Reducing CO$_2$ Corrosion of Gas Transmission Pipelines by Injection of Mono Ethylene Glycol

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Abstract- Gas Transmission pipelines suffer from internal corrosion in CO$_2$ environments. Addition of Mono Ethylene Glycol (MEG) reduces the corrosion rate by preventing or reducing the condensation rate of the water vapor present in the gas phase and confining the water activity. The addition of MEG also decreases the solubility of CO$_2$ in liquid solution. Consequently, reduces the corrosion rate by limiting the formation of carbonic acid H$_2$CO$_3$ that is responsible for higher corrosion rate in CO$_2$ media. Furthermore, in the presence of MEG, a thin layer forms on the steel surface that can reduce the iron dissolution rate and thus protect the pipeline from further corrosion.

Keywords- *CO$_2$ Corrosion, Gas Pipeline, Top of the Line Corrosion, FeCO$_3$*

I. INTRODUCTION

The operational conditions of gas fields can cause severe internal corrosion to carbon steel tubular. However, carbon steel pipelines are widely used in oil industry since they are inexpensive in comparison to pipelines made of stainless steel and/or corrosion resistance alloys (CRAs). The weakness of carbon steel pipelines can be compensated by applying appropriate corrosion control methods. Corrosion inhibitors and MEG are two popular chemicals used by oil companies to protect their tubular assets from internal corrosion.

Dry CO$_2$ is not corrosive in any forms (gas, liquid, etc). However, when it commingled with water, carbonic acid (H$_2$CO$_3$) will form. H$_2$CO$_3$ is a weak acid and is widely believed to be the reason for corrosion attacks in aqueous CO$_2$ environments.

The magnitude of CO$_2$ corrosion of carbon steel pipelines is influenced by important factors such as water chemistry, fluid velocity, CO$_2$ concentration, temperature, etc. corrosion of gas pipelines made of carbon steel can be mitigated by formation of protective corrosion product layers on the steel surface, use of film forming corrosion inhibitors, use of glycol dehydration and pH stabilization.

II. CO$_2$ CORROSION MECHANISM

Carbon steel can growingly be corrode when exposed to aqueous CO$_2$ environments. There a number of parameters that need to be considered to understand the mechanism of CO$_2$ corrosion for carbon steel pipelines, these are briefly described below.

A. Chemical Reactions

Water chemistry is considered one of the important parameters that affect CO$_2$ corrosion. Gaseous CO$_2$ can dissolve in water and convert to aqueous phase as described in Equation (1) [1]:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}, \qquad K_{sol} = \frac{c_{CO_2}}{pCO_2} \qquad (1)$$
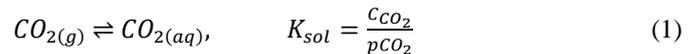
Where K_{sol} is the temperature-dependent solubility constant of CO$_2$.

The dissolved, or aqueous CO$_2$, will then partially be hydrated to form carbonic acid:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}, \qquad K_{hy} = \frac{c_{H_2CO_3}}{c_{CO_2}} \qquad (2)$$
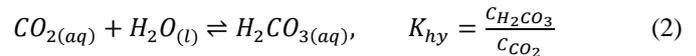
Where K_{hy} is the equilibrium constant for CO$_2$ hydration reaction.

The carbonic acid partially dissociates to provide hydrogen ion and bicarbonate ion:

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}, \qquad K_{ca} = \frac{c_{H^+} c_{HCO_3^-}}{c_{H_2CO_3}} \qquad (3)$$
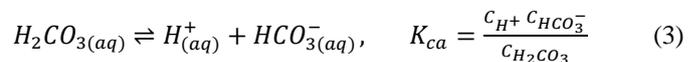
Where K_{ca} is the equilibrium constant of the first dissociation of carbonic acid.

Bicarbonate ions then partially dissociate to provide carbonate and hydrogen ions:

$$HCO^-_{3(aq)} \rightleftharpoons H^+_{(aq)} + CO^{2-}_{3(aq)}, \qquad K_{bi} = \frac{c_{H^+} c_{CO_3^{2-}}}{c_{HCO_3^-}} \qquad (4)$$
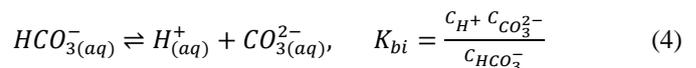
Where K$_{bi}$ is the equilibrium constant.

Hydrogen ion can also be derived from dissociation of water molecules:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}, \qquad K_{wa} = c_{H^+} c_{OH^-} \qquad (5)$$

Where K_{wa} is the equilibrium constant of water dissociation reaction.

When glycol, such as MEG is added to the system (gas pipeline), the chemistry of water/MEG mixture and equilibrium constants values, described in the aforementioned reactions, will be different. Mainly because the MEG decreases the CO_2 solubility and thus directly affect the formation rate of H_2CO_3 (Equation 2).

B. Electrochemical reactions

The electrochemical reaction that occurs on the steel surface involves the cathodic evolution of hydrogen (reduction) and the anodic dissolution of iron (oxidation). The cathodic evolution of hydrogen can be described by the following half-reactions [1]:

Reduction of hydrogen ions. The hydrogen ions come from partial dissociation of H_2CO_3, HCO_3^- and H_2O. These can be considered to be transported from the bulk solution to the surface for the subsequent reduction:

$$2H_{(aq)}^+ + 2e^- \rightarrow H_{2(g)} \tag{6}$$

The direct reduction of H_2CO_3:

$$2H_2CO_{3(aq)} + 2e^- \rightarrow H_{2(g)} + 2HCO_{3(aq)}^- \tag{7}$$
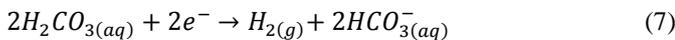
The direct reduction of bicarbonate HCO_3^- at pH<5, where it is a dominant species [2]:

$$2HCO_{3(aq)}^- + 2e^- \rightarrow H_{2(g)} + 2CO_{3(aq)}^{2-} \tag{8}$$
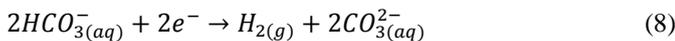
The direct reduction of water, this can be significant if pH>6 and partial pressure of CO_2 (pCO_2) << 1[3]:

$$2\,H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH_{(aq)}^- \tag{9}$$

The anodic half-reaction corresponds to the oxidative dissolution of iron:

$$Fe_{(s)} \rightarrow Fe_{(aq)}^{2+} + 2e^- \tag{10}$$

C. Mass Transfer

The rate of electrochemical reactions at the steel surface is governed by the mass transport rates of the electroactive species coming from the bulk solution and steel surface. In CO_2 corrosion, mass transport occurs *via* molecular diffusion, within a diffusion boundary layer, and *via* convection, due to the movement of solution over a metal surface [3].

In electrochemical processes behind CO_2 corrosion, the concentration of hydrogen ion is depleted thorough cathodic reactions at the steel surface and concentration of ferrous ion increases due to anodic dissolution of iron. These electrochemical reactions are strongly affected by mass transport of Fe^{2+} to bulk solution and H^+ to the steel surface. However, the rate determining step for such electrochemical reaction behind corrosion is the chemical reaction of CO2 hydration (formation of carbonic acid). Because the chemical reaction of the dissolved CO_2 to form acidic species is much slower than the diffusion rate of H^+ and Fe^{2+} [4].

D. Iron Carbonate as the Main Corrosion Product in CO_2 Environments

The ferrous ion (Fe^{2+}) can pair with the carbonate anions (CO_3^{2-}), which forms due to the dissociation reaction of bicarbonate ions, to form iron carbonate as the main corrosion product. The protectiveness of $FeCO_3$ is dependent on the precipitation rate. When the precipitation and/or formation rate of $FeCO_3$ on the steel surface exceeds the corrosion rate (oxidative dissolution of iron), an adherent and dense iron carbonate layer can form on the steel surface. The precipitation rate of $FeCO_3$ is also dependent on the pressure of CO_2 and temperature. The precipitation rate is described by the saturation equation (SS) of iron carbonate, which is defined as:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}} \cdot c_{CO_3^{2-}}}{K_{sp}} \tag{11}$$

Where K_{sp} is the solubility limit of iron carbonate at the pipeline operational condition.

The saturation value (SS) has to be greater than unity (supersaturation condition) to thermodynamically expect precipitation of $FeCO_3$. That leads to formation of an adherent and dense iron carbonate layer if the precipitation rate is higher than corrosion rate.

III. CORROSION OF INTERNAL GAS PIPELINES AND CONDENSATION PROBLEM

In CO_2 gas pipelines, the CO_2 can be transported in gas, liquid, or supercritical form. The water is always present as a liquid at the temperature/pressure typically experienced in a gas field. When the gas is transported in the pipeline all free water is removed at the gas field/offshore platform. However, if temperature decreased during transportation, some of the water vapor will be condensed on the top of the internal wall, as shown in Figure 1. This condensed water will cause severe corrosion to the top and bottom wall of the pipeline.

The condensed water will form a thin film of liquid which is enriched in carbonic acid H_2CO_3 coming from the hydration reaction of CO_2.

There are many studies discussed the internal CO2 corrosion of oil and gas pipelines [5]–[13]. Gunaltan et al. divided the corroded pipe wall in to three parts; the bottom, the side, and the top of the line. The top of the line corrosion (TLC) is the most important part, because an unprotected iron carbonate layer can be formed and leads to localized corrosion that is more dangerous than uniform corrosion [14].

In addition to water condensation, if temperature decreased to less than 10° C, water start to form hydrates which can block the flow by the hydrate plugs inside the gas pipeline. To overcome condensation and hydrate problems, glycol dehydration, such as monoethylene glycol (MEG) can be injected with the gas stream to absorb the water and reduce its dew point.
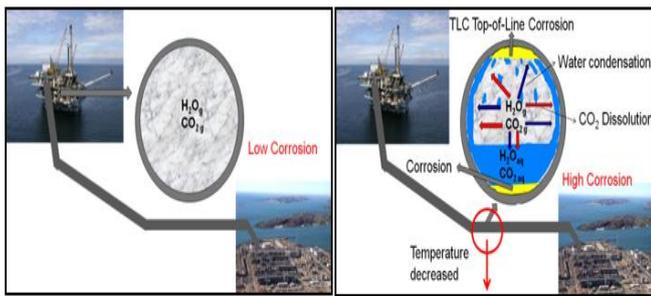
Figure 1. Drop in temperature leads to condensation of water vapor on the steel surface

The addition of glycol will help to reduce the top of the line corrosion (TLC) corrosion and the corrosion in the bottom of the pipeline. However, if the temperature has not been decreased to lower than the vapor temperature of the water, the high concentration of the glycol can lead to absorb more water and increase the solubility of CO_2 and corrosion rate. Therefore, a good assessment of the amount of glycol that has to be added must be taken into account.

A. Glycol Dehydration

To avoid the formation of hydrates, large quantities of glycol dehydration are injected with the gas stream to inhibit hydrate formation which can cause plugging problems in the gas pipelines. The most known glycol dehydrations which are mainly used are Methanol, Diethylene glycol (DEG), Monoethylene glycol (MEG), and Triethylene glycol (TEG). The use of methanol is economically favorable because it is difficult to recover in most cases. MEG and TEG are preferred over DEG, since MEG and TEG has lower vapor temperature (less than −10 °C). All glycols can be recovered and recycle again.

B. Mono ethylene Glycol (MEG)

MEG is considered the most used and efficient glycol dehydrations that used in oil and gas industry. When MEG injected in the gas stream, it will absorb water vapor from the gas and reduce the water vapor temperature [15].

Because corrosion inhibitor is not effective in the case of TLC, MEG can help to prevent the water vapor condensation and reduce the corrosion. There are many studies reported that the MEG can help to reduce the corrosion rate in most cases, and most of these studies stated that the addition of MEG reduce the solubility of CO_2 that leads to reduce the corrosion rate [16], [17]. *Gulbrandsen et al.* assumed that MEG can decrease CO_2 corrosion by reduce the solubility of the CO_2, which leads to decrease the activity of water and corrosion rate [16]. In another study, Oyevaar et al. reported that the solubility of CO_2 decrease as increase the concentration of MEG until 60% MEG is reached, then the solubility start to increase again [17].

IV. CONCLUSION

CO_2 corrosion is a major concern for oil and gas pipelines. Injection of MEG is one of the efficient method to mitigate the internal corrosion of gas pipelines. MEG affects the CO_2 corrosion mechanisms. Formation of MEG film on the steel surface reduces the solubility of CO_2 in the water phase and decrease iron dissolution rate and thus corrosion rate. Presence of MEG increase the local pH and favors the precipitation of $FeCO_3$. $FeCO_3$ is widely believed to be a protective layer against further corrosion for carbon steel pipelines. The optimum concentration of MEG for mitigating corrosion of gas pipelines should be determined based on the operational parameters of the pipelines.

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