Scale Build-Up Prediction of FeS and FeCO₃ in Gas Production Pipes

R. K. Santosoi, S. D. Rahmawati1, A. Gadesa1, D. Wahyuningrum2
1Petroleum Engineering Study Program, Institut Teknologi Bandung, Indonesia
2Chemistry Study Program, Institut Teknologi Bandung, Indonesia

Abstract. The existence of passive layer is important to control the corrosion-erosion rate in gas production pipes. However, passive layer can lead to two possible conditions: corrosion-erosion protection or scale build-up. Accurate prediction of scaling tendency is needed to plan treatment and operating condition during the production from gas field. In this study, we develop mathematical model to predict the scaling tendency in gas production pipes. The model consists of two basic equations: precipitation rate and erosion equation. Precipitation rate is calculated using semi-empirical correlation and erosion is calculated using Salama (2000) equation. Then, a modified parameter of scaling tendency (ST), which is the ratio between net precipitation rate and corrosion rate, is introduced to measure the scaling tendency in each segment of production pipe. From simulation, it was found that the interaction between pressure, temperature and fluid composition affected the scaling tendency at most. However, when sand was introduced in the pipe flow, scale formation occurred at low rate. Every segment of production tubing and pipeline gave different tendency condition.

1. Introduction

Passive layer is defined as corrosion product formed on the inner surface of pipes under the nature of corroding environment [21]. Passive layer could be advantageous as giving protection from further corrosion or disadvantageous as blocking the fluid flow. In protection mechanism, passive layer forms diffusion barrier for any species involved in corrosion process [27]. It covers and prevents the underlying steel from further dissolution. However, when the growth rate of passive layer is big, passive layer can block the fluid flow. It becomes scale that builds up and fills the internal pipe volume.

The common types of passive layer formed in the inner surface of the pipes are siderite for sweet corrosion and mackinawite for sour corrosion. When both CO₂ and H₂S exist in the gas stream, the formed passive layer is determined by the competitiveness of mackinawite and siderite. The layering arrangement is also various, depends on the supersaturation of mackinawite and siderite and temperature [4] [33].

When moving fluid is introduced in the corrosion system, there will be erosion phenomenon that affects the growth of passive layer. Erosion can be caused by liquid particle or solid particle impingement [16]. In gas flow, liquid impingement is possibly triggered by the liquid condensation from the gas and solid impingement by produced sand. This erosion will reduce the thickness of passive layer or increase the material removal by direct damaging. Therefore, in order to predict the rate of material...
removal of the pipe accurately, the interaction between corrosion process, growth of passive layer and erosion process need to be further investigated.

In this paper, we present a mathematical model to predict the growth of mackinawite and siderite in CO$_2$/H$_2$S system and the tendency to form scale. The mathematical model relates the corrosion rate directly with the growth of passive layer using Faraday’s Law and semi-empirical approach. Through the model’s results, we will be able to see the effect of passive layer towards fluid flow and material removal in pipes.

2. Mathematical Model

The prediction model is built using Faraday’s law and semi-empirical approach. Faraday’s law is used to estimate the amount of Fe$^{2+}$ ion in half-cell reaction. Several semi-empirical equations are utilized then as the main function to calculate the growth rate of passive layer. Scaling Tendency (ST) parameter, which is defined as the ratio of net growth rate and corrosion rate, is used to predict the tendency of scale to form. Therefore, the model is divided into three parts: calculation of Fe$^{2+}$ ion, calculation of net growth rate of passive layer and calculation of scaling tendency. We also assume that

- corrosion and erosion occur uniformly in a specific segment of production pipe
- passive layer grows uniformly in the inner surface of the pipe
- reaction has reached its equilibrium condition at certain pressure and temperature

2.1. Calculation of Fe$^{2+}$ Ion

Faraday’s Law stated that the amount of dissolved cathode in liquid was proportional to the corrosion current [8]. Therefore, 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

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

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)

\[
MW_{metal} = \frac{1}{\sum_{i=1}^{n} \left( \frac{f_i \times a_i}{n_i} \right)}
\]

where

$\hat{f}_i$ : mass fraction of an atom, fraction
$a_i$ : molecular weight of an atom
$n_i$ : valence
2.2. Calculation of Net Growth Rate of Passive Layer

In H$_2$S environment, the formation of mackinawite can be expressed by the following reaction

$$Fe^{2+}_{\text{(aq)}} + S^{2-}_{\text{(aq)}} \leftrightarrow FeS_{(s)}$$  \hspace{1cm} (3)

Therefore, the formation of mackinawite is related to its solubility product, which can be expressed mathematically by the following equation

$$K_{sp_{FeS}} = \left[Fe^{2+}\right] \left[S^{2-}\right]$$  \hspace{1cm} (4)

There are also many researchers that introduce supersaturation parameter (ratio between concentration product of each ion that possibly contribute to form a solid and solubility product constant) as the contributed one in calculating the growth rate of mackinawite. Therefore, most of prediction equations relate solubility product, supersaturation and temperature to the growth rate of mackinawite. The growth of mackinawite can be calculated using Harmandas & Koutsoukos, 1996. In CO$_2$ environment, the formation of siderite can be expressed by the following reaction

$$Fe^{2+}_{\text{(aq)}} + CO_3^{2-}_{\text{(aq)}} \leftrightarrow FeCO_{3(s)}$$  \hspace{1cm} (5)

Therefore, the solubility limit can be mathematically expressed as

$$K_{sp_{FeCO_3}} = \left[Fe^{2+}\right] \left[CO_3^{2-}\right]$$  \hspace{1cm} (6)

The semi-empirical equations of siderite formation rate also relate supersaturation, solubility product and temperature. Several correlations can be used: Tomson & Johnson, 1991; Greenberg & Tomson, 1992; Van Hunnik et al., 1998; Yean et al., 2008; and Gao et al., 2011.

When there is flowing fluid in the pipes, erosion occurs. The common equation used in petroleum industry for predicting erosion rate caused by either solid or liquid impingement is presented by Salama, 2000.

$$ER = \frac{M \times V_m^2 \times d_p}{S_m \times \rho_m \times D^2}$$  \hspace{1cm} (7)

where
- $ER$ : erosion rate, L T$^{-1}$
- $S_m$ : a geometry dependent constant
- $M$ : amount of flowing sand, M T$^{-1}$
- $V_m$ : fluid mixture velocity, L T$^{-1}$
- $\rho_m$ : mixture density, M L$^{-3}$
- $d_p$ : sand particle diameter, L
- $D$ : pipe diameter, L

Finally, the net growth rate for each passive layer can be expressed mathematically by the following equation

$$NR_i = R_i - ER$$  \hspace{1cm} (8)

where
- $NR_i$ : net formation rate of passive layer i, L T$^{-1}$
- $R_i$ : formation rate of passive layer i, L T$^{-1}$
When the value of erosion rate is bigger than formation rate, it can be concluded that net formation rate of passive layer is zero. Thus, there is no passive layer on the inner surface of the pipes and moving fluid is directly in touch with the pipes surface.

2.3. Calculation of Scaling Tendency
Scaling Tendency is used to determine whether the passive layer will protect the underlying surface from further corrosion or block the fluid flow. Nesic, Lee and Ruzic, 2002 have defined scaling tendency as the ratio of film growth rate and corrosion rate. However, when there is a fluid flow in the pipes, the definition should be changed into

$$ ST_i = \frac{NR_i}{CR} $$

where

$CR$ : corrosion rate, LT-1

3. Model Implementation
The execution step for the model follows the algorithm in Figure 1.

![Figure 1. Algorithm for Execution](image)

The input parameters for the model are pressure, temperature, fluid PVT and corrosion rate in every partition. One should measure them accurately to get good prediction of scaling tendency. Pressure and temperature in every partition can be measured directly using pressure and temperature log or calculated using empirical correlations. Corrosion rate can be measured directly using coupons or calculated using empirical correlations.

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 inside the case study can be seen at Table 1. The production data is shown at Table 2.

| 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     |
Propane (C₃) 0.03
Water (H₂O) 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 | - |
| 11 Sand Concentration (Assumed)| 10  | ppm    |

| **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 | - |
| 11 Sand Concentration (Assumed)| 10  | ppm    |

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, concentration of $\delta^2$ and $CO_3^{2-}$ ion are determined using multiple step reaction. Mackinawite growth rate is calculated using Harmandas and Koutsoukos, 1996 and siderite growth rate is calculated using Greenberg and Tomson, 1992. Several constants in the equations are calculated using: Sander et al., 2011; Suleimenov & Seward, 1997; Kharaka et al., 1989; Sun et al., 2008; Prieto & Millero, 2002; Roy et al., 1993; and Benezeth et al., 2009.
5. Results and Discussions

Pressure and temperature calculation results using commercial software are shown at Figure 2. The corrosion rate profile is presented at Figure 3.

![Pressure and Temperature Profile in Tubing Flow](a) ![Pressure and Temperature Profile in Flowline Flow](b)

**Figure 2.** Pressure and Temperature Profile in: Tubing Flow (a) and Flowline Flow (b)

![Corrosion Rate Profile in Tubing Flow](a) ![Corrosion Rate Profile in Flowline Flow](b)

**Figure 3.** Tubing’s Corrosion Rate Profile (a) and Flowline’s Corrosion Rate Profile (b)

Corrosion rate occurs worst at tubing because it has higher pressure and temperature than in flowline. Based on the deWaard prediction, corrosion rate has its biggest value at the near-outlet location of the pipes. Because the small amount of sand concentration in the field, the calculation results using Salama (2000) equation show small value of erosion rate in both tubing and flowline. It is presented at Figure 4.
The erosion rate values are the highest at the near-outlet of the pipes, compared to all partitions. It is caused by the expanding of gas volume. Increase in gas volume will increase the gas superficial velocity, thus, erosion rate value will grow higher.

The formation rate of mackinawite in tubing and flowline are presented at Figure 5.

Both graphs at Figure 5 depict the increasing mackinawite formation rate as increasing pressure and temperature. As going deeper from wellhead in tubing flow and going nearer to the wellhead in flowline flow, temperature and pressure tend to increase. Therefore, supersaturation value will be high. High value in supersaturation means that there are many mackinawite formed at specific section (high formation rate) and it also increases the possibility to deposit scale on the inner surface of pipes. Moreover, as increasing in time step, the supersaturation value will also grow high, thus, the formation rate will be increasing.

However, the formation rate of siderite is different as it is presented at Figure 6.
The formation rate of siderite is strongly affected by the amount of $Fe^{2+}$ ion in the solution. As going deeper from wellhead in tubing flow and going nearer to wellhead in flowline flow, the corrosion rate becomes smaller. Therefore, the concentration of $Fe^{2+}$ ion will be also low. This condition will reduce the amount of siderite formed on the inner surface of the pipes. Moreover, the formation rate is increasing as the time is increasing. It is caused by the increasing amount of $Fe^{2+}$ ion in the solution that can lead to high supersaturation value.

As carbon dioxide concentration in the system is higher than hydrogen sulfide and the formation rate of siderite is much higher than mackinawite, it can be said that siderite dominates the passive layer. Therefore, the scaling tendency is measured based on the siderite layer only. The scaling tendency profile in tubing and flowline are presented at Figure 7.

As going deeper from the wellhead in tubing flow and going nearer to the wellhead in flowline flow, the scaling tendency increases. Thus, it explains why the corrosion rate is high at near the wellhead. Passive layer thickness is thin in near wellhead in tubing flow and far from wellhead in flowline flow. It makes corrosive agent easily attack the surface of the pipe.

Figure 7 also describes that the possibility of scale to block the fluid flow will only happens after 1 hour exposure because the scaling tendency value is greater than one. Corrosion will no longer exist anymore after 1 hour.

From all of the simulation results, it can be said that corrosion rate and formation rate of passive layer depend on each other. Corrosion rate determines the amount of $Fe^{2+}$ ion in the solution, thus, it affect the supersaturation condition, then, the formation rate of passive layer. Formation rate of passive
layer determines the thickness of passive layer that can reduce the value of corrosion rate. Thus, iteration process has to be involved to calculate the interaction between corrosion rate and passive layer formation rate in the future.

Brown and Nesic, 2005 has investigated the possibility of mixed siderite and mackinawite in the passive layer. However, the interaction of siderite and mackinawite when they exist at the same time is very complicated and hard to be predicted. Therefore, the proposed model has a limitation in predicting this condition. When using the proposed model, one has to assume type of passive layer that has high possibility to form on the inner surface of the pipe.

6. Conclusion

From the discussion above, it can be concluded that the proposed model successfully predicts the scaling tendency in tubing and flowline flow. However, the model is still limited in prediction when mackinawite and siderite exist at the same time.

Formation rate of passive layer is affected by three major parameters: pressure, temperature and supersaturation. Pressure and temperature determine the kinetic of reaction and the amount of $S^{2-}$ and $CO_3^{2-}$ ion in the solution, then, affect the supersaturation value. Supersaturation value is also affected by the corrosion rate.

Scaling tendency has increasing trend as going deeper from the wellhead in tubing flow and going nearer to the wellhead in flowline flow. Therefore, corrosion in the tubing flow at near wellhead and in flowline flow far from the wellhead happens worst.

Acknowledgement

This research was funded by DIKTI 2016.

References

[1] 1989 ASTM G 102 (Philadelphia: American Society for Testing and Materials) p 416-422
[2] Andrzej Anderko and Robert D. Young 1999 Corrosion 99 No. 31 (Houston: NACE International) p 1-19
[3] Bénézeth, P., Dandurand, J. L. and Harrichoury, J. C. Solubility product of siderite (FeCO$_3$) as a function of temperature (25–250 °C). Chemical Geology Volume 265, Issues 1–2, 15 July 2009, Pages 3–12.
[4] B. Brown and S. Nesic 2005 Corrosion 2005 No. 05625 (Houston: NACE International) p 1-29
[5] Carlos A. Palacios, Corpoven S. A., Valoy Chaudary 1996 Fourth Latin American and Caribbean Petroleum Engineering Conference No. SPE 36127 (Port of Spain: Society of Petroleum Engineers, Inc.) p 501-511
[6] Denny A. Jones 1996 Principles and Prevention of Corrosion 2nd edition (New Jersey: Prentice-Hall, Inc.) p 5
[7] E. W. J. van Hunnik, B. F. M. Pots and E. L. J. A. Hendriksen 1996 Corrosion 96 No. 6 (Houston: NACE International) p 1-22
[8] F. C. Strong 1961 J. Chem. Educ. 1961, 38 (2), p 98
[9] Gao, M.; Pang, X.; and Gao, K. The growth mechanism of CO2 corrosion product films. Corrosion Science 53, 2011, 557–568.Greenberg, J. and Tomson, M. Precipitation and dissolution kinetics and equilibria of aqueous ferrous carbonate vs temperature. Appl. Geochem. 1992, 7, 185–190.
[10] G. H. Al-Aithan, F. M. Al-Mutahar, J. R. Shadley, S. A. Shirazi, E. F. Rybicki and K. P. Roberts 2014 Corrosion 2014 No. 3854 (San Antonio: NACE International) p 1-15
[11] G. H. Nancollas 1979 Advances in Colloid and Interface Science 10 (1979), p 215-252
[12] J. Greenberg and M. Tomson 1992 Applied Geochemistry 1992, Vol. 7, p 185-190
[13] Johnson, M. L.; and Tomson, M. B. Ferrous Carbonate Precipitation Kinetics and Its Impact on CO2 Corrosion. CORROSION/91, paper no. 268, (Houston, TX: NACE International, 1991).
[14] Kharaka, Y. K.; Perkins, E. H.; Gunter, W. D.; Debral, J. D.; and Bamford, C. H. Solmineq 88:
A Computer Program for Geochemical Modeling of Water Rock Interactions; Alberta Research Council: Menlo Park, CA, 1989.

[15] M. B. Tomson and M. L. Johnson 1991 *SPE International Symposium on Oilfield Chemistry* No. SPE 21025 (Anaheim: Society of Petroleum Engineers) p 1-8

[16] M. M. Salama 2000 *Corrosion* 2000 No. 00085 (Houston: NACE International) p 1-18

[17] N. G. Harmandas and P. G. Koutsoukos 1996 *Journal of Crystal Growth* 167 (1996) p 719-724

[18] O. A. Nafday and S. Nesic 2005 *Corrosion* 2005 No. 05295 (Houston: NACE International) p 1-27

[19] Oddo, J. E.; and Tomson, M.B. Simplified Calculation of CaCO$_3$ Saturation at High Temperatures and Pressure in Brine Solutions, *J. of Petroleum Technology*, 1982, pp.1583-1590.

[20] Prieto, F. J. M.; and Millero, F. J. The values of pK$_1$ + pK$_2$ for the dissociation of carbonic acid in seawater. *Géochimie et Cosmochimica Acta* Vol. 66, 2002, No. 14, pp. 2529–2540.

[21] Richard Woollam, Kavitha Tummala, Jose Vera and Sandra Hernandez 2011 *Corrosion* 2011 No. 11076 (Houston: NACE International) p 1-14

[22] R. K. Santos, I. Faizi and S. D. Rahmawati 2015 *SPE Asia Pacific Oil and Gas Conference and Exhibition* No. SPE 176192 (Bali: Society of Petroleum Engineers, Inc.) p 1-17

[23] Roy, R. N.; Roy, L. N.; Vogel, K. M.; Porter-Moore, C.; Pearson, T.; Good, C. E.; Millero, F. J.; and Campbell, D. M. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mar. Chem.* 1993, 44, 249–267.

[24] Sander, S. P.; Abbatt, J.; Barker, J. R.; Burkholder, J. B.; Friedl, R. R.; Golden, D. M.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Moortgat, G. K.; Orkin, V. L.; and Wine, P. H. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 17, JPL Publication 10-6, 2011, Jet Propulsion Laboratory, Pasadena, available at: http://jpldataeval.jpl.nasa.gov (last access: 22 June 2016).

[25] Sander, R. Compilation of Henry’s law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.*, 2015, 15, 4399–4981.

[26] S. Nesic, S. Wang, H. Fang, W. Sun and K. K-L. Lee 2008 *Corrosion 2008 Conference and Expo* No. 08535 (Houston: NACE International) p 1-16

[27] S. Nesic, K. J. Lee and V. Ruzic 2002 *Corrosion* 2002 No. 02237 (Houston: NACE International) p 1-35

[28] S. Nesic, M. Nordsveen, R. Nyborg and A. Stangeland 2001 *Corrosion* 2001 No. 01040 (Houston: NACE International) p 1-28

[29] Suleimenov, O. M.; and Krupp, R. E. Solubility of hydrogen sulfide in pure water and in NaCl solutions, from 20 to 320 °C and at saturation pressures. *Geochim. Cosmochim. Acta* 1994, 58, 2433-2444.

[30] Suleimenov, O. M.; and Seward, T. M. A spectrophotometric study of hydrogen sulfide ionization in aqueous solutions to 350 °C. *Geochim. Cosmochim. Acta* 1997, 61, 5187-5198.

[31] Sun, W.; Nesić, S.; Young, D.; and Woollam, R. C. Equilibrium Expressions Related to the Solubility of the Sour Corrosion Product Mackinawite. *Ind. Eng. Chem. Res.* 2008, 47, 1738-1742.

[32] Wei Sun and Srdjan Nesic 2007 *Corrosion 2007 Conference and Expo* No. 07655 (Houston: NACE International) p 1-26

[33] W. Sun, S. Nesic and S. Papavinasam 2006 *61ST Annual Conference & Exposition* No. 06444 (Houston: NACE International) p 1-26

[34] W. Sun, S. Nesic and S. Papavinasam 2006 *Corrosion* July 2008, Vol. 64, No. 7, p 586-599

[35] Yean, S.; Saiari, H.; Kan, A.; and Tomson, M. "Ferrous Carbonate Nucleation and Inhibition, in SPE International Oilfield Scale Conference," Society of Petroleum Engineers, Aberdeen, UK, 2008.