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การกัดกร่อนของเหล็กกล้าภายใต้สภาวะบรรยากาศก๊าซคาร์บอนไดอ็อกไซด์ของอุตสาหกรรมผลิตน้ำมันและก๊าซ: กลไกและการทำนายการกัดกร่อน

Review of Corrosion of Carbon Steel in CO_2 – Containing Environment of the Oil and Gas Industry: Mechanism Understanding to Prediction Model

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บทคัดย่อ

การกัดกร่อนโดยบรรยากาศคาร์บอนไดอ็อกไซด์ก่อให้เกิดความเสียหายต่ออุปกรณ์การผลิต ในอุตสาหกรรมการผลิตสารไฮโดรคาร์บอน ซึ่งอุปกรณ์ดังกล่าวโดยมากนั้นผลิตโดยใช้วัสดุหลักคือเหล็กกล้า ดังนั้นความเข้าใจในกลไกการเกิดการกัดกร่อนประเภทนี้ สามารถนำไปสู่ การออกแบบอุปกรณ์การผลิตที่ถูกต้อง การกำหนดเงื่อนไขในการผลิตที่มีความเหมาะสม และ กระบวนการผลิตในอุตสาหกรรมปิโตรเคมีและการกลั่นที่มีประสิทธิภาพ ดังนั้น บทความนี้จึงนำเสนอ กลไกการกัดกร่อนของเหล็กกล้าในบรรยากาศคาร์บอนไดอ็อกไซด์ รวมทั้ง ตัวแปรต่างๆ ในการผลิตที่ส่งผลกระทบต่อประสิทธิภาพการป้องกันการกัดกร่อนของเหล็กกล้า นอกจากนี้

Review Paper
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บทความยังกล่าวถึงแบบจำลองทางคณิตศาสตร์ที่ใช้ในการทำนายอัตราการกัดกร่อนของเหล็กกล้าในบรรยากาศคาร์บอนไดอ็อกไซด์ของการกัดกร่อนประเภทนี้อีกด้วย

คำสำคัญ: การกัดกร่อนโดยบรรยากาศคาร์บอนไดอ็อกไซด์ การผลิตไฮโดรคาร์บอน เหล็กกล้า

Abstract

CO_2 corrosion has been known as one of the major mode of failure in a lot of the steel process equipment of hydrocarbon production all over the world. Hence, the comprehensive understanding of CO_2 corrosion is essential to establish the robust design, operations and integrity of the hydrocarbon production process. This paper highlights the modern understanding of CO_2 corrosion mechanisms for steels used in oil and gas production. The special attention is also paid to the important parameters affecting the protectiveness of steel under the attack of CO_2 corrosion. Besides, the empirical model for practical engineering application to predict the rate of this specific damage is also presented.

Keywords: CO_2 Corrosion, Hydrocarbon production, Steel

1. Introduction

In oil and gas industry, steel has widely been used as a pipelines and process material due to its availability and usefulness to meet the requirements of mechanical performance, fabrication, and cost [1-2]. This material is regarded as the economical material for oil-gas equipment. However, the major drawback of its efficient utilization is its insufficient corrosion resistance in the corrosive environment, i.e. CO_2 environment [2-3]. Accordingly, thorough design, operation and integrity of hydrocarbon process equipment are essential to control corrosion degradation on this material.

CO_2 corrosion has an enormous economic impact on many industries, particularly the oil and gas industry. In Thailand, for instance, the total cost of corrosion in the oil and gas industry was estimated at around 23,000 million baht in 2011 [4]. Surprisingly, almost half of this cost was related to CO_2 corrosion [5]. For this reason, CO_2 corrosion is evidently a main barrier to successful operation in oil and gas production. It can cause severe localized damages on the steel piping and pressure vessel used for the production of hydrocarbon substances, leading to unexpected shutdown of many production processes [6]. Technically, CO_2 corrosion is a very complicated process, which deals with many electrochemical reactions and ion diffusing process taking place on the interface of the steel and the CO_2- containing solution [5-7]. In addition, its behavior is affected by a variety of different factors, e.g. environmental parameters, the retarding effect of the corrosion product layers, the flow conditions of the solution as well as alloying elements in steel [7-8]. From the engineering point of view, the effective design and operation based on the comprehensive understanding in this particular attack is useful to maintain or control the degradation rate of steel under this environment [9]. Nowadays, many efforts from corrosion scientists have been made to shade the light on the CO_2 corrosion of the steel, but a comprehensive review on this specific damage, particularly on its mechanism and the empirical model for practical design and operating, seems to be lacking. This paper is aimed to fill this gap by outlining the current mechanisms of CO_2 corrosion occurring on the steel and emphasizing on influential parameters of the protective ability of steel subjected to this degradation. Furthermore, the mathematic model used as a practical engineering guideline to predict CO_2 corrosion rate is also introduced.

2. The mechanism of CO_2 Corrosion

CO_2 corrosion is very complex. It deals with a number of chemical, electrochemical, and physical processes, simultaneously taking place on the steel / solution interface. The schematic diagram for CO_2 corrosion mechanism of steel is schematically shown in Fig.1. Generally, CO_2 is a weak acidic gas and it becomes corrosive when it is dissolved in water [9-10]. From Fig.1 CO_2 in gas phase initially dissolves in water containing in solution and then hydrated in water to form a carbonic acid (H_2CO_3).

$$CO_2\,(g) \rightarrow CO_2\,(aq) \tag{1}$$

$$CO_2(aq) + H_2O\,(l) \rightarrow H_2CO_3(aq) \tag{2}$$

H_2CO_3 is not stable and then dissociated to form Bicarbonate (HCO_3^-) and Carbonate ion (CO_3^{2-}).

$$H_2CO_3(aq) \rightarrow H^+\,(aq) + HCO_3^-\,(aq) \tag{3}$$

$$HCO_3^-(aq) \rightarrow H^+\,(aq) + CO_3^{2-}\,(aq) \tag{4}$$

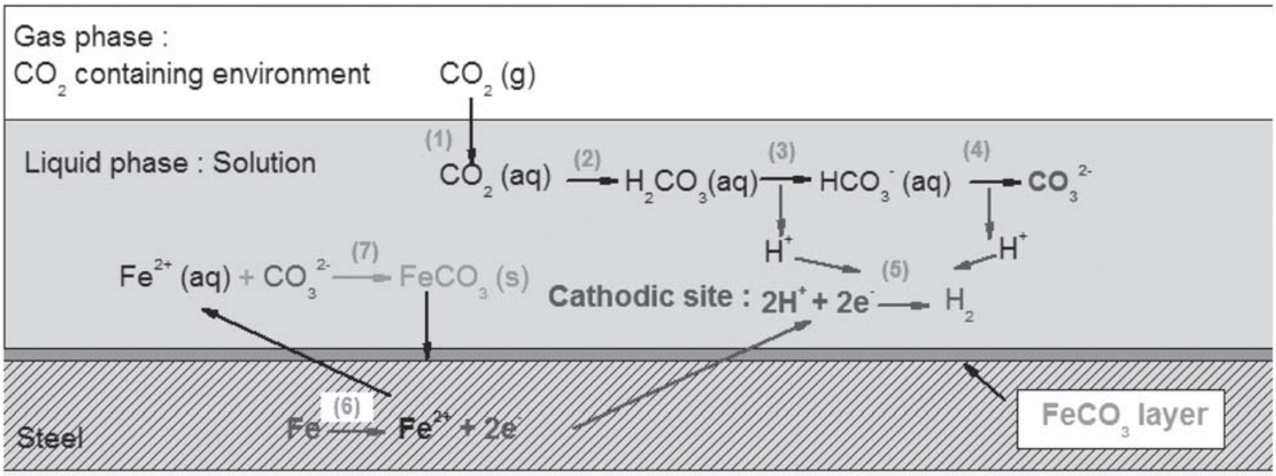

Fig.1 The schematic diagram of feasible reactions in CO_2 corrosion of steel: the numbers (1) – (7) in this figure indicates the sequence of reactions, corresponding to Eqs. (1) – (7) in this content.

Hence, the dissociation of H_2CO_3 acts as a source of H^+, which continuously attacks the steel surface. The hydrogen evolution reaction in Eq. (5) is believed to be the primary cathodic reaction. H^+ from Eq. (3) and (4) can be diffused to the steel surface. Steel in this environment is then anodically dissolved. At the same time, its electrons are cathodically consumed by H^+. Finally, Fe^{2+} from Eq. (6) reacts with CO_3^{2-} to form Iron carbonate ($FeCO_3$) in Eq. (7) as a new phase in steel-solution system [10-11].

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{5}$$

$$Fe\,(s) \rightarrow Fe^{2+}(aq) + 2e^- \tag{6}$$

$$Fe^{2+}\,(aq) + CO_3^{2-} \rightarrow FeCO_3(s) \tag{7}$$

Whether or not CO_2 corrosion of steel can be controlled or uncontrolled depends significantly on a number of different factors governing the deposition rate and retention of the $FeCO_3$ layers [12]. Normally, the deposition rate determines the protectiveness of the $FeCO_3$ layers. If the deposition rate of these layers is sufficiently high, dense and adherent protective layers can be formed and inhibit the CO_2 corrosion process of steel. On the other hand, if the solubility of Fe^{2+} and CO_3^{2-} is high, the porous and discontinuous layers can be precipitated on the steel substrate. The pores in the layers can facilitate the transport of hydrogen or other aggressive anion toward the steel surface and thus accelerating corrosion process [13-15].

3. Parameters affecting CO_2 corrosion

The protectiveness of the corroding steel under the CO_2 –containing environment is critically depends upon the characteristics of $FeCO_3$ layers. To clearly illustrate the formation of the $FeCO_3$ layers, Eq. (7) is re-written in Eq.(8)

$$Fe^{2+}(aq) + CO_3^{2-} \rightarrow FeCO_3(s) \qquad (8)$$

The reaction in Eq. (8) causes the nucleation of $FeCO_3$, taking place on the interface of steel and solution. From this reaction, it is clear that the high super-saturation of Fe^{2+} and CO_3^{2-} brings together with the high deposition rate of $FeCO_3$ layers [16-17], which is important for the formation of the protective $FeCO_3$ layers. Basically, the formation of the thick and dense $FeCO_3$ layers can decrease the corrosion kinetics by providing the barrier to resist the ingress of corrosive agents, such as Hydrogen. At the same time, these layers can also inhibit the steel dissolution [18-20]. The operating conditions related to the formation of the protective $FeCO_3$ are pH, temperature and partial pressure of CO_2. In addition to the properties of $FeCO_3$ corrosion products, the retention of these layers is also vital [21-22]. The presence of turbulence often prevents the retention and the formation of these layers [23-24].

3.1 Operating conditions

Three most influencing parameters on the CO_2 corrosion of steel are pH, partial pressure, and temperature. Many researches pointed out the consistency results that increasing in the pH of solution can lower the solubility of Fe^2 [24-25]. This favors the high saturation of Fe^{2+} and CO_3^{2-} . Hence, dense protective layer can be formed on the steel substrate, resulting in the decreased corrosion rate of steel. A. Dugstad [26] reported that the possibility of the formation of protective layers is increased when pH of solution is greater than 5. The effect of the partial pressure of CO_2 on the formation of the $FeCO_3$ protective layer has also been studied by a number of scientists [27-28]. Their works suggested that increasing partial pressure of CO_2 tends to increase the concentration of H_2CO_3, which can subsequently be dissociated to liberate hydrogen ions and cause the increased corrosion rate of carbon steel. Nevertheless, the useful work from B. Kermani et al [29] reported that in case of the high pH condition, increasing partial pressure of CO_2 can increase the concentration of Fe^{2+} and CO_3^{2-} , and thus promoting the formation of the corrosion product layers. For the effect of temperature, it has been known from Arrhenius Equation that increasing temperature accelerates all chemical reactions [30-31]. From this reason, corrosion rate of steel tends to increase. However, the results from C. deWarrd et al [32-33] exhibited that for high pH solution, increasing temperature decreases the solubility of $FeCO_3$ and CO_2.

Therefore, increasing temperature in such condition accelerates the precipitation kinetics of $FeCO_3$, enhancing the formation of the protective $FeCO_3$ layers.

3.2 Alloying elements

In many special conditions, the corrosion resistance of ordinary steel cannot meet the demand of the production system. For examples, Acidic conditions prevent the formation of dense $FeCO_3$ layers of the steel. Hence, it is necessary to improve the corrosion resistance of the ordinary steel. To achieve this goal, Cr-steels have been developed and employed in the severe corrosion environments. B. Kermani at al [34] found that adding the carbide-forming elements and lowering the carbon content in the alloyed steel can improve the protectiveness of the corrosion product layers. This is because the carbide-forming elements preferably react with carbon to form the carbide compound [35], which allows the high amount of free Cr in the corrosion product to provide enhanced corrosion protection.

3.3 The flow of solution

Usually, the effect of the solution flow is to disturb the formation of the adherent corrosion products, or remove them, causing the increased corrosion rate [36]. Flow disturbances, such as valves, and U-bends can induce the shear stress, which can destroy the protective layers. Excessive turbulence prevents the formation and retention of the protective $FeCO_3$ layers. In reality, the presence of the multiphase flow of CO_2-containing solution quickly removes the corrosion products, promoting the accelerated corrosion process [37].

4. CO_2 corrosion prediction model

Principally, steel under the attack of CO_2 corrosion is subjected to two basic types of corrosion: General corrosion and localized corrosion [38].

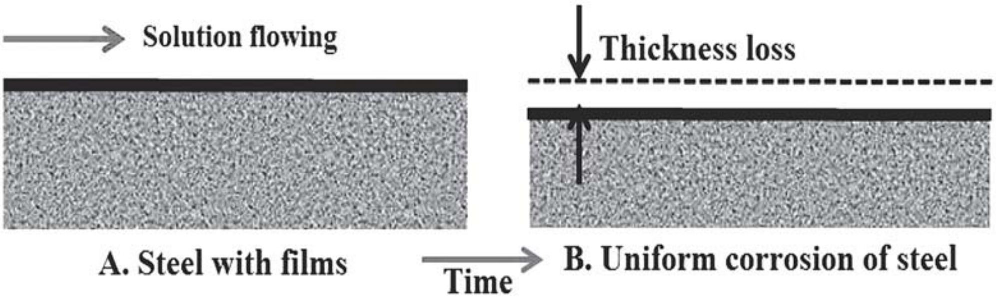

Fig.2 Schematic diagram for General or uniform corrosion of CO_2 corrosion.

General or uniform corrosion is regarded as the uniform dissolution of the corroding surface, as schematically shown in Fig.2. Uniform corrosion of CO_2 corrosion is one of extensively researched researches in corrosion community. The most widely used model for estimating CO_2 corrosion of steel in this corrosion form is proposed by De Waard and Milliams [39-40]. In this model, estimated corrosion rate of steel is a function of temperature and CO_2 partial pressure. The assumption of this model is that H^+ ions in the solution come from the dissociation of H_2CO_3. This model has been proven to be an effective model, which is still be used in the engineering design and inspection purpose for hydrocarbon production pipelines and equipment. This model is given in Eq. (9).

$$\text{Log } V = 7.96 - (230 / T+273) – (5.58 \times 10^{-3} T) + 0.67 \log P \tag{9}$$

Where V is an estimated corrosion rate (mm/year), T is temperature (degree of Celsius) and P is the partial pressure of CO_2 (bar).

Although this model can offer the estimated corrosion rate of steel under the attack of CO_2, the limitations of this model is also realized [41-42]. Firstly, the model is based on the corrosion rate of bare steel surface. However, in reality, steel is covered with the $FeCO_3$ layers. So, the corrosion rate in the real situation should be less than that from model. Secondly, the model does not take the role of turbulence. So, the estimated corrosion rate from the model may not correspond to that from the application with turbulence.

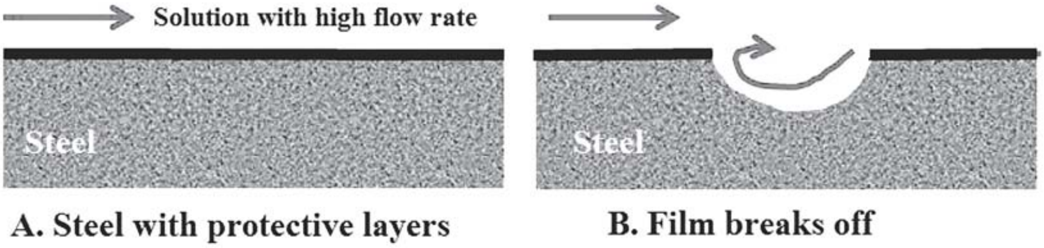

Fig. 3 The schematic illustration of the localized CO_2 corrosion.

In contrast to the general corrosion, steel subjected to the CO_2 corrosion can also be locally attacked. In this particular form, the anode and cathode area varies randomly, but only small areas are severely attacked. Thus, a number of small pits can be formed, leading to the failed steel piping or equipment in hydrocarbon production. Fig. 3 shows the schematic illustration of the localized CO_2 corrosion. This damage starts with the dissolution of steel under the corrosion product layers, subsequently breaking these layers at certain positions.

The solution with the high flow rate accelerates the dissolution of steel and prevents the re-formation of the corrosion layers [43]. So, the effect of high flow rate as well as turbulence is enormous on the protective $FeCO_3$ layers. Up to now, no specific models can efficiently estimate the localized attack [44]. In practice, to prevent this effect, engineers may add the corrosion allowance up to 6.4 mm [45], or use alloyed steel, i.e. Cr-Steels to withstand the severity of CO_2 corrosion.

5. Conclusion

In this paper, the mechanisms, the influential parameters and the predictive model of CO_2 Corrosion of steel were already reviewed. It is obvious that the CO_2 corrosion behavior of steel is greatly related to the formation of the protective $FeCO_3$ layers, which are dominated by operating conditions. The formation of the protective $FeCO_3$ layers can potentially be enhanced by following suggestions.

- Operating at high temperature: This condition can decrease corrosion products solubility, CO_2 solubility, and thus increasing the precipitation rate of corrosion products.
- Increasing pH of solution: This situation can decrease solubility of corrosion products, and promote the precipitation of corrosion layer.
- Avoiding turbulence

The model given by De Waard and Milliams cannot provide an exact corrosion rate. Instead, it can be used just a guideline for design and operation because important effects, i.e. the role of flow rate and the corrosion product layers, are not included in this model. When the turbulence or high flow problem is unavoidable, increasing the corrosion allowance is usually a choice to extend the remaining service life of steel pipelines and equipment. The use of the high resistance alloyed steel, such as Cr-steels, as an alternative material is also an effective option to minimize the severity of the CO_2 corrosion.

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