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CO_2 corrosion control in steel pipelines. Influence of turbulent flow on the performance of corrosion inhibitors

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ABSTRACT

Corrosion associated with aqueous environments containing carbon dioxide (CO_2) and/or hydrogen sulphide (H_2S), is a well-known phenomenon in oil and gas industries. This type of corrosion is of particular importance in transportation through steel pipelines. This transportation process could involve the movement of a complex mixture of gas and liquids. This moving mixture is in close contact with the inner surface of the steel pipelines and corrosion can occur. It has been demonstrated that this corrosion is influenced by flow.

In oil and gas industries, film-forming corrosion inhibitors are the main tool used to control inner corrosion in pipelines. The movement of the environment generates mechanical shear stresses on the surface of the steel that can interfere with the formation of the film. This phenomenon is frequently not taken into account in corrosion control strategies and could cause problems. Despite the importance of this, there are few scientific studies available, which can provide control criteria.

This work presents some ideas developed in order to understand the influence of flow on the corrosion process, making emphasis in the corrosion process associated with carbon dioxide (CO_2).

1. Introduction

In the oil and gas industries, hydrocarbons containing a certain amount of dissolved carbon dioxide (CO_2) are known as “sweet”. On the other hand, hydrocarbons containing a certain amount of dissolved hydrogen sulphide (H_2S) are known as “sour”. From a geological point of view, the presence of carbon dioxide (CO_2) and hydrogen sulphide (H_2S) in oil and gas reservoirs is a consequence of several physicochemical processes that takes place in the formation. H_2S can also be generated by microbial activity, phenomenon known as “reservoir souring”.

Although oil and gas that are transported in pipelines are subjected to various treatments to remove impurities, they still retain some contaminants that can affect the physical integrity of the steel pipelines due to corrosion processes (CO_2, H_2S, microorganisms, etc.). When a steel pipeline transports a mixture of hydrocarbons and water containing dissolved CO_2 or H_2S, these gases can dissolve in the aqueous phase, decreasing pH and increasing their corrosive tendency.

These problems have led to the implementation of various methods to control corrosion. These methods include the use of corrosion resistant materials, modification of the aggressive medium and the use of corrosion inhibitors. Due to various technical and economic advantages, the method most commonly used to control internal corrosion of pipelines transporting hydrocarbons is the addition of chemical compounds known as corrosion inhibitors. The effectiveness of these chemical compounds depends on different parameters, such as environment composition, temperature, shear stresses generated by the movement of the fluid, etc. In the oil and gas industries, film-forming corrosion inhibitors are the main tool used to control inner corrosion of transport steel pipelines. This type of corrosion inhibitors is organic chemical compounds that form a thin film on the surface of the steel, isolating it from the corrosive environment and thus decreasing corrosion rate.

Understanding the corrosion process that occurs at the interface of a metallic surface in contact with an aqueous environment containing dissolved CO_2 or H_2S and the influence of different parameters such as temperature, pressure, water content, pH, chemical composition of the environment, presence of corrosion

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products on the metal surface and corrosion inhibitor present is an important research area, leading to ensure the integrity of transport pipelines.

On the other hand, transport pipelines handle fluids in constant motion. This movement generates shear stresses on the inner wall of the pipeline. These stresses can affect the adhesion of a corrosion inhibitor film to the metal surface. Nevertheless, there is little scientific and technical information concerning the behaviour of an inhibitor film formed on a metal surface, which is in contact with a moving fluid. Additionally, the flow regime most commonly present in pipelines transporting hydrocarbons is turbulent.

Turbulent flow increases the mass transport of corrosive species, from the bulk of an aggressive environment towards the metal surface. Turbulent flow may also cause the removal from the metal surface of films formed from corrosion products or corrosion inhibitors. From a theoretical point of view, the analysis and prediction of turbulent flow is complex due to its random nature.

All these issues make the description, understanding and control of a corrosion phenomenon in a flowing environment, a complex topic.

2. Carbon dioxide (CO_2) chemistry in water

When CO_2 gas is in contact with water, the following chemical equilibria take place (Quinn and Jones, 1936; Kern, 1960).

a) CO_2 gas ($CO_{2(g)}$) dissolves in water ($CO_{2(aq)}$) according to:

$$CO_{2(g)} \rightarrow CO_{2(aq)} \tag{1}$$

This reaction follows Henry's law defining the dissolution constant (K_d) as:

$$K_d = \frac{\left[CO_{2(aq)}\right]}{P_{CO_2(g)}} \tag{2}$$

where $[CO_{2(aq)}]$ is the molar concentration of dissolved CO_2 (mol dm^{-3}) and $P_{CO_2(g)}$ is CO_2 partial pressure (bar).

b) A fraction of dissolved CO_2 reacts with water (hydration) producing carbonic acid (H_2CO_3):

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \tag{3}$$

From the above reaction, it is possible to determine a forward (k_1) rate constant and a backwards (k_{-1}) reaction rate constant. Then, the hydration constant (K_{hyd}) is defined as:

$$K_{hyd} = \frac{k_1}{k_{-1}} \tag{4}$$

Estimated values of K_{hyd} indicate that this hydration rate can be considered as slow process and, therefore, the determining step for subsequent reactions.

At pH > 10, direct reaction with OH^- predominates (equation (5)), and an instantaneous reaction takes place (equation (5a)):

$$CO_{2(aq)} + OH^- \rightarrow HCO_3^- \tag{5}$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \quad \text{(Instantaneous)} \tag{5a}$$

c) Once the carbonic acid is formed (H_2CO_3), it dissociates according to:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{6}$$

For this reaction, the dissociation constant (K_{a1}) is defined by the concentration (mol dm^{-3}) of the species in solution according to:

$$K_{a1} = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]} \tag{7}$$

Due to experimental issues involved in the measurement of this constant, a second expression for this constant ($k_{a1'}$) can be found in the literature:

$$k'_{a1} = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right] + \left[CO_{2(aq)}\right]} \tag{8}$$

This expression considers the total H_2CO_3 dissolved.

d) Further dissociation of bicarbonate ion (HCO_3^-) can proceed, generating carbonate ions (CO_3^{2-}):

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{9}$$

Fig. 1 shows a graphic representation of these equilibria, as a function of solution pH.

A common representation of the equilibria is like a relative concentration, mol fraction (Xmol), as a function of solution pH (Fig. 2).

3. Turbulent flow

When a liquid is moving its molecules interact with them, and transport phenomena are altered (momentum, mass, heat, etc.)

Under some circumstances, the movement of the liquid can be described considering that its molecules form a uniform series of liquid layers, slipping one over other. In this description, it is assumed that molecules belonging to a liquid layer do not move to another layer, that is; there is not mixing. This kind of movement, without a mix, is known as "laminar flow".

When the liquid is moving in a solid container (as it is in most of the cases), molecules interact with the walls of the container. Due to this interaction, the fluid adheres to the solid walls of the

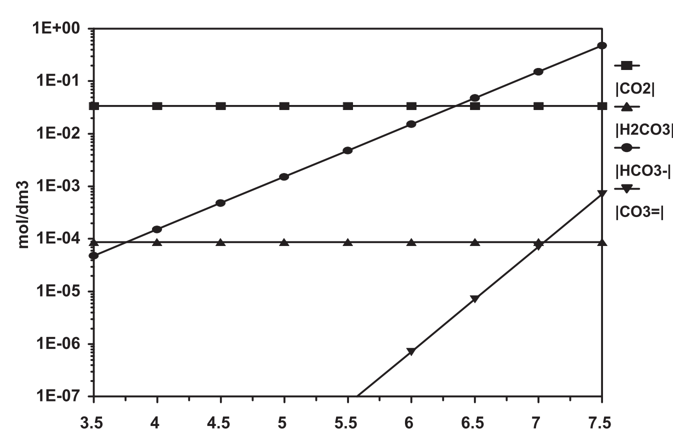

Fig. 1. Concentration of carbonic species in water as a function of pH, 25 °C, 1 bar.