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Chemical and Electrochemical Mechanisms behind Aqueous CO_2 Corrosion of Mild Steel- a Basic Review

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Abstract : *Sweet corrosion (CO_2) is a major concern in internal corrosion of pipelines in oil industry. Dissolution of CO_2 in water facilitates formation of a weak acid, H_2CO_3. Dissociation of carbonic acid provides proton and bicarbonate ions. Furthermore, bicarbonate's dissociation leads to formation of carbonate and hydrogen ions. The thermodynamics and kinetics of such chemical reactions depends on temperature, solution pH, ionic strength, etc. Corrosion process has an electrochemical nature and it is widely agreed that presence of CO_2 in aqueous environments increases corrosion rate of mild steel via accelerating cathodic reactions involved in the corrosion processes. Although mechanism of chemical reactions involved in CO_2 corrosion is widely agreed, disagreement exists on the electrochemical part. This paper reviews the basics of chemical and electrochemical mechanisms in CO_2 corrosion. With the emphasis on the "buffering behavior" and "direct reduction" mechanisms proposed for the presence of carbonic acid at the bulk solution and/or metal surface.*
Keywords: *CO_2 corrosion, Cathodic reaction, H_2CO_3 reduction, buffering behavior, direct reduction.*

I. INTRODUCTION

Non-hydrocarbon gases such as CO_2, H_2S, N_2 are present in oil and gas extraction form reservoirs [1], [2]. Dissolution of CO_2 and H2S in brine (water phase) facilitates formation of weak acid and thus increase corrosion rate. Corrosion caused by CO_2 is called "sweet corrosion" while corrosion by H_2S is known as "sour corrosion" [3]–[6]. Acidic corrosion is a destructive and cost-bearing phenomenon for every industry dealing with metallic structures, especially petroleum industry. Corrosion imposes significant cost of repair and replacement of the damaged infrastructures [7]–[9]. Understanding the exact chemical and electrochemical mechanisms behind acidic corrosion, especially CO_2 corrosion as one of the common causes of corrosion attack in oil industry, is essential in corrosion modeling [10], [11]. This paper provides a basic review on chemical and electrochemical mechanisms behind CO_2 corrosion and discusses the difference between "buffering behavior" and "direct reduction" mechanisms proposed for the presence of carbonic acid at the bulk solution and/or metal surface.

II. CO2 CORROSION MECHANISM

CO_2 is not a corrosive species in any forms (gas, liquid, etc.). The corrosion story begins when dissolved CO_2, in water phase, reacts with water to form carbonic acid. There has be a lot of research to understand CO_2 corrosion mechanisms [12]–[14]. Concisely, CO_2 corrosion comprises a number of chemical and electrochemical reactions. The chemical reactions occurs in the bulk solution, therefore; they are all homogeneous as listed in table 1.

Table 1. Homogeneous chemical reactions taking place in CO_2 aqueous environments

Reaction	Name
$CO_{2(g)} \rightleftharpoons CO_2$ (1)	dissolution of carbon dioxide in water phase
$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (2)	carbon dioxide hydration; formation of carbonic acid
$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ (3)	carbonic acid dissociation
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$ (4)	bicarbonate anion dissociation
$H_2O \rightleftharpoons H^+ + OH^-$ (5)	water dissociation

Hydration of CO_2 (reaction 2) is a slow process (in the order of millisecond) in compare to the other listed chemical reaction in table 1. Moreover, only a very small portion of dissolved CO_2 converts to H_2CO_3

(around 0.1 percent). Dissociation of carbonic acid and bicarbonate anion are the fastest equilibria in table 1 (in the order of sub microsecond) [15], [16].

The electrochemical reactions involved in CO_2 corrosion happen at the steel surface, therefore; they are categorized as heterogeneous reactions. Table 2 shows the main heterogeneous electrochemical reactions taking place at the steel surface (anodic and cathodic).

Table 2. Electrochemical reactions behind mild steel CO_2 corrosion

Reaction	Name
$Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$ (6)	anodic reaction; oxidation of iron
$2H^+ + 2e^- \rightarrow H_{2(g)}$ (7)	cathodic hydrogen evolution; reduction of free hydrogen ions
$2H_2CO_3 + 2e^- \rightarrow 2HCO_3^- + H_{2(g)}$ (8)	cathodic hydrogen evolution; reduction of carbonic acid
$2HCO_3^- + 2e^- \rightarrow 2CO_3^{2-} + H_{2(g)}$ (9)	cathodic hydrogen evolution; reduction of bicarbonate ions
$2H_2O + 2e^- \rightarrow 2OH^- + H_{2(g)}$ (10)	cathodic hydrogen evolution; reduction of water

A sequence of chemical and electrochemical reactions, listed in Table 1 and Table 2 work together to proceed CO_2 corrosion. Electrochemical reactions are faster, in nature, than chemical reactions. Hydration of CO_2 (the slowest chemical reaction) is the rate determining factor in the whole process of CO_2 corrosion.

One can write the overall descriptive reaction in CO_2 corrosion as following

$$Fe_{(s)} + H_2CO_3 \rightarrow FeCO_{3(s)} + H_{2(g)} \qquad (11)$$

Fe (iron) from the steel is oxidized in presence of H_2CO_3 (carbonic acid). H_2 (hydrogen gas) is evolved as a result of H^+ (hydrogen ions) reduction at the steel surface. And $FeCO_3$ (iron carbonate) is the main corrosion product in CO_2 environments which can conditionally provide corrosion protection when it forms [17].

III. BUFFERING EFFECT OR DIRECT REDUCTION OF H_2CO_3

The mechanism of chemical reactions listed in Table 1 is widely accepted. However, three are uncertainties in quantification of reaction constants, thermodynamically and/or kinetically. For instance, different values for equilibrium constant of CO_2 hydration (reaction 2) can be found in literature, ranged from 01×10^{-3} to 2.84×10^{-3} [18]. However, slight differences in the thermodynamic and kinetic constants do not cast doubt on the overall corrosion process.

The anodic dissolution of iron (reaction 6) and two other cathodic reactions (reaction 7 and reaction 10) are agreed by different researchers. However, the "direct reduction mechanisms" proposed for carbonic acid and bicarbonate ion (reaction 8 and reaction 9) have been challenged recently. This mechanism originally proposed by deWaard and Milliams. Then, it was widely accepted and used in corrosion models. However, recently, researchers have cast doubt on "direct reduction mechanism" by claiming another alternative possibility. There is a postulation that the only cathodic reaction is the reduction of free hydrogen ions (reaction 7) in the vicinity of the steel surface. When the H^+ in consumed near the steel surface, carbonic acid dissociates and provides an alternative source of H^+. This mechanism is known as the "buffering behavior". These two conflicting mechanisms are discusses in more details.

a. Direct Reduction

In 1975deWaard and Milliams observed a higher corrosion rate for solutions saturated with CO_2 when compared with HCl solutions at the same condition (pH, temperature, ionic strength, etc.). HCl is a strong acid that dissociate completely in water whereas H_2CO_3 is a weak acid with partial dissociation (protonation). They justified the higher corrosion rate with the direct reduction mechanism of H_2CO_3 at the steel surface.

Later on, the direct reduction of carbonic acid at the steel surface was adopted by many researchers [13], [19]. Figure 1 shows theortical potenthiadynamic sweeps that justify direct reduction of carbonic acid. In this mechanism, the increase of H_2CO_3 concentration in the bulk solution increases both charge transfer current and limiting current (mass transfer zone).
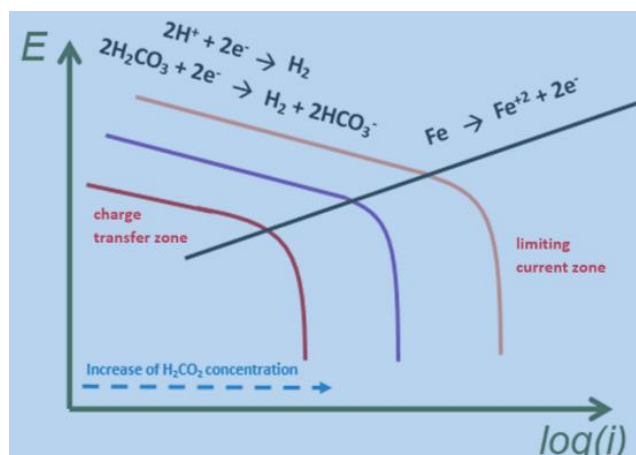
Figure 1. Description of direct reduction mechanism- effect of H_2CO_3 direct reduction on both charge transfer current and limiting current

b. Buffering Behavior & le Chatelier's principle

In the buffering behavior mechanism, reduction of carbonic acid and bicarbonate ion (reaction 8 & 9) do not contribute in the cathodic reaction. Reduction of free hydrogen ion (reaction 7) is considered as the only cathodic reaction. Here, H_2CO_3 and/or HCO_3^- partially protonates (dissociates) to provide most of H^+ (reaction 8 & 9). Then the free hydrogen ions transported and adsorbed on the steel surface to participate in hydrogen evolution process (reaction 7). In this mechanism, carbonic acid behaves as a hydrogen ion reservoir by compensating for the depleted H^+ as a result of hydrogen reduction at the steel surface. This is in accordance with Le Chatelier's principle. In reaction 8 & 9, when the H^+ is consumed by reaction 7 the equilibrium shifts to the right direction and results in more dissociation of carbonic acid and/or bicarbonate ion.

First indication for the buffering behavior of dissolved CO_2 on reduction of hydrogen ions, was made by Hulen *et al*. [20]. Later on, Linter et al. agreed the Hulen *etal*'s work and concluded that the H_2CO_3 reduction is not participating in the cathodic reactions because it is thermodynamically unstable in compare to the H^+ reduction [21]. Recently, Remita *et al*. concluded the buffering behavior of carbonic acid is more evident than its direct reduction in CO_2 saturated solutions. They postulated that in the case of direct reduction of H_2CO_3, the pH at the steel surface should increase in compare to a N_2 saturated solution with the same bulk solution pH. However, they did not observe a different pH at the steel surface of the two solutions. Therefore, they concluded that the buffering behavior of carbonic acid was sufficient to justify the mechanism of sweet corrosion [22].

Figure 2 illustrates the theatrical potenthiadynamic sweeps that justifying buffering behavior of carbonic acid. In this mechanism, the increase of H_2CO_3 concentration only influences mass transfer current.

The true behavior of H_2CO_3 in CO_2 corrosion still have uncertainty and more systematic experiments needed to quantify the contribution of buffering effect and direct reduction of H_2CO_3 behind CO_2 corrosion.
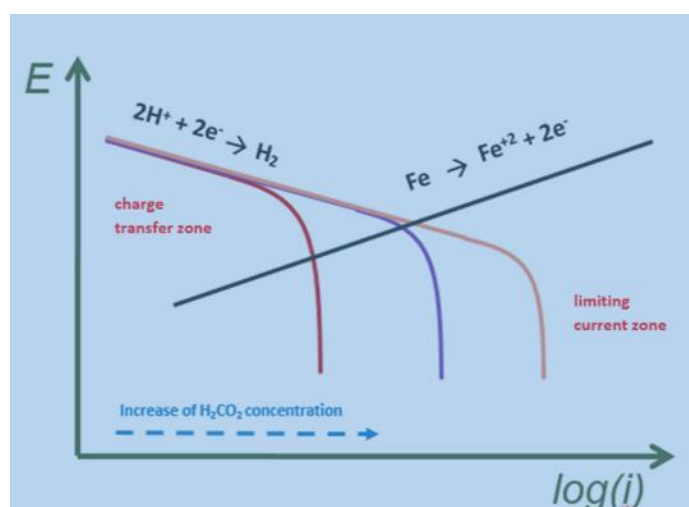

Figure 2. Description of buffering behavior mechanism- H_2CO_3 direct reduction only increases the limiting current.

IV. CONCLUSION

o   Two series of homogeneous chemical reactions and heterogeneous electrochemical reactions are involved in CO_2 corrosion.

o   The Slow hydration of CO_2 is the rate determining factor in corrosion rate calculation

o   The overall mechanism of chemical reactions involved in sweet corrosion are agreed, but disagreement exists on the electrochemical mechanism.

o   There two possibilities to justify the higher corrosion rate in presence CO_2 compared with a HCl solution with the same pH, Temperature, etc.

•   Direct reduction of carbonic acid and/or bicarbonate ion at the steel surface, proposed first by de Waard & Milliams.

•   Buffering behavior of H_2CO_3 by replenishing H^+, proposed first by Hulen *et al*.

o   Experiments that are more systematic needed to quantify the contribution of the two mechanisms.

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