Scale Build-Up Prediction of FeS and FeCO$_3$ in Gas Production Pipes

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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 CO$_2$ and H$_2$S exist in the gas stream, the formed passive layer is determined by the competiveness 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_2S 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

$$\left[Fe^{2+}\right] = \frac{CR \times A \times \rho_{metal} \times \Delta t}{MW_{metal} \times HU \times V_{pipe}} \tag{1}$$

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

Based on ASTM G102 [1], in half-cell reaction, molecular weight of a metal is determined using (equivalent molecular weight)

$$MW_{metal} = \frac{1}{\sum_{1}^{n} \frac{f_i}{\left(a_i \big/ n_i\right)}} \tag{2}$$

where
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_2S environment, the formation of mackinawite can be expressed by the following reaction

$$Fe^{2+}_{(aq)} + S^{2-}_{(aq)} \Leftrightarrow FeS_{(s)} \qquad (3)$$

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

$$Ksp_{FeS} = \left[Fe^{2+} \right]\left[S^{2-} \right] \qquad (4)$$

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

$$Fe^{2+}_{(aq)} + CO_3^{2-}_{(aq)} \Leftrightarrow FeCO_{3(s)} \qquad (5)$$
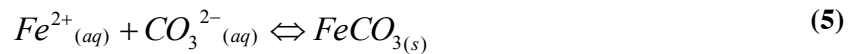
Therefore, the solubility limit can be mathematically expressed as

$$Ksp_{FeCO_3} = \left[Fe^{2+} \right]\left[CO_3^{2-} \right] \qquad (6)$$

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.

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

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, $L\ T^{-1}$
ρ_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

$$NR_i = R_i - ER \qquad (8)$$

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
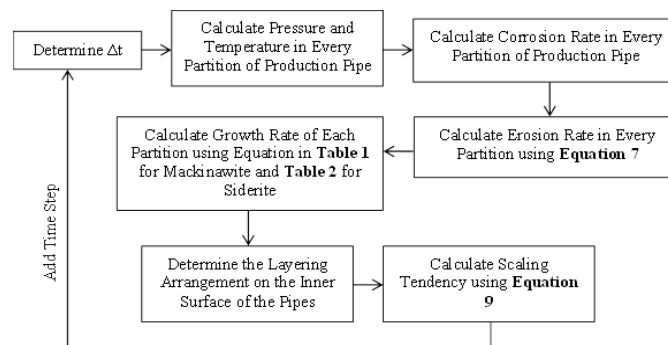
$$ST_i = \frac{NR_i}{CR} \qquad (9)$$

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

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.

Table 1. Gas Composition Data

	Composition	Mole (%)
1	Hydrogen Sulfide (H_2S)	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	-
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 S^{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.
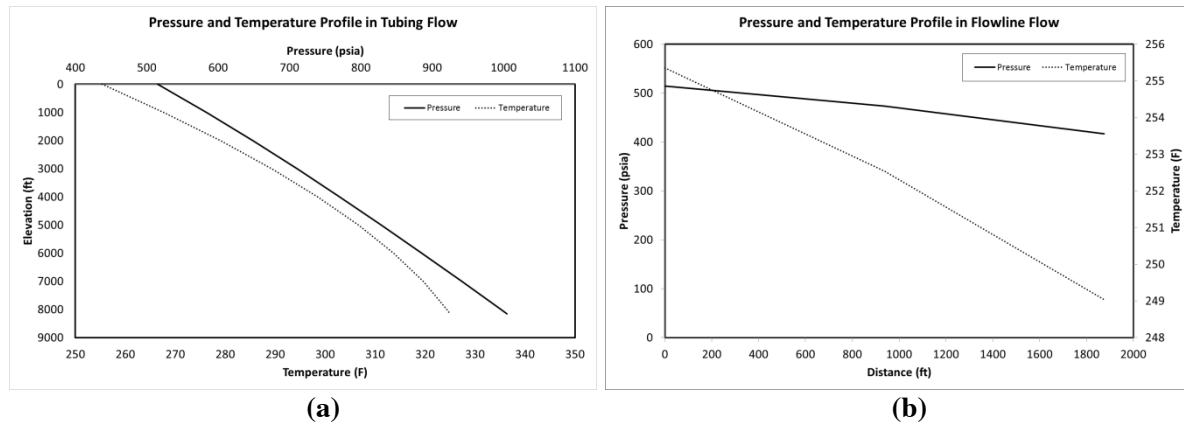

Figure 2. Pressure and Temperature Profile in: Tubing Flow **(a)** and Flowline Flow **(b)**
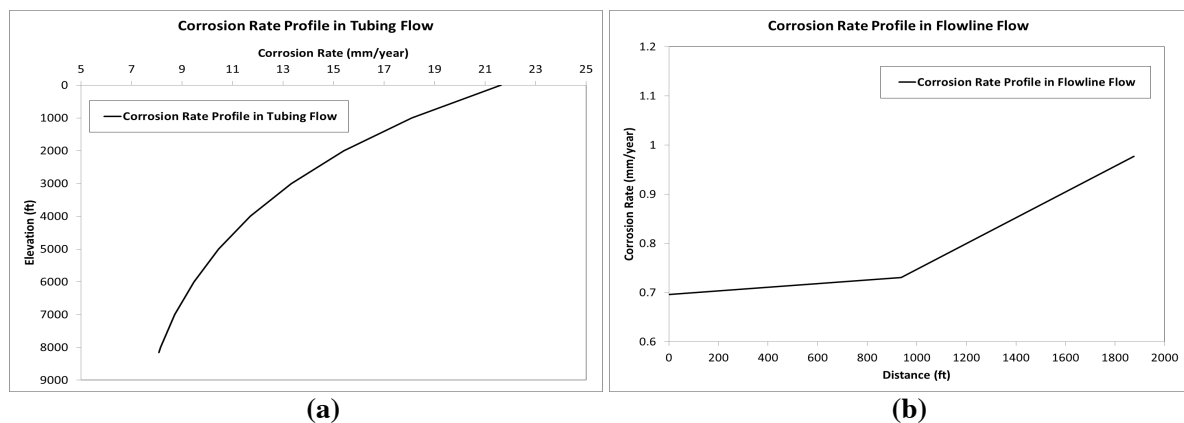
Figure 3. Tubing's Corrosion Rate Profile **(a)** and Flowline's Corrosion Rate Profile **(b)**

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.
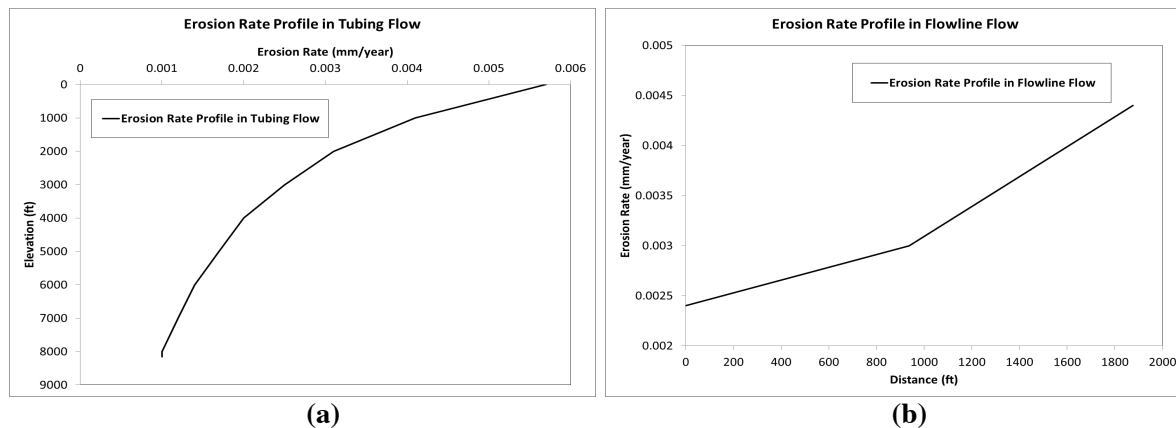
Figure 4. Tubing's Erosion Rate Profile **(a)** and Flowline's Erosion Rate Profile **(b)**

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.
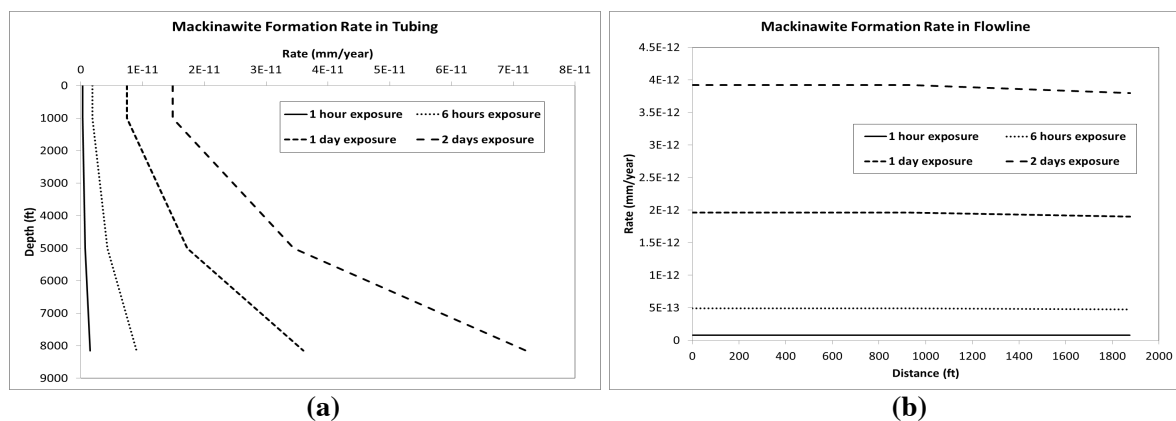
Figure 5. Tubing's Mackinawite Formation Rate Profile **(a)** and Flowline's Mackinawite Formation Rate Profile **(b)**

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.
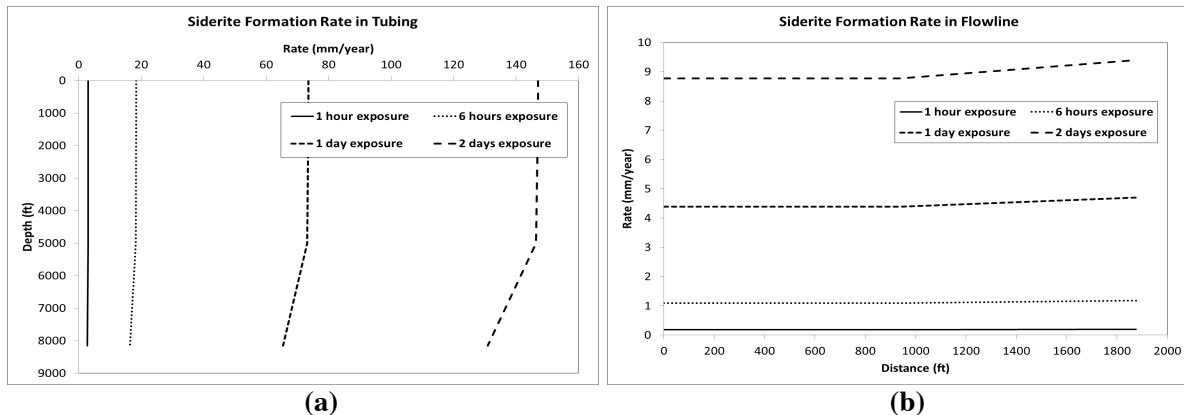
Figure 6. Tubing's Siderite Formation Rate Profile **(a)** and
Flowline's Siderite Formation Rate Profile **(b)**

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**.
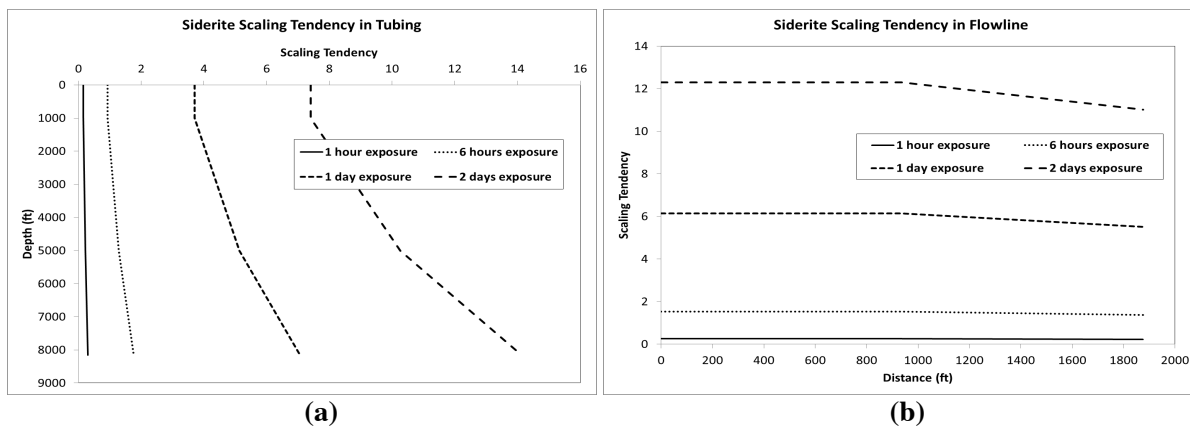
Figure 7. Tubing's Scaling Tendency Profile **(a)** and Flowline's Scaling Tendency Profile **(b)**

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.

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