

Role of Conductive Corrosion Products in the Protectiveness of Corrosion Layers

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ABSTRACT

In carbon dioxide (CO_2) corrosion of steels, the bicarbonate ion (HCO_3^-) is simultaneously the buffer for carbonic acid (H_2CO_3), the source of iron carbonate (FeCO_3) precipitation, and the product of the cathodic reaction. In addition to spatial separation of the production of Fe^{2+} and HCO_3^- , galvanic coupling between the steel and cementite (Fe_3C) layers is the principal cause of internal acidification in these layers, since the HCO_3^- ions are removed from the steel surface by electromigration. This can facilitate localized corrosion by lateral galvanic coupling. This mechanism explains the role of traces of free acetic acid (CH_3COOH , or HAc) and the existence of multiple steady states. Transposition to corrosion of iron by hydrogen sulfide (H_2S) or to corrosion of copper is discussed.

KEY WORDS: acetic acid, acidification, bicarbonate, carbon dioxide corrosion, carbonic acid, cementite, copper, electromigration, galvanic coupling, hydrogen sulfide, steel

INTRODUCTION

In the general paradigm of the study of carbon dioxide (CO_2) corrosion of steel, recent developments have revealed the decisive influence of variations in the protectiveness of corrosion layers.¹ Thus, corrosion layers containing the same solid components can be extremely protective,² very little so, or even corro-

sive.³ For a carbon-manganese steel, such as the St52 grade⁽¹⁾ used in some studies,²⁻³ the corrosion layers are composed of an insoluble corrosion product, iron carbonate (FeCO_3), and/or an undissolved component from the steel, namely cementite (Fe_3C). Like the metal, Fe_3C is an electronic conductor. The cathodic corrosion reaction, therefore, can occur as readily on Fe_3C as on the surface of the steel itself. This leads to the possibility of galvanic coupling between the steel substrate and the layer of undissolved Fe_3C .

Based upon the general electrochemical characteristics of the reduction of hydrogen (H^+) ions and the anodic dissolution of iron, the first study on the aggravation of corrosion by layers of undissolved Fe_3C led to the conclusion that galvanic coupling between the steel and the Fe_3C was only of a marginal nature and suggested that local acidification must occur in the aqueous medium trapped within the pores of the solid layer.³ However, it has since been realized that these basic electrochemical properties, which had been observed in strong acid solutions and assumed to be general, cannot be transposed to CO_2 media.⁴ Under specific conditions of this sort, different orders of reaction for the reduction of H^+ and different slopes of the individual Tafel lines leads to a situation where it is impossible to distinguish between the effect of galvanic coupling and that of internal acidification.⁴ It is now necessary to consider that one or the other may occur, or even both together.

The aim of the present work was to show that it is not possible for one effect to occur without the

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⁽¹⁾ A common construction steel corresponding to ASTM A537, Grade 1, with minimum tensile strength of 510 MPa.

other. Thus, galvanic coupling between the steel and Fe_3C is seen to be a powerful source of internal acidification and, therefore, its most probable cause. Moreover, the random irregularities of such coupling during uniform corrosion potentially can be extremely effective in promoting more enhanced coupling (i.e., between small pits and their surroundings or between corroded and uncorroded areas in "mesa-type" attack). In general, the presence of conductive compounds in a corrosion layer plays an essential role in their protectiveness and the risk of uniform corrosion degenerating into localized attack. The underlying reasons are the local pH and the water chemistry.

EFFECT OF LOCAL WATER CHEMISTRY ON PROTECTIVENESS

Mechanisms Determining Protectiveness

In addition to the two electrochemical reactions, anodic and cathodic, the system represented by a metal corroding beneath a corrosion layer involves two or three transport processes, corresponding to the supply of reactants for the cathodic process and the evacuation of the products of both reactions.⁵ The transport between the external corrosive medium and the metal is accounted for mainly or partially by diffusion through the liquid contained in the pores of the corrosion layer, with the remainder resulting from the permanent growth of the layer in contact with the metal and its permanent redissolution in the external medium. If precipitation and redissolution are the majority processes, the corrosion layer is called soluble. Conversely, if diffusion in the liquid phase is the predominant mechanism, the layer is called insoluble. Depending upon whether the overall process is governed by diffusion of the metal cation or by that of the precipitable anion, the layers are designated as insoluble cationic (IC) or insoluble anionic (IA), respectively. Any imposed polarization obviously will modify interaction between the electrochemistry and the transport mechanism greatly.⁶ From this standpoint, galvanic coupling between the metal and a conductive corrosion product already will cause a major modification in the mechanisms of protectiveness.

These diffusion fluxes naturally imply marked gradients in concentration of the different species involved, particularly those of the metal cation M^{n+} and the corresponding precipitable anion X^{m-} . This leads to local solubility equilibria inside the layer that can differ vastly from what might be expected in the external medium. In particular, in an IA layer, local depletion of the precipitable anion X^{m-} causes a corresponding increase in the local solubility of the metal ion M^{n+} and, therefore, allows higher M^{n+} concentration gradients and fluxes (i.e., faster steady state corrosion rates).^{2-3,5}

CO₂ Corrosion in Steels

In this case, the insoluble corrosion product is FeCO_3 , for which the solubility product conventionally is written:

$$\left[\text{Fe}^{2+}\right]\left[\text{CO}_3^{2-}\right]=K_s \quad (1)$$

where K_s is the solubility constant of FeCO_3 . Nevertheless, in the presence of significant concentrations of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-), the effective carbonate ion (CO_3^{2-}) content becomes of second order compared to these species. Where transport phenomena are concerned, it is never advisable to reason in terms of trace components whose excessively low concentration completely excludes the possibility of direct transport. For example, at pH 6, the transport capacity of acidity via the highly mobile H^+ (or H_3O^+) ions is negligible compared to the indirect effect of diffusion of tens or hundreds of mM/L of dissolved CO_2 , even though mobility of the latter is low, and the kinetics of the final hydration of CO_2 and dissociation of H_2CO_3 are slow.^{4,7} Thus, to conserve a realistic physical meaning for each solubility product, they are written systematically in terms of the majority independent species, which can be transported directly. For example, HCO_3^- ions are concentrated enough to be transported directly, but the CO_3^{2-} mainly are formed or removed locally by chemical reaction. From this local equilibrium between HCO_3^- and CO_3^{2-} , Equation (1) can be rewritten:

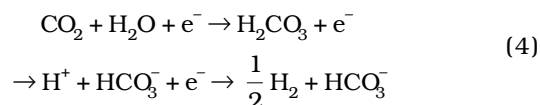
$$\left[\text{Fe}^{2+}\right]\left[\text{HCO}_3^-\right]=K_2K_s\left[\text{H}^+\right]=K\left[\text{H}^+\right] \quad (2)$$

where K_2 is the equilibrium constant for the second dissociation of H_2CO_3 .

At a given pH, the HCO_3^- anion then appears mathematically in Equation (2) as the precipitable anion leading to formation of solid FeCO_3 , with a corresponding solubility constant equal to $K\left[\text{H}^+\right]$. At the same time, HCO_3^- naturally remains the anion that buffers the H_2CO_3 and is in solubility equilibrium with the CO_2 partial pressure (P_{CO_2}):⁸

$$\left[\text{H}^+\right]\left[\text{HCO}_3^-\right]=K_1\left[\text{CO}_2\right]=K^*_1P_{\text{CO}_2} \quad (3)$$

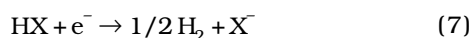
Finally, HCO_3^- is also the reduction product of CO_2 . Actually, the mass balance of the oxidizing power (i.e., the whole ensemble involving all transport of acidity-carrying species, their direct reduction, or the in-situ generation of H^+ just before reduction, which are equivalent in a mass balance) can be expressed as:



The three roles respectively represented by Equations (2) through (4) are naturally inseparable and occur simultaneously in the corrosion layer. Therefore, there is a strong and complex interaction between the local pH, the solubility of iron, the transport of Fe^{2+} and HCO_3^- , and the respective localization of their electrochemical productions.

Generalization to Other Metals and Acids

From CO_2 to Hydrogen Sulfide (H_2S) — Given the completely parallel situation between CO_2 and H_2S ,⁹ the previous information concerning FeCO_3 can be transposed immediately to all ferrous sulfides, FeS or $\text{FeS}_{1\pm}$ (i.e., in practice, to all the sulfides other than pyrite and marcassite). It is sufficient to rewrite Equations (2) through (4), where X^- represents HCO_3^- or HS^- :



From CO_2 to Acetic Acid (CH_3COOH , or HAc) — The mathematics involved in the transposition of Equations (2) through (4) to Equations (5) through (7) are not related to the diacid character of H_2CO_3 and H_2S but solely to the valency ratio between Fe^{2+} and X^- . In these conditions, Equations (5) through (7) can be transposed to all monoacids, particularly to HAc , and to all the carboxylic acids of similar pK_a known to be present in produced waters, either directly or in the form of the corresponding anions (X^-).¹⁰ The solubility product for ferrous acetate (FeAc_2), $[\text{Fe}^{2+}] \times [\text{Ac}^-]^2 = K_s$, can be reduced back to Equation (5), with $K_1 = K_a$ and $K = (1/[\text{HAc}]) \times K_s/K_a$.

However, while the mathematical forms are the same, there are two fundamental differences between CO_2 and HAc . First, for the same in-situ pH, the solubility of FeAc_2 is considerably higher than that of ferrous carbonate (FeCO_3) (K_s increases), while the concentrations usually encountered ($[\text{HAc}] = 10^{-3}$ M) and the acid strength ($\text{pK}_a = 4.6$) enhance the effect ($K_2 = 10^{-10.4}$, $([\text{HAc}] \times K_2)^{-1} = 10^{7.6}$). Consequently, at a given pH, any replacement of a concentration or a flux of HCO_3^- by an equivalent quantity of acetate will considerably increase the local solubility of iron. This decreases the protectiveness of the corrosion layer in proportion by increasing the iron concentration gradients allowed and raising the fluxes of corrosion products that potentially can be removed through the layer.

Furthermore, when the carbonic buffer is the major constituent, the acetate concentration of the

water no longer affects the pH.¹¹ Whereas the cathodic reduction of CO_2 produces HCO_3^- (Equation [4]) and leads to local alkalization, the cathodic reduction of HAc produces acetates (Equation [7]), which have no effect whatsoever on pH. Thus, substituting the cathodic reduction of CO_2 with that of HAc doubly decreases the protectiveness of the corrosion layer by increasing the solubility of iron due to both the replacement of HCO_3^- by acetate and the elimination of alkalization (Equations [4] and [7]).

Since the cathodic reduction of CO_2 and HAc can occur simultaneously and even competitively, it is quite natural that the corrosiveness of CO_2 wells often is related to the concentration of free HAc in the water and not to the acetate content.

From Monoacids to Water — Since the precipitation of ferrous hydroxide ($\text{Fe}[\text{OH}]_2$) is a necessary precursor for formation of protective oxides, Equations (5) through (7) again can be extended to the case $\text{X}^- = \text{OH}^-$, with $K_1 = K_w$ and $K = K_s/K_w$. Indeed, in the cathodic Reaction (7), the replacement of the direct reduction of water by that of O_2 would not change the e^-/OH^- ratio. In a neutral medium, the cathodic alkalization is exactly the same in aerated and deaerated water.

From Iron to Other Metals — By adjusting the stoichiometric coefficients in Equations (5) through (7) to other valencies, the whole of the above approach can be transposed to other metals. The most interesting example is probably that of the anodic dissolution of copper to Cu^+ in aerated water, followed by the precipitation of a porous layer of cuprous oxide (Cu_2O). Like Fe_3C in CO_2 corrosion of steels, Cu_2O is an electrically conducting compound and is known to play a decisive role in the protectiveness of corrosion layers on copper.¹²

Conversion of Uniform Corrosion Into Localized Attack

In CO_2 corrosion of steels, the maximum transport capacity is always that resulting from the CO_2 itself.³ Furthermore, in uniform corrosion, the anodic and cathodic current densities are equal at all points. Equation (4) consequently indicates that Fe^{2+} and HCO_3^- always are produced simultaneously (i.e., in the same amounts [in meq/L] and at the same place, Figure 1⁽²⁾). This equality maximizes the solubility product of FeCO_3 shown in Equation (2), and from the resulting precipitation, this ensures the greatest possible protectiveness of the deposit.

If for any external reason whatsoever a temporary local anode appears, the local equality between the anodic and cathodic currents would no longer hold. With respect to Figure 1(a), the production of Fe^{2+} in Figure 1(b) would increase at this local anode and that of HCO_3^- would decrease. Because of the associated rise in the solubility of iron, the corrosion layer on the anode would become less and less pro-

⁽²⁾ The scale in Figure 1 is not "nanoscopic" but micro- or macroscopic.

tective. Conversely, on the cathode, the production of Fe^{2+} would decrease and that of HCO_3^- would increase. The corresponding drop in the solubility of iron then would enhance the protectiveness of the deposit formed on the cathode.

Therefore, there should be a threshold beyond which any disturbance in the local balance between the respective anodic and cathodic current densities (i_A/i_K) would tend to intensify spontaneously. This eventually leads to a situation where the presence of the galvanic couple enables iron to be produced at the anode without HCO_3^- being formed. Therefore, Fe^{2+} becomes more soluble, and HCO_3^- less soluble. Consequently, if the bulk medium is itself buffered by some HCO_3^- content, a possible local depletion in HCO_3^- at the anode, at constant CO_2 , will locally decrease pH below its value in the bulk. Conversely, the excess HCO_3^- formed at the cathode will decrease the local solubility of Fe^{2+} and prevent significant amounts of Fe^{2+} from being produced there.

This process naturally would explain the random nature of the nucleation of pits, the difficulty of reproducing mesa attack in the laboratory, and the fact that certain water compositions stabilize such galvanic cells more than others.¹³ In fact, this all depends upon whether the following chain reaction is triggered:

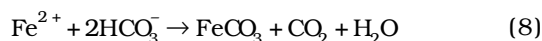
- The presence of a galvanic cell spatially separates the anodic and cathodic reactions,
- This separation locally modifies the water chemistry and the protectiveness of the corrosion layers, and
- The difference in local protectiveness enhances the galvanic coupling.

In localized corrosion, galvanic coupling occurs in a relatively visible manner, since it takes place on a macroscopic scale in a direction parallel to the surface of the steel.¹³ In the case of a layer of undissolved Fe_3C , galvanic coupling between the Fe_3C and the steel necessarily will have similar effects. Until now, these have remained hidden since they occur on a microscopic scale and in a direction perpendicular to the metal surface.

ROLE OF CONDUCTIVE COMPOUNDS

Localization of FeCO_3

In the same way as Equation (4) represents the solubility of FeCO_3 as a function of HCO_3^- anion concentration, the precipitation reaction can be expressed in the form:



Thus, FeCO_3 can precipitate not only on the steel but also directly on the Fe_3C , as a result of the ambient concentration in Fe^{2+} and the additional HCO_3^- anions produced on Fe_3C by the cathodic reduction of

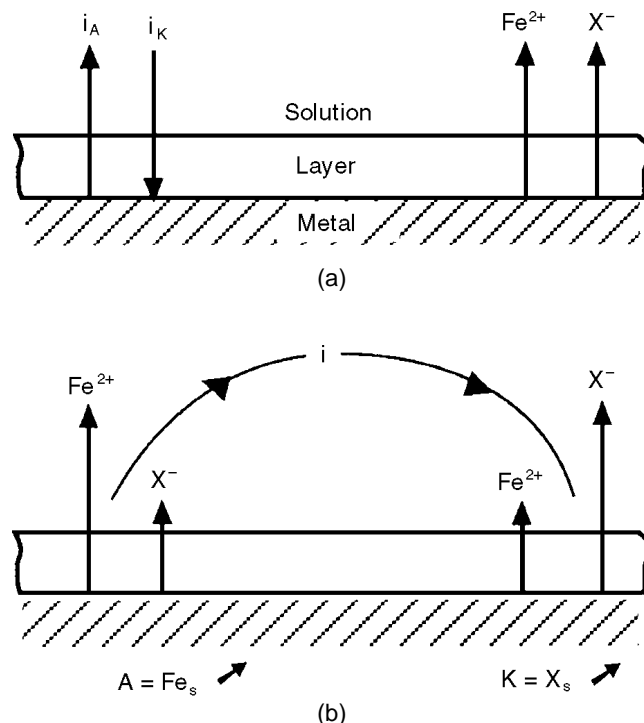
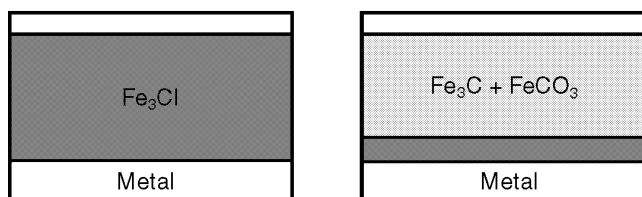


FIGURE 1. (a) Breakdown of uniform corrosion and (b) onset of local attack resulting from interaction between local water chemistry and the protectiveness of corrosion layers ($X^- = \text{HCO}_3^-$, HS^- , and OH^-).

CO_2 . A first consequence of the galvanic coupling between the steel and the Fe_3C , therefore, is the possibility of FeCO_3 precipitation at a certain distance from the steel; whereas in the absence of coupling, it can form only on the steel, where the local Fe^{2+} and HCO_3^- concentrations are a maximum. Among all the corrosion layer morphologies observed,^{2-3,14} the main difference between protective and unprotective forms is the presence of empty Fe_3C in contact with steel in the protective case, and its absence, in the unprotective one (Figure 2). However, in unprotective layers, the thickness of empty Fe_3C does not appear to exert a decisive influence, no more so than does the presence or absence of FeCO_3 further from the steel surface. Similarly, for protective layers, the existence of empty Fe_3C elsewhere than on the steel seems to be of no importance.

It is naturally very difficult to imagine even qualitatively the distribution of coupling currents on the Fe_3C . The continuity and the electrical conductivity of this carbide network are difficult to predict. High resistance frequently is observed in Fe_3C layers, which thus reveal to be poor effective conductors. Similarly, it has been found that stable potential gradients can exist in the aqueous solution that permeates the layers.⁵ Finally variations in the extent to which the pores in the Fe_3C are obstructed by FeCO_3 can influence the distribution of current densities. Therefore, it is impossible, even by numerical model-

Nonprotective



Protective

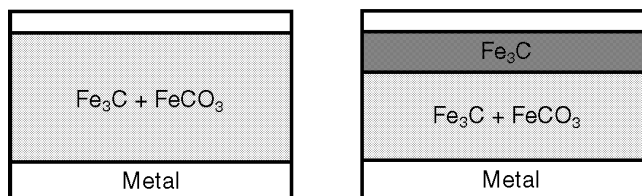


FIGURE 2. Morphologies observed for protective and unprotective corrosion layers.

ing, to determine whether the cathodic current density is uniform in the Fe_3C or whether it increases on approaching the metal.

Indeed, the ohmic drops (ΔU) within the solution are growing from the metal outward, but the gradients of the reducible species are in the opposite direction.

Whatever the situation, the presence of empty Fe_3C in contact with the steel at present can be explained only by galvanic coupling, which is either sufficiently strong or whose range is sufficiently long. Conversely, its absence indicates that galvanic coupling is either inexistent or only slight or occurs over only a very short range. Consequently, unprotective corrosion layers always are associated with significant galvanic coupling between steel and Fe_3C .

Galvanic Coupling and Internal Acidification

Another constant characteristic of unprotective corrosion layers is the existence of oblique pseudo-polarization curves, with slopes close to $120 \text{ mV}/\log$.²⁻³ The most recent analyses have shown that this can be explained by the presence of galvanic coupling or by internal acidification, without it being possible to decide between one, the other, or both.⁴

Furthermore, in the general models for protectiveness, the precipitable anion is considered to come solely from the external medium, by diffusion or electromigration.⁵⁻⁶ However, in CO_2 corrosion of steels, the precipitable anion HCO_3^- is itself a corrosion product and is formed directly within the porous layer. Like Fe^{2+} , it must be evacuated by diffusion into the external medium (i.e., in the opposite direction with respect to the original models). In this situation, galvanic coupling and acidification necessarily are related closely.

For example, in the sense acidification-coupling, the density, and distribution of the coupling current naturally depend on the pH profiles, since the effect of pH on the values of i_A and i_K on the steel is different, and perhaps also on the values of i_K on Fe_3C . The interaction is even more marked in the reverse sense coupling-acidification, since coupling itself appears as a major source of acidification.

Completely Empty Fe_3C Layer

This case has been described previously.³ The assumption that the concentration of dissolved CO_2 is sufficient for its transport capacity to be greater than that of all other species will be conserved here. In the absence of coupling (Figure 3[a]), HCO_3^- will be produced only on the steel. Because of the similarity of all the diffusion coefficients in water (except H^+), its removal by diffusion requires a dynamic enrichment in HCO_3^- of the same order as that for Fe^{2+} .⁵ This leads to an at least hyperbolic decrease in the local solubility Fe_s and the impossibility of evacuating large iron fluxes. Figure 3(a) illustrates this assumption of the absence of coupling to be unrealistic for a layer of empty Fe_3C . It would be compatible only with particularly low electrochemical activities.

On the contrary, in the presence of coupling, the nearer to the outer surface the production of HCO_3^- , the easier it is to remove by diffusion (Figure 3[b]). The dynamic enrichment necessary to evacuate a given flux decreases with the distance between the point of formation and the external medium. Since the total flux remains the same as in Figure 3(a), the HCO_3^- concentration profile is leveled rapidly. However, this can explain the absence of alkalinization (dotted line in Figure 3[b]), but not internal acidification due to complete disappearance of HCO_3^- . As before, an electromigration effect is necessary to "force" the HCO_3^- anions out of the layer.³ In fact, a phenomena of this sort does exist, due to the galvanic coupling.

In the case of a plane P parallel to the metal at a distance x from the surface (Figure 4), the fluxes of Fe^{2+} and HCO_3^- ions crossing this plane correspond to ionic currents, for which the same sign convention is used as for the electrochemical currents:

— The flux of Fe^{2+} ions is conservative (i.e., there is no FeCO_3 precipitation). Expressed in mA/cm^2 , the flux ($J_{\text{Fe}^{2+}}$) through any plane P, therefore, corresponds to the current i_A for the anodic reaction on the steel:

$$J_{\text{Fe}^{2+}} = i_A \quad (9)$$

— The coupling current $i_c(x)$ through this same plane P (i.e., the electronic current closing the circuits of the cathodes on the left of P) is equal to that necessary to cancel out the sum of i_A and the overall current $i_K(x)$ representing the sum of the cathodic

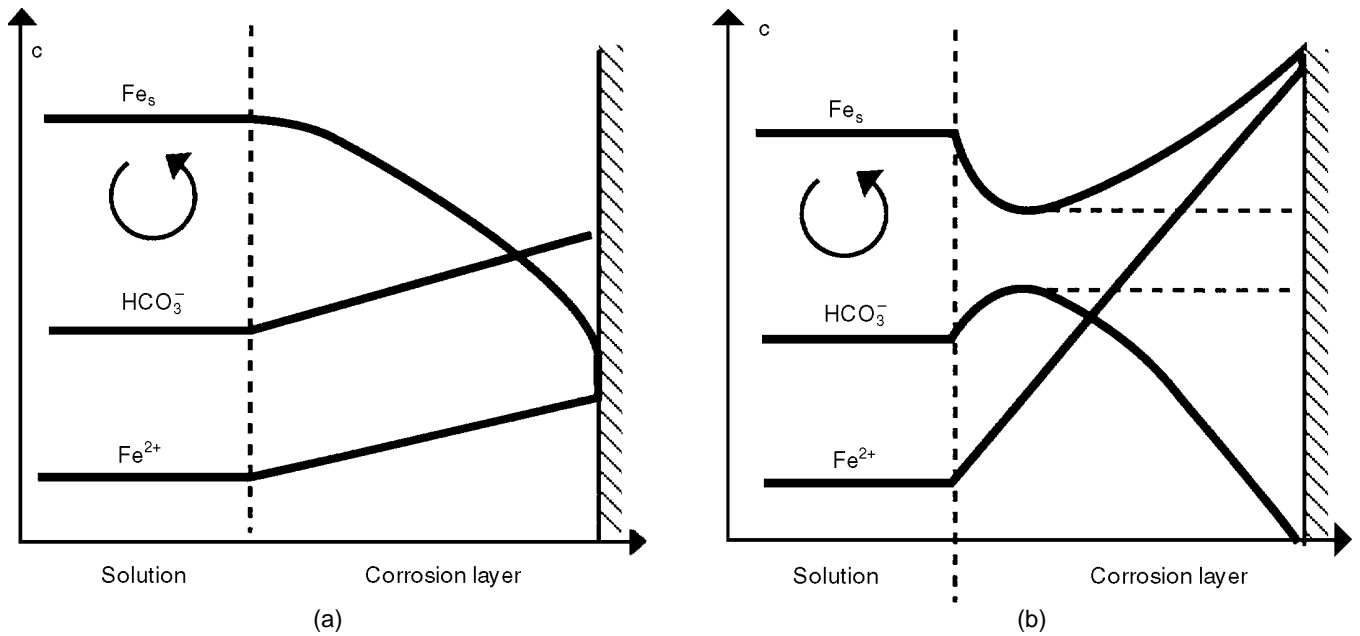


FIGURE 3. HCO_3^- anion concentration profile in the: (a) absence or (b) presence of galvanic coupling between the steel and Fe_3C .

reactions taking place on the right of P. Consequently, the total ionic current through plane P is positive (i.e., from the right to the left in Figure 4):

$$i_A + i_K(x) = -i_C(x) > 0 \quad (10)$$

In the steady-state regime, the species not involved in the reactions have no corresponding fluxes. The net ionic current in Equation (10) corresponds simply to the difference in the fluxes of Fe^{2+} and HCO_3^- , whose signs are opposite. The flux of HCO_3^- resulting from galvanic coupling (J_C) is thus:

$$J_C = J_{\text{Fe}^{2+}} + i_C(x) < J_{\text{Fe}^{2+}} \quad (11)$$

The problem is that Equation (11) is written in terms of free ions (or electric charges), while it is known that, close to the saturation in FeCO_3 and even more beyond it, there is necessarily a strong effect of ion pairing. It is not known whether the precursor of FeCO_3 precipitation is a neutral triplet $\text{Fe}(\text{HCO}_3)_2^0$ or already a neutral pair $\text{Fe}(\text{HCO}_3)$, but in both cases, the two corresponding fluxes $J_{\text{Fe}^{2+}}$ and $J_{\text{HCO}_3^-}$ cannot be but equal (in mA/cm^2). As a result of ion pairing, the apparent fluxes of Fe^{2+} and HCO_3^- are no longer independent as would be the case for free ions, but they are strongly coupled. It follows that, despite the presence of galvanic coupling, there is no possible net ionic current flowing through the solution.

This has three major consequences:

— Since the actual flux of HCO_3^- ions through plane P actually is forced to be greater than the rate of their cathodic production on the right of P (Equa-

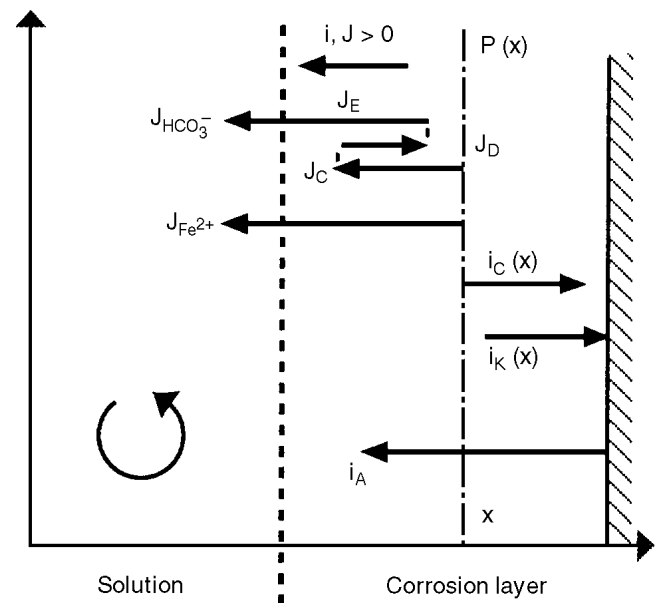


FIGURE 4. Representation with respect to a plane $P(x)$ parallel to the metal surface of the steel- Fe_3C coupling current $i_c(x)$ and the cation and anion fluxes $J_{\text{Fe}^{2+}}$ and $J_{\text{HCO}_3^-}$ crossing P, together with the anodic and cathodic currents i_A and $i_K(x)$ occurring on the metal or to the right of P.

tion [11]), this induces a depletion of HCO_3^- close to the metal. At constant CO_2 concentration, this signifies a local acidization with respect to the external medium.

— This depletion induces a diffusion flux (J_D) of HCO_3^- from the outside toward the metal. This still

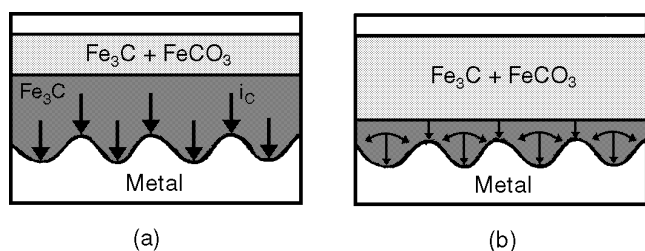


FIGURE 5. Variation of the galvanic coupling between steel and Fe₃C resulting from undulations in the dissolution front: (a) relatively negligible effect on a thick layer of empty Fe₃C and (b) development of macroscopic lateral coupling in a layer effectively thinned by obstruction of the pores with FeCO₃.

increases the difference between $J_{\text{Fe}^{2+}}$ and $J_{\text{HCO}_3^-}$ already brought about by galvanic coupling (Equation [11]).

— The final zeroing of the net ionic current is achieved by an electromigration term (J_E) that adjusts the total flux ($J_{\text{HCO}_3^-}$) to the value of $J_{\text{Fe}^{2+}}$ (Figure 4):

$$J_{\text{HCO}_3^-} = J_C + J_D + J_E = J_{\text{Fe}^{2+}} \quad (12)$$

with $J_D = -D \text{ grad } [\text{HCO}_3^-]$ and $J_C = J_{\text{Fe}^{2+}} + i_c(x)$ (Equation [11]).

J_E does not necessarily have a strong physical meaning. It is just the way to replicate for independent free ions Fe²⁺ and HCO₃⁻ the coupling of their fluxes actually introduced by ion pairing. However, the root cause of internal acidification in both cases is the presence of galvanic coupling between steel and Fe₃C.

Then, if galvanic coupling is basically the driving force for acidification, it is its dependence on pH that will define the exact pH profile in the steady state. Precise numerical modeling, therefore, will not be easy and must take into account recently published results concerning the electrochemistry in CO₂ media.⁴

Case of a Layer of Fe₃C Partially Filled with Siderite

In Figure 3(b), the inverted Fe²⁺ and HCO₃⁻ concentration profiles are perfectly able to maintain a lower degree of saturation in FeCO₃ within the layer than in the outside solution. This explains why CO₂ corrosion can continue in a medium saturated in corrosion product¹ and even why only the corrosion of steels by CO₂ can lead to high FeCO₃ supersaturations without the use of artificial means. However, with these profiles, the solubility limit of FeCO₃ can also be exceeded at some point within the layer. During the resulting precipitation transient, the two species Fe²⁺ and HCO₃⁻ are removed from their respective fluxes in equal amounts (in meq/cm²). It is also possible that this precipitation might not occur

within the pores, but directly on the surface of the Fe₃C, due to local alkalization by the cathodic reduction of CO₂.

By locally isolating the Fe₃C from the water and by reducing the porosity of the corrosion layer, the precipitation of FeCO₃ causes an overall decrease in the galvanic coupling and, above all, profoundly modifies its spatial distribution. In particular, coupling with an empty external Fe₃C layer is probably highly attenuated by the screen of ohmic drop represented by the region obstructed with FeCO₃. The empty outer layer, therefore, is theoretically not very dangerous, in agreement with actual observations (Figure 2).

Conversely, Equations (10) and (11) show that the process of internal acidification begins by electromigration whenever there is a deficit of cathodic reaction on the steel. Therefore, there is no need for large "diffusion distances." A thin layer of empty Fe₃C in contact with the steel is sufficient to cause at least the onset of internal acidification. Only layers obstructed by FeCO₃ directly in contact with the metal can be protective. Again, this corresponds to what is found in practice (Figure 2).

These considerations explain the existence of multiple steady states,² together with the sometimes erratic influence of the iron content in the corrosive medium:

— If the iron content in the test medium is high from the moment of immersion of freshly polished specimens, FeCO₃ can precipitate on the metal, and the layer is protective. If the iron concentration subsequently falls and a certain amount of external redissolution of FeCO₃ exposes an outer layer of empty Fe₃C, this has no effect on the overall protectiveness of the corrosion layer.

— If, on the other hand, the iron content of the medium becomes high only after an initial phase of corrosion leading to the formation of an empty Fe₃C layer, then internal acidification prevents further precipitation of FeCO₃ in contact with the metal, even though the outer part of the layer becomes obstructed. The layer then is unprotective, and even enormous iron supersaturations cannot subsequently render it protective.²

Lateral Stability of Galvanic Coupling

Uniform corrosion does not necessarily leave the surfaces concerned rigorously planar. Random fluctuations of various types occur as a result of a number of causes (segregations, inclusions, crystal texture, turbulence, fretting, etc.). However, in general, after a small disturbance, a stable system reverts naturally to its initial state. There is an average statistical compensation of all past disturbances at any given point. Conversely, a disturbance may take on an amplitude that is no longer negligible compared to the scale on which the system is regu-

lated naturally. In the presence of multiple steady states,² the system path can incorporate a number of irreversible branches.

For example, in an empty layer of porous Fe_3C , a local undulation in the metal dissolution front will not change the uniform nature of the corrosion (Figure 5[a]). In contrast, gradual clogging by FeCO_3 can reduce the thickness of the empty part to a value close to the depth of the undulation (Figure 5[b]). In addition to the galvanic coupling and electromigration flux strictly perpendicular to the initial metal surface, parallel components then arise. This leads to the possibility of spontaneously initiating the lateral galvanic coupling shown in Figure 1. In the same way as spinodal decomposition in alloys is a precursor to the precipitation of separate phases, lateral fluctuations of the galvanic coupling between steel and Fe_3C can give rise to the macroscopic coupling involved in localized corrosion.

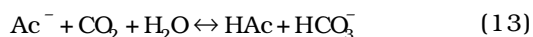
Again, the proposed mechanism is in perfect agreement with the observation of the initiation of mesa attack by intense nucleation of pits,¹⁵ with the presence of empty Fe_3C layers on the corroded "canyons" and sealed Fe_3C layers on the unattacked plateau (Figure 6).¹⁴

INFLUENCE OF HAC

Field experience shows that, except for very high CO_2 partial pressures, the presence of very small amounts of free HAC (or other carboxylic acids) can change the corrosivity of a well dramatically.¹⁰ Until now, the extremely low minimum threshold (0.1 mM/L) has not been explained. In particular, the conventional interpretation in terms of the oxidizing power and the "acidity reservoir" of weak acids does not stand up to comparison between the 0.1 mM/L HAC threshold and the tens of mM/L of dissolved CO_2 , at least in the conditions of the external corrosive medium.

Effect on Uniform Corrosion

Nevertheless, such a low concentration of free HAC signifies that the external medium is potentially able to regenerate HAC from acetate, via the usual reaction for the transfer of acidity between two buffers:



Initially, external HAC diffuses toward the metal, where it is cathodically reduced to Ac^- . The acetate anion, which is completely soluble, then diffuses back outward, where it is reconverted to HAC by Reaction (13). Furthermore, in the presence of galvanic coupling and electromigration, Ac^- is affected in the same way as HCO_3^- . Thus, in addition to internal acidification, there is also local depletion of Ac^- . How-

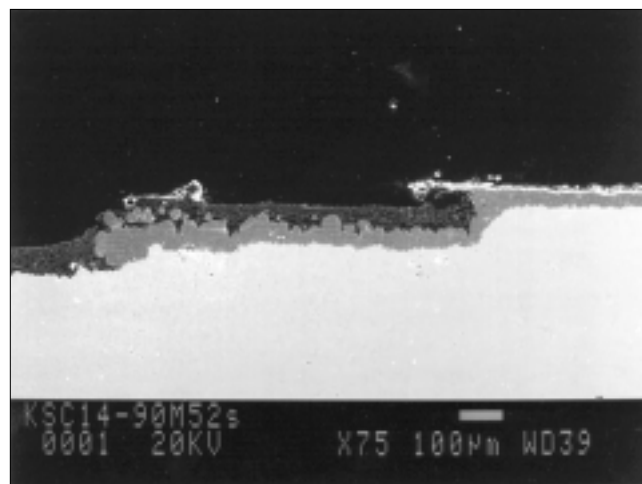


FIGURE 6. Observation of galvanic coupling between empty and sealed Fe_3C layers.¹⁴

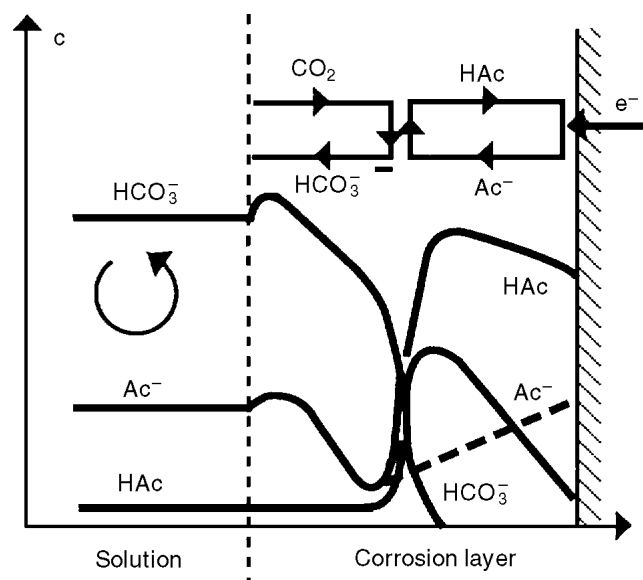


FIGURE 7. Illustration of HAC enrichment in a corrosion layer resulting from internal acidification and galvanic coupling between steel and Fe_3C .

ever, since HAC is a stronger acid than H_2CO_3 , the HCO_3^- ions disappear before the Ac^- ions. Although the acetic buffer is always a minority component in produced waters, at low pH levels, the internal acidification of corrosion layers could very well make it the majority species with respect to the H_2CO_3 buffer. Consequently, the acetate ion would be converted to HAC inside the corrosion layer, without needing to diffuse back into the external medium. The HCO_3^- effectively would be removed from the layer by electromigration but not the acetates (Figure 7). Thus, in the presence of only traces of free HAC in the external medium, internal acidification could

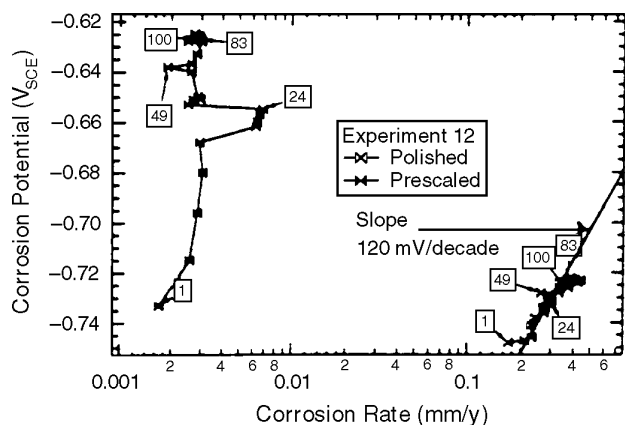


FIGURE 8. Experimental pseudo-polarization curve attributable to passivation beneath a protective corrosion layer.²

produce high local concentrations of HAC in contact with the steel. The high solubility of FeAc_2 would then give free rein to dissolution in this local acetate-rich, HCO_3^- -depleted solution.

Now, since FeAc_2 is much more soluble than FeCO_3 , it is also possible that ion pairing is much less present between Fe^{2+} and Ac^- than previously with HCO_3^- . Then, diffusion fluxes of Fe^{2+} and Ac^- would no longer be coupled through ion pairing. Thus, in an acidized region where HCO_3^- would have disappeared, galvanic coupling can proceed "normally" (i.e., in the presence of a net ionic current $J_{\text{Fe}^{2+}} - J_{\text{Ac}^-}$). In this case, the concentration gradient of Ac^- close to the metallic surface would have the "usual" slope (dashed lined in Figure 7).

Whatever the exact transport process in this acidized region, it remains that, in both cases, the buffering power and the source of acidity close to steel proceed less and less from carbonic species and more and more from acetic ones. This still may increase the detrimental effects of the layers of empty Fe_3C — higher corrosivity and a high difficulty to clog them with FeCO_3 .

Effect on Localized Corrosion

Any substitution of HAC for CO_2 in the cathodic reaction locally replaces the production of a precipitable anion by that of a fully soluble anion. Independently of the Fe_3C and possible coupling and acidification effects, the simple solubility of FeAc_2 thus decreases the protectiveness of corrosion layers. This facilitates the initiation of lateral galvanic coupling. In Figure 1, if the anion X^- is on average a mixture of HCO_3^- and Ac^- , any random fluctuation in their concentration ratio could trigger local coupling, which would become stabilized in the form of permanent localized corrosion. If, as in Figures 7 and 5, this fluctuation occurs in the acid medium already enriched in acetic species, the initiation of local attack would be facilitated.

Comparison Between Service Behavior and Laboratory Experiments

In all cases, the role of HAC with respect to the corrosion product FeCO_3 is like that of a fluxing or complexing agent. However, this action requires already established corrosion layers, in a steady-state regime, and with a certain thickness. This is exactly what is encountered in the field, and it is perhaps the reason why the influence of HAC was discovered by the analysis of service conditions.¹⁰ Conversely, it is perhaps due to the systematic absence of "mature" deposits that the effect of HAC has never been able to be reproduced in the laboratory. What is certain is that the question asked in 1944¹⁶ — "Corrosion by CO_2 or by Acetic Acid?" — and assumed to have been answered in 1951,¹⁷ remains more pertinent than ever.

Passivation

Beneath a Protective Corrosion Layer

The present approach also sheds new light on the question of whether high corrosion resistance results from the intrinsic protectiveness of the corrosion layer itself or to passivation beneath a moderately protective layer.¹ In particular, it has been seen that a layer of Fe_3C sealed by FeCO_3 in direct contact with the metal behaves exactly like a protective deposit of pure FeCO_3 . In both cases, there is no galvanic coupling whatsoever with the steel, and in both cases, the HCO_3^- anion concentration profiles are equivalent to those shown in Figure 3(a).

Compared to general models of protectiveness, where the precipitable anion comes from the outside, the production of HCO_3^- by cathodic reduction precludes the existence of insoluble anionic layers (IA), with exhaustion of the anion due to precipitation. These unprotective layers are replaced by the Fe_3C layers (C), with a conductive compound and galvanic coupling. In practice, their properties and performances are quite similar to those of IA layers, but the prime reason for the depletion of precipitable anion is markedly different. In contrast, insoluble cationic layers continue to exist. Their protectiveness is even enhanced considerably by the increased insolubility of FeCO_3 due to a precipitable anion concentration profile parallel to that of the cation (Figure 3[a]).

While galvanic coupling and electromigration can cause internal acidification for a constant CO_2 level, the absence of coupling and pure diffusional fluxes lead on the contrary to internal alkalization of the liquid in direct contact with the metal (Figure 3[a]). Conditions of this sort, therefore, can combine both an anodic current with a low activity peak due to the high local pH¹⁸ and a cathodic reaction whose limiting current is maintained at a high level by the high local dissolved CO_2 content. Thus, passivation is

possible beneath protective corrosion layers.¹ This is probably the origin of the almost vertical pseudo-polarization curves which are observed sometimes, with low currents and high potentials² (Figure 8). Their explanation by passivation beneath a corrosion layer also would account for the extraordinary inertia of this type of layer,¹ particularly with regard to aggressions of a chemical nature, such as a reduction in pH or in the dissolved iron content.²

CONCLUSIONS

❖ In the study of CO₂ corrosion in steels,¹ the consideration of galvanic coupling between the steel and a layer of undissolved Fe₃C provides the missing link in many mechanistic models. It explains the possibility of local depletion of the precipitable anion in spite of the absence of any precipitation (C instead of IA layers). It also explains how HCO₃⁻ can be produced within the corrosion layer itself, by cathodic reduction of CO₂, and then forcibly removed by electromigration. It shows how unprotective layers can even become corrosive, due to internal acidification.³ Finally, it accounts for the decisive influence which slight traces of free HAc can have on the corrosivity of a medium, by becoming concentrated to almost pure HAc in contact with the metal.

❖ Lateral galvanic coupling explains the breakdown of uniform corrosion and the onset of localized attack, such as pitting and mesa corrosion. Fluctuations in the cells formed between the steel and the Fe₃C, thus, can lead to the stable lateral coupling associated with localized corrosion.

❖ Although the above phenomena are related naturally to the particular chemistry of iron and CO₂, the underlying principles are not limited to this specific case. They can be transposed immediately to the corrosion of steels by H₂S.⁵⁻⁶ Less obviously, this

approach can be applied to the corrosion of copper in aerated water and to the specific role of the semiconducting compound Cu₂O among the numerous copper corrosion products.¹²

❖ With regard to the practical implications for CO₂ corrosion of steels, it will be necessary to make a thorough reassessment of the influence of steel composition and corrosive medium chemistry and to reexamine the effect of time and initial surface condition in laboratory tests.

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