodic protection, and regions where the deposit has become anionic, and which will be both less protected and under conditions of galvanic corrosion. This is typical of situations where pitting corrosion is encountered.

It follows that the existence of a pitting potential is an inherent feature of the growth-controlling mechanism for insoluble cationic deposits. Moreover, a marked analogy will be noted with the case of stainless steels [7]. In both situations, pitting corrosion corresponds to local failure of the protection system. In both cases also, this failure, and the corresponding critical potential, are due to a kinetic instability between the electrochemical control of the current and the variation of the composition of the local medium due to a sudden supply of corrosion products.

It should be noted that the properties described here on a theoretical basis have already been observed experimentally in $CO_2$ media: existence of local galvanic couples in cases of localized corrosion [1, 6]; initiating effect of anodic polarization [2].

In general, all the experimental evidence concerning the theoretical mechanisms described in both the present work and in the previous paper [5] correspond to $CO_2$, $H_2S$ or calcium-rich media, i.e. to $HCO_3^-$, $HS^-$ or $OH^-$ precipitatable anions interacting with the oxidizing cation, $H^+$. In all these cases, the solubility of the corresponding corrosion products is sensitive to the local pH, resulting in an additional reaction between the anodic and cathodic systems (cf. Section 3.1.2). Before attempting to draw general conclusions from these studies, it is thus preferable to give more detailed consideration to the case of corrosion product deposits whose solubility is sensitive to pH.

## 4. Deposits whose solubility is sensitive to pH

### 4.1. Transport and local equilibria

### 4.1.1. *Water chemistry*

In concentrated chloride or sulphate media, precipitation of the iron salt involves only the anion

$$Fe^{2+} + SO_4^{2-} \rightarrow FeSO_4 \qquad (2)$$

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \qquad (3)$$

In $CO_2$ media, even if the iron salt is $FeCO_3$, the precipitatable anion is not necessarily $CO_3^{2-}$. In effect, at pH $< 7$, $CO_3^{2-}$ is an extremely minority species, and is therefore untransportable. In the transport phenomena, the precipitatable anion is $HCO_3^-$, or even the carbonic acid molecule itself in highly acidic media

$$Fe^{2+} + HCO_3^- \rightarrow FeCO_3 + H^+ \qquad (4)$$

$$Fe^{2+} + (CO_2 + H_2O) \rightarrow FeCO_3 + 2H^+ \qquad (5)$$

In effect, for transport purposes, it is of little importance whether Equations 4 and 5 represent the direct reactions, or the overall reactions simply expressing the *in situ* generation of $CO_3^{2-}$ by successive dissociation of $H_2CO_3$ and $HCO_3^-$.

The same is true for the local equilibria, where the mass action laws and the solubility must be expressed as a function of the species effectively present (and transportable), and not of the quasi virtual species $CO_3^{2-}$. The solubility product (Equation 6) will therefore be replaced by the equivalent forms (Equations 7 and 8) [8]

$$Fe^{2+} \cdot CO_3^{2-} = K_s \qquad (6)$$

$$Fe^{2+} \cdot HCO_3^- = H^+ \cdot K_s/K_2 \qquad (7)$$

$$Fe^{2+} \cdot CO_2 = (H^+)^2 \cdot K_s/K_1 K_2 \qquad (8)$$

where $K_1$ and $K_2$ are, respectively, the rate constants for the first and second dissociations of carbonic acid [8].

### 4.1.2. *Effect on the fluxes*

In a soluble deposit, any iron flux injected by the anodic reaction is precipitated on the spot. Adding the electrochemical Reactions 9 and 10

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (9)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (10)$$

to the precipitation Reactions 4 and 5 yields the overall Reactions 11 and 12 at the metal-solution interface

$$Fe + HCO_3^- + H^+ \rightarrow FeCO_3 + H_2 \qquad (11)$$

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2 \qquad (12)$$

Compared to Reaction 10, Reactions 11 and 12 thus correspond, in fact, to a partial or total regeneration of the $H^+$ ions consumed by the corrosion.

On bare metal, a phenomenon designated "$H^+$ transport" is already known in $CO_2$ media [9]. In effect, the diffusion polarization corresponds not only to diffusion of the $H^+$ ion itself, but also to that of the $CO_2$ or $H_2CO_3$ molecules, with local generation of $H^+$ by hydration and dissociation *in situ*. However, in the experimental conditions studied, this additional transport of $H^+$ remained marginal, although it was not clear whether this was due to reduced $CO_2$ mobility or to slow hydration and dissociation kinetics.

It can be seen that this same effect of $H^+$ transport can also exist under a soluble deposit, the additional supply of $H^+$ this time being related to total or partial regeneration after the cathodic reaction itself. For the moment, there are no indications as to the potential amplitude of this latter phenomenon. It can simply be stated that, in the limiting conditions of free corrosion, if $CO_2$ and $HCO_3^-$ migrate sufficiently quickly, a soluble deposit could remain relatively unprotective up to quite large thicknesses. As long as there is no local exhaustion of $CO_2$ and $HCO_3^-$, the cathodic reaction is not impeded by an increase in deposit thickness.

Thus, contrary to an insoluble deposit, a soluble deposit whose solubility is sensitive to pH may only become protective once the system has converted to anionic control. This type of effect may well contribute to the well-known corrosivity of weak acids.

### 4.1.3. *Effect on local solubilities*

The first consequence of the sensitivity of the corrosion product solubility to pH is that the local iron solubility no longer depends only on the local concentration of the transported anionic species, but also on the local $H^+$ level [5]. This has two types of effect on growth control of corrosion deposits:

(i) in free corrosion, the local iron solubility depends on the existence or absence of a diffusion polarization for the cathodic reaction;

(ii) under imposed polarization, whatever the free corrosion situation, a transition in the local iron solubility occurs, at the transition potential, $U_T$, where the instantaneous cathodic Tafel line intersects the limiting instantaneous current line. This transition may occur for either cathodic or anodic polarization, depending on the respective positions of $U_T$ and the free corrosion potential $U_{corr}$. Moreover, both $U_T$ and $U_{corr}$ depend on the deposit thickness when polarization is applied.

Under these conditions, imposed polarization modifies not only the instantaneous rate of $Fe^{2+}$ production, but also the rate of consumption of $H^+$ ions. For corrosion product deposits whose solubility depends on pH, determination of the growth-controlling mechanism therefore requires the comparison of the respective values of five gradients: $Fe^{2+}$, $H^+$, $H_2X$ acid, $HX^-$ anion and the local solubility:

$$Fe_s = K_s \cdot H^+ / K_2 \cdot HX^- \text{or } K_s \cdot (H^+)^2 / K_1 K_2 \cdot H_2X$$

## 4.2. The different types of carbonate, sulphide and hydroxide deposits

In order to be able to treat indifferently the case of carbonates, sulphides, hydroxides or other salts of weak acids, the following notation will be adopted: acid, $H_2X$; hydrogenous anion, $HX^-$; bivalent anion causing insolubility, $X^{2-}$.

In order to consider all cases (free corrosion and both anodic and cathodic polarizations) a graphical demonstration mode will be employed.

### *4.2.1. Soluble deposits*

Fig. 8 represents the various possible cases. In a highly acid water (case 1), or whenever $pH < pK_1$, the "precipitatable anion" is the acid $H_2X$ itself, so that the $H^+$ ions consumed by the corrosion are completely regenerated in contact with the metal. Such a deposit thus confers no protection, even for large thicknesses. It is therefore a profuse deposit.

However, contrary to profuse deposits of the insoluble anionic type [5], profuse soluble deposits cannot become protuberant whenever the medium is turbulent. In effect, the rate of redissolution increases markedly as soon as the deposit projects beyond the metal surface. Such deposits therefore tend to fill exactly the corrosion craters and may even have the polished appearance of a metal subjected to erosion–corrosion.

In sufficiently concentrated media closer to neutrality (pH between $pK_1$ and $pK_2$), the precipitatable anion $HX^-$ is largely sufficient for the permanent build up of a deposit (case S2). When the deposit thickness increases, $H^+$ diffusion polarization impedes corrosion, and further decreases the local iron solubility. Nevertheless, even if the $HX^-$ anion concentration is locally exhausted (case S3), provided that this exhaustion occurs after that of $H^+$, iron is not made locally soluble.

### *4.2.2. Insoluble cationic deposits (Fig. 9)*

In the steady state at the free corrosion potential (case $IC_0$), the precipitation rate attains a virtually zero residual level. Consequently, the precipitatable anion concentration becomes uniform everywhere, and there is no regeneration whatsoever of $H^+$. The case is therefore strictly identical to that of an $Fe_nX_2$ salt with a solubility insensitive to pH.

On the contrary, under cathodic polarization (case $IC_-$), the local acidity decreases, reducing the local iron solubility. The apparent cathodic protection can

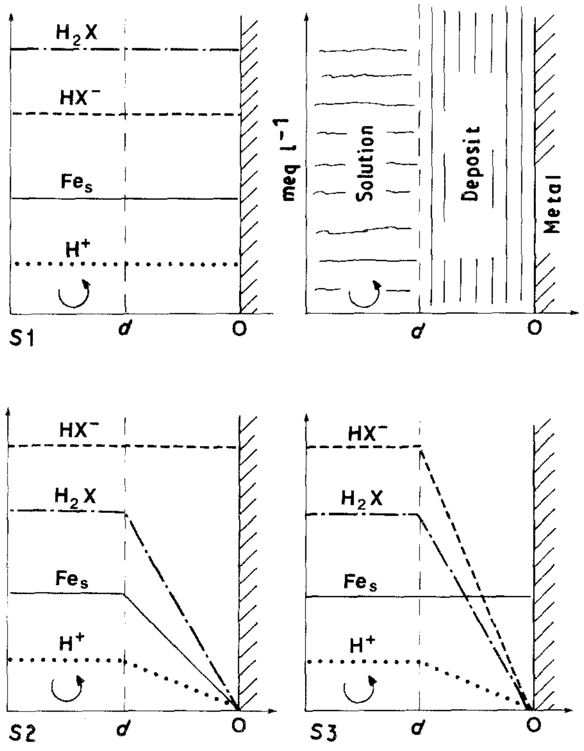

*Figure 8* $Fe^{2+}$, $H^+$, $HX^-$ anion and $H_2X$ acid concentration gradients and variation of local iron solubility $Fe_s$ through a soluble deposit. *S*1, a highly acid medium ($H_2X \gg HX^-$); *S*2, a concentrated "neutral" medium ($HX^- \gg H_2X$ and $Fe_s$); *S*3, a dilute "neutral" medium ($Fe_s \gg HX^- \gg H_2X$).

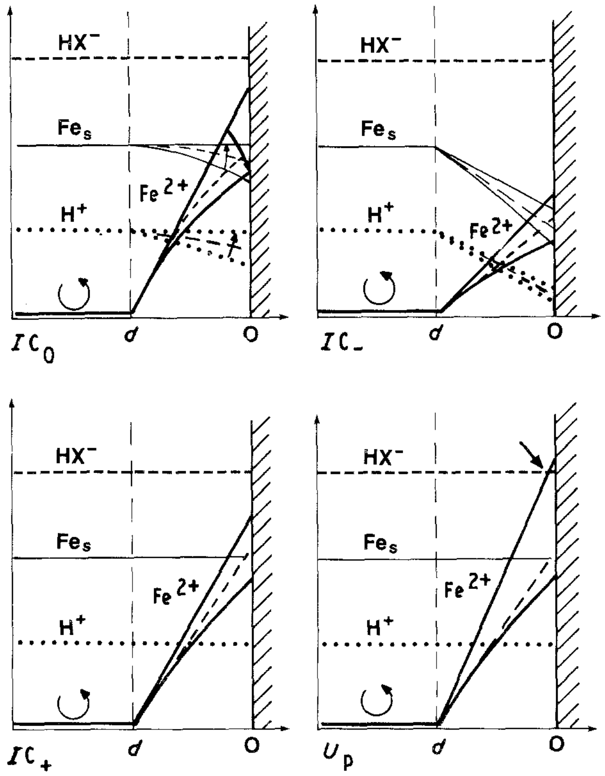

*Figure 9* $Fe^{2+}$, $H^+$, $HX^-$ anion and $H_2X$ acid concentration gradients and variation of local iron solubility $Fe_s$ through an insoluble cationic deposit. $IC_0$, free corrosion; $IC_-$, cathodic polarization; $IC_+$, anodic polarization; $U_p$, pitting potential.

then be due just as easily to a transport effect (decreased $Fe^{2+}$ gradient) as to the usual electrochemical effect.

With anodic polarization (case $IC_+$), any $H^+$ diffusion polarization disappears very rapidly, so that the mean local iron solubility remains constant, while the fluctuations with time increase. The lower limit remains the same (under-saturation threshold for the redissolution of FeX), but the upper limit increases with potential (iron production more and more rapid). When the upper fluctuation limit of the local iron concentration attains the $HX^-$ anion content (case $U_p$), precipitation causes local anion exhaustion, and the system converts to an insoluble anionic regime.

Because the latter type is not at all protective, depending on the resultant topography, $U_p$ will be either a pitting potential or a general anodic depassivation potential.

### *4.2.3. Insoluble anionic deposits (Fig. 10)*

At the free corrosion potential (case $IA_0$), the local solubility of iron obviously depends on the local acidity induced by the variable $H^+$ diffusion polarization.

Under anodic polarization (case $IA_+$), this diffusion polarization disappears. The deposit then becomes totally transparent, both for the transport of corrosion products and as regards electrochemical effects.

Under cathodic polarization (case $IA_-$), the local acidity decreases. It thus gradually reduces the local iron solubility down to its normal level in the outside medium.

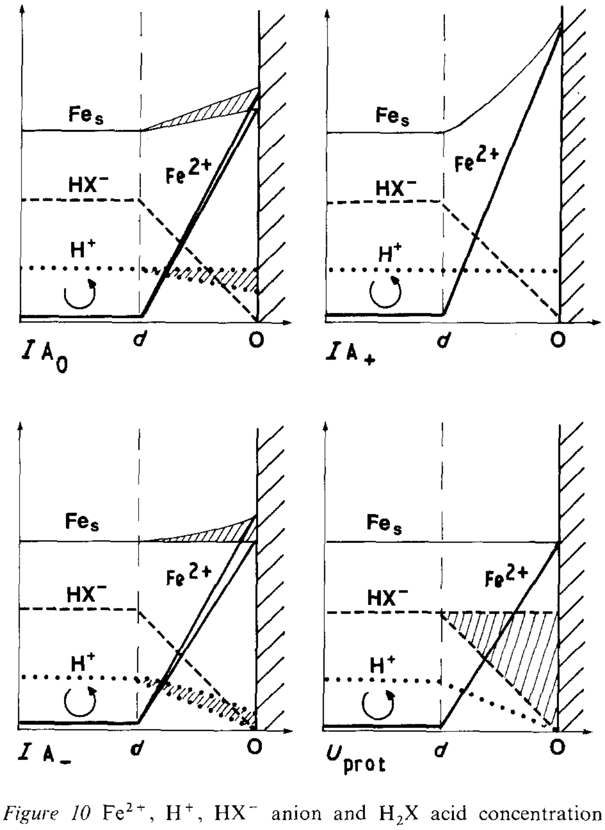

*Figure 10* $Fe^{2+}$, $H^+$, $HX^-$ anion and $H_2X$ acid concentration gradients and variation of local iron solubility $Fe_s$ through an insoluble anionic deposit. $IA_0$, free corrosion; $IA_-$, cathodic polarization; $IA_+$, anodic polarization; $U_{prot}$, protection potential.

At the protection potential (case $U_{prot}$), the production of iron approaches the flux which can be transported by diffusion and the residual precipitation diminishes. The necessary anion supply therefore also decreases, leading to a gradual reduction in the anion gradient, and eventually to a completely uniform distribution.

From this point, if the potential rises again, the residual precipitation also increases. Depending on the place where it occurs, on an internal surface of the deposit or on the surface of the metal, the insoluble deposit will remain anionic or will become cationic. Because the latter case is protective, $U_{prot}$ is therefore a protection potential. Depending on the initial topography, $U_{prot}$ will be a pitting repassivation potential or a cathodic passivation potential.

In conclusion, compared to the general corrosion product $Fe_nX_2$ already described [5], the carbonates and sulphides encountered in $CO_2$ or $H_2S$ corrosion show three additional properties:

(i) in acid media, profuse deposits occur, exactly filling corrosion craters;

(ii) a pitting or general depassivation potential exists for insoluble cationic deposits;

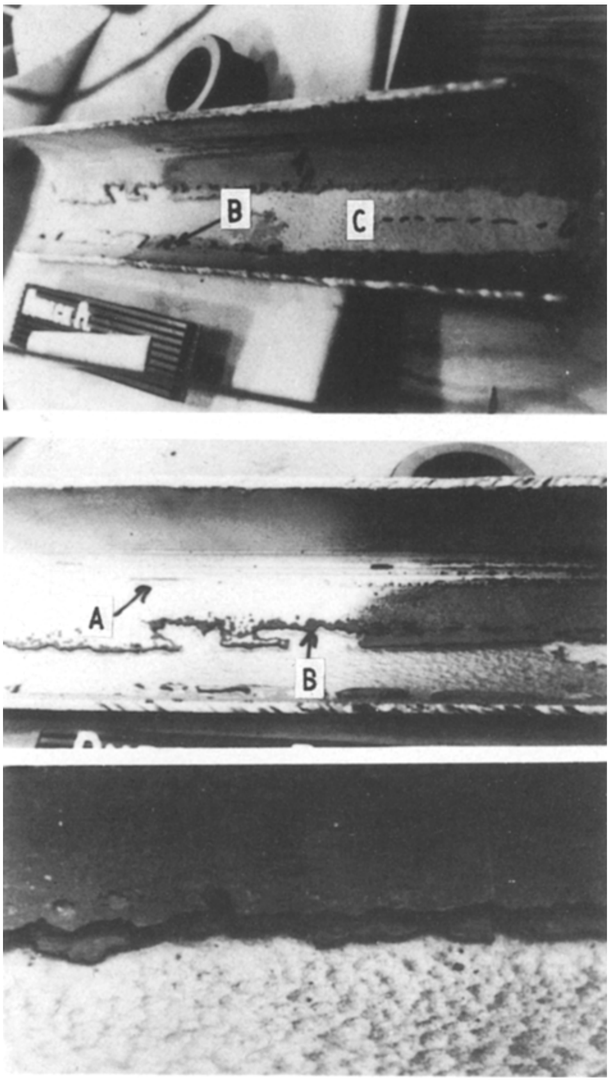

*Figure 11* Massive deposit of $FeCO_3$ corrosion product along the edge of a region of erosion–corrosion attack in a $CO_2$-containing raw-gas pipeline.

(iii) a protection potential exists for insoluble anionic deposits.

## 5. Discussion

### 5.1. Experimental evidence

In the same way that non-protective insoluble anionic deposits, described previously [5], had already been encountered in calcium-rich brines, and profuse insoluble anionic deposits in $H_2S$ media, unknowingly, three of the processes considered above have already been observed in $CO_2$ environments.

#### *5.1.1. Profuse soluble deposits*

From time to time, thick, black, dense and sometimes polished deposits are found along the edges of localized corrosion craters. Externally, these thick unprotective deposits are not readily distinguished from uncorroded metal covered by a thin protective deposit. At the present time, it is therefore difficult to say whether this type of feature is indeed rare, or whether it has simply escaped notice. Fig. 11, presented at a NACE T-1-4 Technical Committee meeting on erosion-corrosion [10], corresponds quite closely to this morphology.

#### *5.1.2. Pitting potential*

The initiation of localized $CO_2$ corrosion by anodic polarization, together with the obvious existence of irreversibilities, has been described by Videm and Dugstad [2]. In this case, the "natural" localized corrosion was undoubtedly the result of exceeding the pitting potential, for anodic polarization on a protective deposit (probably of the insoluble cationic type).

#### *5.1.3. Protection potential*

Conversely, "artificial" localized corrosion has been obtained in the laboratory by locally stabilizing a cathode [1, 6], and was presumably caused by exceeding the protection potential, for cathodic polarization on an unprotective deposit (probably of the insoluble anionic type).

#### *5.1.4. Analysis of field deposits*

Differences in composition have also been observed in the deposits coating anode and cathode regions of in-service $CO_2$ corrosion [1, 6]. The fact that the major difference is the presence of calcium is perfectly coherent with the proposed models.

### 5.2. Consequences

Together with the previous study, the present work both predicts and theoretically analyses certain types of behaviour and corrosion morphologies. Certain of them, extremely specific and precise, or even paradoxical, have already been encountered unknowingly, and their descriptions in the literature show remarkable agreement with the proposed theoretical model. Such concordance is a powerful incitement to extend this approach to include all uniform or pitting corrosion problems in non-passivatable metals.

The possibility of using normal electrochemical methods, not simply for measuring corrosion rates, but for studying the dynamic stability of deposits and their growth control, opens up a wide new area for future research. When Brennert discovered the pitting potential of stainless steels in 1935 [11, 12], he could certainly not have imagined to what extent this change in experimental technique was going to extend and revolutionize the use of these materials.

In the oil industry, the prediction of localized corrosion in both $CO_2$ and $H_2S$ media, or even the prediction of uniform corrosion, and particularly the real long-term corrosivity, becomes a more and more pressing requirement. In effect, corrosion monitoring in wells is both difficult and costly. In the entirely submerged production units of the future, efficient monitoring becomes practically impossible, so that reliable prediction is increasingly essential. Indeed, in view of the enormous expenditure involved, it is desirable to avoid resorting systematically to noble materials in media which are often either little or uncorrosive. Accurate prediction of the corrosion behaviour of ordinary steels is therefore required, and this could be provided by the approach described above.

## 6. Conclusions

Based on the uniform corrosion mechanisms beneath corrosion deposits described in a preceding theoretical study, the present paper shows that certain deposits attain a steady state only at the free corrosion potential. Under imposed polarization, soluble or insoluble anionic deposits grow or shrink indefinitely, depending on the direction of the applied polarization.

Except for the natural corrosion potential, electrochemical investigation techniques can therefore only be used to study quasi-stationary states, where the electrochemical reactions and transport phenomena are in dynamic equilibrium with the instantaneous thickness of the deposit.

Soluble or insoluble anionic deposits are totally "transparent" to the electrochemical effects of interest. Over a wide range of conditions, i.e. as long as they are not themselves destabilized by the imposed polarization, they do not counteract the electrochemical phenomena under investigation. The electrochemistry of a metal covered by such deposits is therefore the same as that normally encountered for bare metal.

Conversely, deposits of the insoluble cationic type conserve the same steady state with or without polarization, the electrochemical effects of the polarization being completely compensated by the change in the deposit growth regime. Thus, insoluble cationic deposits not only are the most protective but also behave as veritable passive layers.

Extremely rapid variations in the applied polarization can lead to irreversibilities in the system. Multiple quasi-stationary states may then exist, depending on both the polarization path and on the rate of application. Thus, anodic or cathodic pulses can cause an insoluble deposit to change from cationic to anionic, or vice versa.

A particular consequence is the existence of a pitting or general anodic depassivation potential for insoluble cationic deposits. Similarly, there is a protection or cathodic passivation potential for insoluble anionic deposits.

Finally, in $CO_2$ or $H_2S$ media, there is an additional effect of polarization, related to the influence on the local solubility of carbonate and sulphide corrosion products of variations in acidity, due to diffusion polarization induced by the reduction of $H^+$. In highly acidic media, completely unprotective profuse soluble deposits may occur, exactly filling the corrosion craters on the metal surface.

Numerous experimental observations of the basic mechanisms described in both the present work and in the previous study have already been reported unknowingly in the literature, representing a strong incitement to generalize this approach. In particular, as in the case of stainless steels, electrochemical methods could be used, not only to measure corrosion rates, but also to study the dynamic stability and the growth-controlling mechanisms of corrosion deposits, so as to determine the long-term reliability of the protective behaviour observed in the laboratory.

In the oil industry, corrosion monitoring is already difficult and costly in wells. It will be even more so on future uninhabited platforms and submarine production units. The continued use of cheap ordinary steels then demands reliable prediction of real effluent corrosivity. The present approach renders this objective realistic, even though a great deal of work remains to be done.

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