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The Role of Acid Gas Partial Pressure on Corrosion Processes in Oil and Gas Production Systems

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ABSTRACT

The role of partial pressure ratio of $\text{CO}_2/\text{H}_2\text{S}$ is often used to define whether the system is sweet and controlled by the partial pressure of CO_2 or sour and controlled by the partial pressure of H_2S , however, this greatly simplifies the role that partial pressure plays in the corrosion processes. This paper offers an overview of the complete role that partial pressure ratio plays in determining the controlling processes in oil and gas production systems. In particular, the paper reviews the role of partial pressure in determining,

- the solution pH
- dominant water chemistry species
- controlling corrosion reaction
- prevalent corrosion product
- sour service regime

The presentation is intended to be a consistent and unified view of the relationships between partial pressure, water chemistry and corrosion product solubility.

Key words: Acid Gas, pH, Equilibrium Constants, Oil and Gas Corrosion

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INTRODUCTION

As illustrated in Figure 1 corrosion in the oil and gas industry consists of a complex and interwoven series of reactions all of which, to some extent or other, are influenced by the partial pressure of the acid gases CO_2 and H_2S .¹ This review explores some of these interactions in terms of the influence of partial pressure in the gas phase, on solution pH, the water-chemistry, surface corrosion reactions, corrosion product precipitation and the sour service regime.

HYDROGEN ION CONCENTRATION

Dissolution and Dissociation

Dissolution and dissociation of CO_2 and H_2S are the first steps in the corrosion process. Initially CO_2 and H_2S dissolve in water as per the Henry's Law constants and as illustrated in Figure 1, dissolution is followed by hydration in the case of CO_2 , and followed subsequently by two dissociation steps yielding H^+ ions. The release of H^+ ions increases acidity, reduces the pH, and hence the term acid gas.

For a solution containing no-buffering, the pH, $-\text{Log}_{10}[\text{H}^+]$, can be calculated directly from the acid gas partial pressure in the gas phase over the solution. Solving Equations (13) and (15) in Table 1 for the hydrogen ion concentration it is possible to develop a parametric chart of lines of constant pH with the partial pressure of CO_2 and H_2S , Figure 2. As can be seen from the chart when $P_{\text{CO}_2} \gg P_{\text{H}_2\text{S}}$ then the pH is controlled by P_{CO_2} , and equally $P_{\text{H}_2\text{S}} \gg P_{\text{CO}_2}$ then the pH is controlled by $P_{\text{H}_2\text{S}}$.

A curious feature of the CO_2 and H_2S system is that while the CO_2 and H_2S dissolution processes are different, CO_2 having a very slow hydration process, the aggregate equilibrium constants controlling pH, see Table 1 Equations (8) and (9), are approximately the same.^{8,9,10} That is, the pH of a solution with gas phase partial pressure of 1 bar CO_2 and zero H_2S has approximately the same pH as a the system with 1 bar H_2S and zero CO_2 - see Figure 3.

ANSI/NACE MR0175/ISO 15156-2:2015

Annex D of the International Standard ANSI/NACE MR0175/ISO 15156 2:2015 provides guidance on the determination of in-situ pH.^{11,12} In particular, the guidance chart, redrawn in Figure 4, shows pH as a function of the sum of P_{CO_2} and $P_{\text{H}_2\text{S}}$, this is only reasonable because the aggregate equilibrium constant for the two systems are approximately equal.

In additional to the original plot shown in Figure 4, the figure also shows a number of values derived from Figure 3 where either the P_{CO_2} or $P_{\text{H}_2\text{S}}$ is dominant. The data derived from Figure 3 is in good agreement with the vales from MR0175. ^{11,12} It should be noted that these calculations are valid only for a condensed system where there is no-buffering e.g. carbonate and acetate free. The effect of buffering will be to increase the pH from the base value calculated for the condensed water as discussed in detail in NACE, Bonis and EFC.^{11,12,13}

WATER CHEMISTRY

Weak Acids

Besides the acid gases themselves, the primary buffering agents in oil and gas produced water systems are,

- Acetic acid/acetate system
- Carbon dioxide/carbonic acid/bicarbonate/carbonate system

The speciation dependence on pH of acetic acid is shown in Figure 5 and of carbon dioxide in Figure 6.^{14,15,16,17} H₂S system is not shown but behaves in a very similar manner to CO₂ with the dissociation to bi-sulfite and then to sulfide. However, the second dissociation for H₂S occurs at a much higher pH than that for CO₂.³

As a result of adding a buffer the pH is generally higher than the original condensed water pH as shown in Figure 7. The buffering agent only has an effect on the pH response when there is sufficient buffer present to “overwhelm” the controlling partial pressure of acid gas. This is reflected in the inflexion of the buffered curves in Figure 7.

However, care is needed in analyzing water sample to correctly identify the controlling buffering agent to ensure that correct amount of carbonate or acetate are added to the solution for either testing or for in-situ pH estimation.¹⁸

An additional factor to consider in the water analysis and simulation is how the buffering agent is added. Figure 8 shows the difference in pH if the buffer, in this case acetic acid/acetate system, is as the salt or as the acid. In this case, if the acetate is added as 0.01 M acetic acid then the pH is approximately 3.4, whereas, if the acetate is added as the salt then the pH will be approximately 8.4.

Normally, for routine oil and gas produced water simulation then the acetate (and other organic acids) would be added as the salt, but in the case of top-of-line corrosion then the acetate would be added as acetic acid which results in a lowered pH and severe corrosion conditions.¹⁹

Top-of-line Corrosion

Iron carbonate formation plays a key role in the top-of-line corrosion process, the solubility of iron carbonate depends on the pH and local [Fe²⁺] system.^{20,21} The pH defined by the speciation of CO₂, in particular the carbonate ion concentration, [CO₃²⁻] from Figure 6, the local ferrous iron concentration [Fe²⁺] produced by the corrosion process, and the solubility product of iron carbonate in Table 1.

CONTROLLING CORROSION REACTION

Controlling Corrosion Reaction in CO₂

The corrosion processes under acid gases has been studied extensively by Nesic and collaborators.^{24,25,26,27,28} One of key features of all these models is that there is a limiting current on the cathodic side. While a detailed review of the kinetics is beyond the scope of this review, it worth looking at the limiting current in the CO₂ system shown in Figure 9.

The dominant species in solution is controlled by the pH which in-turn is controlled in-part by the partial pressure of the acid gases in the gas phase in equilibrium with the produced water. In Figure 9 (a) the dominant cathodic corrosion reaction is the reduction of $[H^+]$ for a partial pressure of 1 bar CO_2 , pH 4 and 30 °C. In Figure 9 (b) the dominant corrosion reaction is the reduction of undissociated carbonic acid $[H_2CO_3]$ for a partial pressure of 1 bar CO_2 , pH 5 and 30 °C. In other words the controlling corrosion reaction is being driven by the water chemistry and speciation of the acid gas as per Figure 6 and Figure 7.

It should be noted that the change in dominant corrosion reaction will greatly affect the way the corrosion process responds, in this case, for the conditions in Figure 9 (a) the corrosion process will be sensitive to flow since the $[H^+] > [H_2CO_3]$. While for the conditions in Figure 9 (b) the corrosion process will be in-sensitive to flow since the $[H^+] < [H_2CO_3]$ as the controlling process is the chemical reaction the hydration of aqueous CO_2 rather than mass transport as detailed elsewhere.^{8,9,10}

CORROSION PRODUCT FILMS

The major corrosion product films in the CO_2 and H_2S system are either iron carbonate and/or iron sulfide which are described in detail in a number of review articles.^{27,30,31} It should be noted that while the second dissociation constants for the CO_2 and H_2S are unimportant for the calculation of solution pH they are critical to the solubility limits of the sparingly soluble iron carbonate (Siderite - $FeCO_3$) and the practically insoluble iron sulfide (Mackinawite - FeS).

The solubility products for Siderite and Mackinawite are given in Table 1.

Specifically, the stability domains for various iron minerals has been discussed in Berner and Curtis.^{32,33} Woollam et al, using updated equilibrium constants, generated iron carbonate and mackinawite stability diagrams over a range of values for pH and $[Fe^{2+}]$ and shown in Figure 10.³⁴

This is a rather simplistic view of the corrosion product mineralogy, while the iron carbonate is straight forward as the only carbonate mineral present, the iron sulfides are much more complex and age with time, temperature, pH and chloride concentration.^{35,36,37,38,39,40,41}

Figure 4.7 in Barnes is of particular interest since it shows the molar volume changes for the progression through the sulfide polymorphs which is very suggestive of a surface film cracking mechanism as illustrated in Freund and Suresh, resulting in localized corrosion.^{42,43}

With respect to corrosion and the influence of corrosion product film, Dunlop has suggested the following, quoting,

Iron Carbonate - Iron Sulfide

Here, a simpler order-of-magnitude guide is proposed. From the values tabulated by Latimer[4] for the appropriate solubility products and ionization constants, co-

existence of siderite and iron sulfide at 25 °C is indicated when the partial pressure ratio of $CO_2/H_2S = 500$. Thus, by ignoring temperature effects and solution imperfections, the conclusion is reached that siderite (iron carbonate) should prevail when the partial pressure ratio of $CO_2/H_2S > 500$; when it is less than 500, iron sulfide can be expected.

Potts provides similar guidance giving the division between CO_2 Regime (Sweet) and the Mixed/Sour Regime for a partial pressure ratio of $P_{CO_2} / P_{H_2S} = 500$. The ratio of 500:1 has been reviewed by Smith and Woollam.^{34,46,47}

However, as suggested by Smith and examined by Woollam and Tamala, the boundaries of the siderite/ mackinawite stability diagram are influenced by the overall pH of the system, and very strongly influenced by the temperature. So while the $P_{CO_2} / P_{H_2S} = 500$ may be valid at approximately 25 °C because of the strong temperature dependence of the solubility constants at 100 °C the ratio is closer to $P_{CO_2} / P_{H_2S} = 10000$.³⁴

SOUR SERVICE REGIME

International Standard ANSI/NACE MR0175/ISO 15156 2:2015 provides guidance on the regions of environmental severity with respect to sulfide stress cracking as shown in Figure 11.

It is important to understand that the two axes, x-axis “Partial Pressure of H_2S ”, and y-axis “pH” do not have the usual relationship of being the independent and dependent variables respectively. Implicit in the x-axis is an associated pH as shown in Figure 3 and Figure 4 where pH is a function of the partial pressure of the acid gas.

Figure 11 shows the implied pH for the given partial pressure of H_2S . This represents the pH for the system for a condensed water with no additional CO_2 . The addition of CO_2 will lower the pH below the H_2S line and the addition of a buffer will raise the pH, as shown in Figure 7.

Indeed the two NACE curves Figure 4 and Figure 11 can be readily overlain.

CONCLUSIONS

The review has presented a unified approach to understanding the corrosion processes influenced by the partial pressure of the acid gases CO_2 and H_2S . In particular,

1. The influence of acid gas partial pressure on the pH of a condensed water system and the approximate equality of the P_{CO_2} and P_{H_2S} in changing pH has been demonstrated
2. The effect of the primary buffering agents, carbonic acid and acetate, has been demonstrated and link to partial pressure
3. The importance of the analysis of water samples in correctly identifying the concentration of the buffering agent and the importance of how the is added to the solution in either a simulation and/or synthetic brine

4. The partial pressure of the acid gases significantly influences the controlling corrosion reaction as demonstrated for the CO₂ system
5. The stability of the corrosion product film is influenced by the water chemistry through the solubility product and the partial pressure of the acid gases.
6. The temperature sensitivity of the partial pressure ratio in controlling the dominant corrosion product film was highlighted
7. The implied pH of the sour service diagram has been shown recognizing the two-axes are not have the dependent -independent variable relationship

Overall, a unified picture is presented of the influence of the acid gas partial pressure on multiple aspects of the corrosion processes in the oil and gas industry.

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