Understanding Passive Layer Formation for Further Corrosion Management in Gas Production Pipes

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Abstract. Corrosion is a critical issue during the development of a gas field, especially wet gas or retrograde gas field. Corrosion affects the management system of a field and further impacts the amount of investment. Therefore, accurate prediction of corrosion rate is needed to plan an effective preventive action before going further to the development phase. One of the important parameters that should be noticed to create an accurate prediction is the formation of the passive layer. In CO\textsubscript{2}-H\textsubscript{2}S environment, there will be three possibilities of passive layer: FeS, FeCO\textsubscript{3} or no passive layer. In this study, we create mathematical models to determine the formed passive layer in each segment of the gas production tubing and pipeline. The model is built using Faraday’s Law and Thermodynamic approach to account the passive layer formation at different temperature, pH, corrosion rate and partial pressure of CO\textsubscript{2} and H\textsubscript{2}S. From the simulation, it was found that there were three boundary conditions: no scale-FeS boundary, no scale-FeCO\textsubscript{3} boundary and FeS-FeCO\textsubscript{3} boundary. The first two boundaries evolved over a time as the concentration of Fe\textsuperscript{2+} ions was increasing. However, FeS-FeCO\textsubscript{3} boundary remained steady as it was not affected by the addition of Fe\textsuperscript{2+} ions. Using sample case study, few variations were noticed at production pipeline and tubing. It was caused by the gas composition, which contained high CO\textsubscript{2} and very low H\textsubscript{2}S. Boundary conditions only changed slightly over two days period.

1. Introduction

Corrosion is defined as the destructive result of chemical reaction between a metal or metal alloy and its environment [18]. It occurs when a metal or metal alloy meets corrosive agents in aqueous solution at certain pressure and temperature. In gas field, corrosion is usually caused by CO\textsubscript{2} gas (sweet corrosion) and H\textsubscript{2}S gas (sour corrosion). The existence of corrosion in production system could affect the amount of production and lead to safety issues. Therefore, early prevention of corrosion is needed before bringing a gas field into production.

In order to plan an effective corrosion management, one should first understand the fluid characteristic and environment condition (ambient temperature, location, etc) of a gas field. Moreover, an accurate prediction of future corrosion phenomenon is also critical. It can be assessed by creating a model that describes the corrosion phenomenon of a field accurately. Many corrosion models have been published so far by researchers [2] [12] [27] [35] [62] [65] [68] [72] and well-known companies to estimate the future corrosion rate in a production system. From all those models, a critical parameter that influences the assumptions inside the models and determines the success of the prediction is the type of passive layer.
Passive layer is known as the corrosion reaction product, formed on the surface of a metal or metal alloy where corrosion reaction occurs. The existence of passive layer could be helpful to protect the metal from further corrosion or harmful because it can block the gas flow. The type of passive layer is determined by the gas composition and thermodynamic condition (pressure and temperature) of production system. As the type of passive layer in a system determines the development of any corrosion models and accuracy in prediction of the future corrosion phenomenon, it is critical to have a mathematical model that can predict the type of passive layer in a gas production system.

As a part of our big research in creating a new corrosion-erosion model that is applicable in any environmental conditions of gas fields, we first developed a mathematical model to predict the type of passive layer using Faraday’s law and thermodynamics approach. This model could simulate the formed passive layer based on the partial pressure of CO$_2$ and H$_2$S in gas production system. The model was applicable in vertical, incline and horizontal flow condition. We also used sample case study from to perform our model calculations.

2. Mathematical Model
The prediction model is built using Faraday’s law and thermodynamic approach. Faraday’s law is used to estimate the amount of $Fe^{2+}$ ion in half-cell reaction. Thermodynamic approach is utilized then as the main foundation to create the model. The model is divided into three parts: no scale-mackinawite (FeS) boundary equation, no scale-siderite (FeCO$_3$) boundary equation and mackinawite-siderite boundary equation. We also assume that

- corrosion occurs uniformly in a specific segment of production pipe
- water is uniformly distributed in a specific segment of production pipe
- reaction has reached its equilibrium condition at certain pressure and temperature

2.1. No Scale-Mackinawite Boundary
In H$_2$S environment, there is a possible formation of mackinawite scale on the surface of the metal or metal alloy. This scale can be formed if the solubility limit of mackinawite is surpassed. The solubility of mackinawite can be expressed as

$$Fe^{2+}_{(aq)} + S^{2-}_{(aq)} \leftrightarrow FeS(s) \quad (1)$$

Therefore, the solubility limit can be represented using solubility product constant of mackinawite

$$K_{sp_{FeS}} = [Fe^{2+}][S^{2-}] \quad (2)$$

The amount of $Fe^{2+}$ ion in solution is related to the amount of metal loss (corrosion rate). Thus, $[Fe^{2+}]$ can be estimated using

$$[Fe^{2+}] = \frac{CR \times A \times \rho_{metal} \times \Delta t}{MW_{metal} \times HU \times V_{pipe}} \quad (3)$$

where
- $CR$ : corrosion rate, L T$^{-1}$
- $A$ : inner pipe area, L$^2$
- $\rho_{metal}$ : metal density, M L$^{-3}$
- $MW_{metal}$ : molecular weight of metal
- $HU$ : liquid hold up, fraction
- $V_{pipe}$ : pipe inner volume, L$^3$
- $\Delta t$ : exposure time, T

Based on ASTM G102 [1], in half-cell reaction, molecular weight of a metal is determined using (equivalent molecular weight)
$$MW_{metal} = \frac{1}{\sum_{i=1}^{n} \left( \frac{f_i}{a_i/n_i} \right)}$$

where

- $f_i$ : mass fraction of an atom, fraction
- $a_i$ : molecular weight of an atom
- $n_i$ : valence

The boundary condition to differentiate the area of no-scale and mackinawite can be calculated using

$$Ksp_{FeS} = \frac{\left( CR \times A \times \rho_{metal} \times \Delta t \right) \times k_{1H_2S} \times k_{2H_2S} \times k_{3H_2S} \times P_{H_2S}}{\left[ H^+ \right]_{aq}}$$

The value of $K_{1H_2S}$ can be estimated using several empirical correlations: Weiss, 1970; Willhelm et al., 1977; Roberts, 1985; Carroll & Mather, 1989; Suleimenov & Krupp, 1994; De Bruyn et al., 1995; Rinker & Sandall, 2000; Nordsveen et al., 2003; Fernández-Prini et al., 2003; and Sander et al., 2011. The value of $K_{2H_2S}$ can be estimated using several empirical correlations: Wright & Maass, 1932; Ringborn, 1953; Pohl, 1962; Ellis & Golding, 1967; Tsonopoulos et al., 1976; Rao & Hepler, 1977; Broderius et al., 1977; Millero, 1986; Kharaka et al., 1989; and Suleimenov & Seward, 1997. The value of $K_{3H_2S}$ can be estimated using several empirical correlations: Ringborn, 1953; Maronny, 1959; Muhammad & Sundarahm, 1961; Pohl, 1962; Kolthoff, 1969; Giggenbach, 1971; Ellis & Giggenbach, 1971; Stephens and Cobble, 1971; Kharaka et al., 1989; and Flaschka et al., 1991. The value of $K_{sp_{FeS}}$ can also be estimated using several empirical equations: Berner, 1967; Doyle, 1968; Tewari et al., 1978; Mors et al., 1987; Davison, 1991; Bagander & Carman, 1994; Davison et al., 1999; Bening et al., 2000; Rickard, 2006; and Sun et al., 2008.

### 2.2. No-Scale-Siderite Boundary

In CO$_2$ environment, siderite will be formed as the passive layer. The solubility of siderite can be expressed as

$$Fe^{2+}_{(aq)} + CO^2_{3-(aq)} \leftrightarrow FeCO_{3(s)}$$

Therefore, the solubility limit can be mathematically expressed as

$$Ksp_{FeCO_3} = \left[ Fe^{2+} \right] \left[ CO^2_{3-} \right]$$

The correlation to identify the area of no-scale and siderite can be expressed mathematically as

$$Ksp_{FeCO_3} = \frac{\left( CR \times A \times \rho_{metal} \times \Delta t \right) \times k_{1CO_2} \times k_{2CO_2} \times k_{3CO_2} \times P_{CO_2}}{\left[ H^+ \right]_{aq}^2}$$

The value of $K_{1CO_2}$ can be estimated using several empirical correlations: Bohr, 1899; Weiss, 1974; Wilhelm et al., 1977; Edwards et al., 1978; Oddo & Tomson, 1982; Yoo et al., 1986; Crovett, 1991; Zheng et al., 1997; Fernández-Prini et al., 2003; and Sander et al., 2011. The value of $K_{2CO_2}$ can be


2.3. Mackinawite-Siderite Boundary

The solubility limit for mackinawite and siderite is simply expressed as the ratio of $K_{sp}^{FeS}$ and $K_{sp}^{FeCO_3}$ [52].

$$K_{sp}^{FeS/FeCO_3} = \frac{k_{1HS} \times k_{2HS} \times k_{3HS} \times P_H^S}{k_{1CO_2} \times k_{2CO_2} \times k_{3CO_2} \times P_{CO_2}}$$

3. Model Implementation

The model is used to predict the type of passive layer in gas pipes through hydrogen sulfide partial pressure vs carbon dioxide partial pressure in log-log plot [52]. The execution step for the model follows the algorithm in Figure 1.

![Algorithm for Execution](image)

The critical parameters during the model’s execution are pressure, temperature, composition and pH changing in each partition of the pipe. One should measure those parameters accurately to obtain good predictions.

4. Case Study

To perform the model’s simulation, we used an example of wet gas field composition. Its fluid is characterized by the significant amount of CO$_2$. The detail fluid’s composition of the case study can be seen at Table 1. The production data is shown at Table 2.
Table 1. Gas Composition Data

| Composition          | Mole (%) |
|----------------------|----------|
| 1 Hydrogen Sulfide (H$_2$S) | 0.05     |
| 2 Carbon Dioxide (CO$_2$)      | 31.67    |
| 3 Nitrogen (N$_2$)            | 0.33     |
| 4 Methane (C$_1$)             | 56.92    |
| 5 Ethane (C$_2$)              | 0.11     |
| 6 Propane (C$_3$)             | 0.03     |
| 7 Water (H$_2$O)              | 10.90    |

Table 2. Production Data

| Parameter                        | Value  | Unit   |
|----------------------------------|--------|--------|
| **Production Tubing**            |        |        |
| 1 Reservoir Pressure             | 1100   | psig   |
| 2 Reservoir Temperature          | 325    | F      |
| 3 Tubing Length                  | 8152.9 | ft     |
| 4 Tubing Internal Diameter       | 6.625  | inch   |
| 5 Inclination (from Vertical)    | 0      | degree |
| 6 Wellhead Pressure              | 500    | psig   |
| 7 Wellhead Temperature           | 255.3  | F      |
| 8 Ambient Temperature            | 85     | F      |
| 9 Gas Rate                       | 57.13  | MMSCFD |
| 10 Tubing Material (Assumed)     | API 5L-X 65 | -    |
| **Production Flowline**          |        |        |
| 1 Wellhead Pressure              | 500    | psig   |
| 2 Wellhead Temperature           | 255.3  | F      |
| 3 Ambient Temperature            | 85     | F      |
| 4 Flowline Length                | 1875.4 | ft     |
| 5 Flowline Outer Diameter        | 8      | inch   |
| 6 Inclination (from Horizontal)  | 0      | degree |
| 7 Outlet Pressure                | 402.28 | psig   |
| 8 Outlet Temperature             | 249.0  | F      |
| 9 Gas Rate                       | 57.13  | MMSCFD |
| 10 Tubing Material (Assumed)     | API 5L-X 65 | -    |

In this study, we assumed steady rate for two days period. We generated the pressure and temperature along tubing and flowline using commercial software with Beggs-Brill correlation for vertical and horizontal flow and black-oil model. The corrosion rate value was also assumed to be steady for two days, even there was passive layer on the surface of the metal. The corrosion rate was calculated using...
deWaard (1995) model. In the proposed model, we calculated all constant using the newest empirical correlation, for instance to calculate the value of $K_{1 H_2 S}$ we used Sander et al. (2011).

5. Results and Discussions

From the simulation using commercial software, the pressure and temperature profile in production tubing and flowline are shown at Figure 2.

![Figure 2. Pressure and Temperature Profile in: Tubing Flow (a) and Flowline Flow (b)](image)

Based on the environment condition in tubing and flowline, the corrosion rate can be seen at Figure 3.

![Figure 3. Tubing’s Corrosion Rate Profile (a) and Flowline’s Corrosion Rate Profile (b)](image)

Corrosion rate occurs worst at tubing because it has bigger pressure and temperature than in flowline. Based on the deWaard prediction, corrosion rate has its biggest value at the outlet location of the pipes. Using the input of corrosion rate and environmental condition, the proposed model can be executed. It can be recognized that there are three boundaries, so that there are three regions [52]: no-scale, mackinawite and siderite region. The arrangement of the boundaries does not change at various conditions, only the value of the boundaries will be different at different conditions. For boundary profile in tubing and flowline, it can be seen at Figure 4.
At each segment, no scale-mackinawite and no scale-siderite boundaries change over time. As time goes longer, the value of those boundaries become smaller. It is caused by the addition of $Fe^{2+}$ ion in the solution (In Equation 5 and 8, $P_{H_2S}$ and $P_{CO_2}$ are reciprocal with the amount of $Fe^{2+}$ ion). However, mackinawite-siderite boundary remains constant since it does not depend on the amount of $Fe^{2+}$ ion.

It can also be seen that at Figure 4, the no scale-mackinawite and no scale-siderite boundary lie on negative side of log-log plot. It means that no scale condition could only occur at low operating pressure or low composition of $H_2S$ and $CO_2$. Since the operating pressure of the pipe is relatively high, there is no doubt that scale is formed. Moreover, the existence of big amount of $CO_2$ makes it sure that siderite layer is formed.

When the whole segments at Figure 4 are compared, it can be seen that there is only small change in boundary and operating point values. It is caused by the significant amount of $CO_2$ in the stream, for about 30%. Therefore, it can be guaranteed that only siderite layer will exist over time in all segments of the production pipes.

Finally, for the case study, we can say that to calculate the corrosion rate, one should involve the existence of siderite passive layer. It is also needed to be noticed that siderite build-up is possible to occur in the future.

6. Conclusion

From the discussion above, it can be concluded that a new boundary model to determine the type of passive layer that is formed inside the gas production pipes has been successfully developed. The model is built using Faraday’s law and thermodynamic approach. The novelty of this study is the easy prediction of type of passive layer using the model. By only plugging in the working pressure and temperature at certain position to the boundary map, one can easily know the type of the passive layer formed at certain time.

In the model, no scale-mackinawite and no scale-siderite boundary are influenced by pressure, temperature, pH, partial pressure of carbon dioxide or hydrogen sulfide and concentration of $Fe^{2+}$ ion (corrosion rate value). Therefore, these boundaries will evolve over time. However, mackinawite-siderite boundary only depends on pressure, temperature and partial pressure of carbon dioxide and hydrogen sulphide. Thus, this boundary will not change over time.

From the case study, it can be concluded that there will be only siderite passive layer formed on the inner surface of the pipes. It is caused by the huge amount of carbon dioxide in the flow.

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