CorrCompilations

CO_2 AND H_2S METAL LOSS CORROSION— 10-YEAR REVIEW

Editor: Yves Gunaltun

NACE INTERNATIONAL

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Foreword

The prediction and control of metal loss corrosion by carbon dioxide (CO_2) and hydrogen sulfide (H_2S) has been one of the big challenges facing the oil and gas industry. Engineers, researchers, and academics working on prediction models have long known that the prediction of CO_2 and H_2S metal loss corrosion is like solving a mathematical equation with 100 interacting parameters. Throughout these efforts, we all understood that the end of the tunnel would not be reached any time soon. However, this understanding was encouraging rather than discouraging, and it sustained research and development (R&D) projects and programs for almost four decades.

By the mid-1990s, the number of publications on the subject started to increase exponentially. Oil and gas producers, universities, and research institutes around the world were conducting studies in the area. Corrosion mechanisms, prediction models, and corrosion control and monitoring systems were proposed and discussed, but the overall task was extensive. The R&D activities at different institutions were directed in different directions. Some researchers favored the study of the interaction at the metal-liquid interface; others chose to investigate the impact of flow, flow regimes, and water and oil chemistries. Additional research projects focused on materials and chemicals. These research activities were complementary but were not sufficiently coordinated. In early 2000, it was not clear what was important and what was not. The magnitude of the overall effort was so large that it was very difficult to perform a gap analysis. As progress was made, it seemed that the end of the tunnel was moving away.

It was in this context that I proposed, in 2004, to review and summarize what had been done and what was known on the subject to guide research institutions and individuals. Through this review, I intended to

- Evaluate the gap between what had been done and what needed to be done
- Reorient research projects for the next 10 years

After receiving the necessary support from some colleagues at different companies and institutions, I proposed to NACE International that it conduct a special symposium with invited authors. This special symposium would cover all aspects of CO_2 and H_2S metal loss corrosion in the oil and gas industry. It took about two years to define the scope, fix the format, identify the papers to be prepared and the potential authors, receive the appropriate NACE approvals, and—finally—organize the first symposium.

The first symposium was presented in 2006. During the one-day symposium, 22 invited specialists, experts, and well-known researchers presented 13 papers on the following topics:

- Fundamental aspects (mechanism, main parameters)
- Oil characteristics, water-oil wetting and flow influence
- Influence of H_2S on CO_2 corrosion
- Field data: collection, evaluation, and use for corrosivity prediction and validation of models
- Corrosion control by inhibition, environmental aspects, and pH control
- Corrosion monitoring and inspection
- Materials review
- Design aspects: best practices

The symposium was a big success.

Several years later some of the participants asked for another symposium on the same subject. After discussion with the authors, it was decided to present a second symposium after about 10 years. The second symposium was presented in 2015 with the same objectives as in 2006. Most of the authors were identical, but some new authors were also invited. Twenty-one authors presented 12 papers that covered the same aspects of CO_2 and H_2S corrosion as in 2006, except for the paper on materials because there had not been sufficient progress since 2006 to justify another paper. The symposium was once again a big success.

The presented papers from both 2006 and 2015 have been widely used in the industry, as well as by research institutions and individuals. To make the papers more available and better contribute to research and operations, some authors suggested proposing that NACE publish the papers as a book. NACE enthusiastically accepted the proposal and, thanks to the support of Jonnie Fuller, the publication of the book became possible.

Yves Gunaltun
Chair of the 2006 and 2015 Sessions

Paper No.
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CORROSION
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Fundamental Aspects of CO_2 Metal Loss Corrosion
Part I: Mechanism

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ABSTRACT

Carbon steel is thermodynamically unstable in water with dissolved CO_2 and the only reason that carbon steel is so attractive and can be so widely used in oil and gas production is that the steel surface becomes covered by a protective layer of corrosion products, oil, mineral scale or inhibitors. It is relatively easy to predict and explain the high corrosion rates on bare steel. The real challenge is to reduce the corrosion and that requires knowledge about the performance of the protective layers, means to predict the breakdown of the layers and methods and techniques to ensure that robust layers form on the surface.

The paper discusses how CO_2 affects the water chemistry, the electrochemical reactions on the bare steel surface, and the initiation and growth of protective corrosion product films. As many sweet systems contain organic acids that affect the solution chemistry and the formation and stability of the $FeCO_3$ corrosion product films, organic acids need also to be considered when the effect of CO_2 is discussed.

Keywords: CO_2 corrosion, carbon steel, internal corrosion, mechanisms, corrosion films

INTRODUCTION

The mechanism of carbon steel corrosion in a CO_2 containing environment has been studied and debated for decades. Hundreds of papers related to CO_2 corrosion have been published and a large variety of corrosion rates and mechanisms have been reported. Oil companies and research institutions have analyzed the data and developed a number of prediction models[1] to take account of the various parameters that determine the corrosion rate. The models give up to two decades difference in the predicted CO_2 corrosion rate and it all depends on how the various parameters are treated and how much conservatism that is built into the model.

In order to explain the confusion and the apparently contradictory observations and results that have been seen and reported, it is important to realize that the term "CO_2 corrosion" and the effect of CO_2 is not related to one mechanism only. A large number of CO_2 dependent chemical, electrochemical and mass transport processes occur simultaneously on and close to the corroding steel surface. The various reactions respond differently to changes in CO_2 partial pressure, temperature, water chemistry, flow and other operational parameters. All the reactions should be taken into account when corrosion in a CO_2 containing environment is to be quantified and explained.

Many researchers have studied and discussed the electrochemical reactions taking place on the bare steel surface. The mechanisms that control the rate of the electrochemical reactions are of great academic interest, but are less important when it comes to the practical application of carbon steel. When carbon steel is directly exposed to water and CO_2 the bare steel corrosion rate will under almost all circumstances become prohibitively high for practical use in oil and gas production. This is illustrated in Figure 1 where the corrosion rate has been predicted[2] for various CO_2 partial pressures and pH values as a function of temperature. The corrosion rate predicted up to 40 °C apply for bare steel, while partly protective films are formed at higher temperature. It is seen that the corrosion rates are in the order of several mm/year, even at CO_2 partial pressures below 0.5 bar, i.e. pressures where the old "rule of thumb" says that carbon steel can be applied without any treatment[3].

In the present paper it is focused on fundamental corrosion mechanisms in sweet systems. Three major effects of CO_2 will be addressed: The effect on the water chemistry, the effect on the electrochemical reactions, and the impact on the initiation and growth of corrosion product films. As many sweet systems contain organic acids that affect the solution chemistry and the formation and stability of the $FeCO_3$ corrosion product films, organic acids also have to be included in the discussion. The effect of other parameters is discussed in the paper "Fundamental Aspects of CO_2 Metal Loss Corrosion, Part II: Influence of different Parameters on the CO_2 Corrosion Mechanism"[4]

CO_2 AND THE EFFECT ON WATER CHEMISTRY AND pH

When CO_2 is dissolved in water it is partly hydrated and forms carbonic acid:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{1}$$

Carbonic acid is diprotic and dissociates in two steps:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \tag{3}$$

The resulting pH is a function of the CO_2 partial pressure. This is illustrated in Figure 2 where the pH has been calculated # as a function of CO_2 partial pressure in unbuffered water and in water with 1, 10 and 100 mM alkalinity respectively. The pH decreases with increasing CO_2 partial pressure. When the water is buffered, the pH increases but the dependency of the CO_2 partial pressure follows the same trend as for pure water.

When the steel corrodes, Fe^{2+} and an equivalent amount of alkalinity are released in the corrosion process.

$$Fe + 2H_2CO_3 \rightarrow Fe^{2+} + 2HCO_3^- + H_2 \tag{4}$$

The pH in the solution increases and when the concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, precipitation of $FeCO_3$ can occur:

$$Fe^{2+} + CO_3^{2-} \Rightarrow FeCO_3(s) \tag{5}$$

When solid $FeCO_3$ is formed at the same rate as the steel corrodes, the pH becomes constant in the corroding system.

The solubility of $FeCO_3$ is strongly dependent on the pH and the CO_2 partial pressure. This is illustrated in Figure 3 where the amount of Fe^{2+} needed to be produced by corrosion to reach $FeCO_3$ saturation is plotted as function of pH at the start of the corrosion process (1 wt% NaCl). It is seen that $[Fe^{2+}]_{sat}$ is much higher in condensed water than in typical formation water with a pH above 5. When the system is pH stabilised at pH 6.5-7.5, $[Fe^{2+}]_{sat}$ is only a fraction of a ppm and is reduced 100 times per unit pH increase. It is important to note that the solubility curves in Figure 3 are not parallel and they cross in the range pH 4.5 to 5. The consequences are illustrated in Figure 4 where the pH is kept constant while the Fe^{2+} solubility is plotted as a function of CO_2 partial pressure. It is seen that the solubility of Fe^{2+} goes through a maximum for pH 5 and 5.5. At lower pH the solubility increases with increasing CO_2 partial pressure while the trend is opposite at pH 6. As the pH is often used as an indicator for the corrosivity of produced water it should be noted that corrosion films form more easily at pH 5 with very high CO_2 partial pressures (>> 1 bar) than with 1 bar CO_2[5]. When comparing the corrosivity of various waters, a higher pH will always give less contribution from the H^+ reduction reaction, but the pH cannot be used directly to predict the likelihood for formation of protective corrosion product films.

The presence of HAc and other organic acids makes the water chemistry much more complex. The interaction of HAc has been discussed in detail in two recent review papers by Crolet and Bonis[6] and by Gulbrandsen[7]. HAc is a weak acid that is readily soluble in water. The equilibrium HAc partial pressure over a 1 mM HAc solution is less than 1 Pa at temperatures up to 100 °C. As pointed out by several authors[7,8], HAc is often referred to as a stronger acid than carbonic acid in the literature. The source of this confusion is that dissolved CO_2, and not only H_2CO_3, is often erroneously included in