The Impact of Time-Varying Operating Parameters on the Corrosion Rate and Depth of Gas Pipelines

Keo Yuan Wu*, Mihai A. Diaconeasa, Ali Mosleh
The B. John Garrick Institute for the Risk Sciences
Department of Materials Science & Engineering
University of California, Los Angeles, USA

Abstract: Corrosion rate and depth predictions in gas pipelines are significant for both safety and economic reasons. Most of the time, the variations of operating conditions on a daily basis are often overlooked and are approximated with their mean values, resulting in non-negligible deviations of the predicted corrosion depth after a long time of operation. This paper introduces a corrosion rate predictive model for internal uniform corrosion of gas pipelines subject to an aqueous CO$_2$ and H$_2$S environment and applies it to wet gas gathering pipelines in Sichuan Province, China, to study the influence of time-varying operating parameters on the corrosion rate and depth. The results show that the proposed model is capable of predicting instantaneous corrosion rates as a function of time in which the instantaneous corrosion rates can reflect the time-varying operating parameters. In addition, it is found that by using mean values for the operating parameters to calculate the corrosion rate it is likely to underestimate the corrosion depth in the long-term prediction by around a factor 2. The underestimation of the corrosion depth prevents engineers to take appropriate mitigating actions in time and thus exposes the pipeline to the risk of failure.

Keywords: Gas Pipeline, Operating Parameters, Corrosion Rate and Depth, Modelling

1. INTRODUCTION

The reduction in wall thickness of gas pipelines as a result of corrosion would lead to pipeline failures either by leaking or bursting and potentially expose operators to tremendous risks [1, 2]. Many mitigation methods such as cathodic protection and anti-corrosion coatings are usually performed to reduce the risk of external corrosion in the industry, however, it is not the case for internal corrosion. Although maintenance and replacement are widely used to prevent internal corrosion, they are not cost-effective if implemented too often or at the wrong time. Therefore, corrosion rate predictive models along with pipeline failure models have become major tools in terms of pipeline reliability for operators to assess and mitigate threats of pipeline corrosion [3-5].

Many efforts have been made to build accurate corrosion rate predictive models for internal corrosion. Among them, many studies have adopted the linear defect-growth model, assuming that the corrosion rate is constant over time for the calculation of corrosion depth in which the corrosion rate is often obtained by the regression of data over a long time interval [6, 7]. In addition, the use of other corrosion models such as the power-law function or linear–growth model with initiation period to represent the lifetime of coatings is also common. The schematic of common corrosion models for corrosion depth prediction is depicted in Fig. 1. However, this type of modelling can hardly reflect the real situation of operating conditions because internal corrosion process inside gas pipelines should be treated as a time-dependent phenomenon. Some studies have proposed using the power law function model to consider time dependence of corrosion rate and depth in which the determination of the parameters of this model is data-driven. Although these parameters are correlated with pipeline operating parameters (e.g., operating years, pH, water content, sulfate, bicarbonate, chloride, etc.) and soil types, temporal variations of these parameters as well as the influence on the corrosion rate are still disregarded [8, 9].

* Corresponding author’s email address: keoyuan0703@ucla.edu.
There are two approaches that have been used for the prediction of corrosion degradation given corrosion rate predictive models and operating parameters as inputs namely in deterministic and probabilistic terms. The deterministic approach considers each input parameter an average value, whereas the probabilistic approach uses a specified probability distribution of each input parameter for corrosion rate calculation, and thereby the corrosion rate is expressed in the form of a specified probability distribution [10, 11]. However, as operating conditions are very likely to change continuously as a function of time merely using an average value or a probability distribution to represent an overall range of variation of the operating parameter may disregard the time-dependent influence of variation of operating conditions on the corrosion rate. Although this issue is often overlooked, and few studies have been done on it, it is no doubt that the results of long-term predictions of corrosion depth may be significantly different if the influence of time-varying operating parameters on the corrosion rate is considered.

This paper aims to give the results of a study that looked at the influence of time-varying operating parameters on the corrosion rate and depth of gas pipelines. A physics-based corrosion rate predictive model of internal uniform corrosion for gas pipelines subject to an aqueous CO$_2$ and H$_2$S environment was introduced as the main tool to estimate the instantaneous corrosion rate based on time-varying operating parameters (i.e., temperature, pH value, flow velocity, partial pressure of CO$_2$ and H$_2$S) on a daily basis. The model is composed of two stages: Stage I and Stage II, where the details of the model description of Stage II has been shown in another paper by authors (Wu and Mosleh 2018, submitted to International Conference on Probabilistic Safety Assessment and Management, PSAM14, Los Angeles). A set of field data from wet gas gathering pipelines in Sichuan Province, China, was used for a demonstration [12]. The calculation of the instantaneous corrosion rate was done via Monte Carlo method by randomly selecting a value from each operating parameter and putting them into the corrosion rate predictive model on a daily basis for a specified operating time.

### 2. MODEL DESCRIPTION

#### 2.1. Corrosion Rate Model Description

The model describes uniform corrosion in terms of two stages: Stage I and Stage II, depending on the formation of corrosion protective layers (i.e., mackinawite sulfide layers). Stage I considers anodic and cathodic reactions at the steel surface. The corrosion rate is assumed to be time-independent in the absence of corrosion protective layers. As the model is developed for gas pipelines made of mild steels, the anodic reaction is the dissolution of iron from the steel surface while cathodic reactions include reduction of hydrogen ion, direct reduction of aqueous H$_2$S, direct H$_2$CO$_3$ reduction, and direct H$_2$O reduction:

![Fig. 1. Common corrosion models for corrosion depth prediction.](image-url)
\[
\begin{align*}
\text{Fe}^{2+}(_\text{s}) & \rightarrow \text{Fe}^{2+}(_\text{aq}) + 2e^- \\
2\text{H}^+(_\text{aq}) + 2e^- & \rightarrow \text{H}_2(\text{g}) \\
2\text{H}_2\text{CO}_3(_\text{aq}) + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2\text{HCO}_3^-(_\text{aq}) \\
2\text{H}_2\text{S}(_\text{aq}) + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2\text{HS}^-(_\text{aq}) \\
2\text{H}_2\text{O}(_l) + 2e^- & \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(_\text{aq})
\end{align*}
\]

It should be noted that in this paper the concentration of each corrosive element in the bulk solution is calculated through their corresponding equilibrium constants and Henry’s Law. Corrosion rate modelling in Stage I is done by using the electrochemical model proposed by previous studies [13, 14]. Each of the electrochemical reactions in Eq. (1-5) contributes to an individual current density (i). The expressions of charge transfer current density and mass transfer limiting current density are given as follows:

\text{Charge transfer control:}
\[i_a = i_0 \times 10^{-\frac{E-E_0}{b}}\]

\text{Mass transfer control:}
\[i_{\text{lim(H}^+\text{)}} = k_m(\text{H}^+)FC_{\text{H}^+}\]
\[i_{\text{lim(H}_2\text{CO}_3\text{)}} = FC_{\text{CO}_2}f_{\text{H}_2\text{CO}_3}\sqrt{D_{\text{H}_2\text{CO}_3}K_{\text{hyd}}k_{\text{hyd}}^f}\]
\[i_{\text{lim(H}_2\text{S) = k}_m(\text{H}_2\text{S})FC_{\text{H}_2\text{S}}\]

\(i_a\) and \(i_0\) are the charge transfer current density and the reference current density in A/m², respectively; \(E\) and \(E_0\) are the corrosion potential of the steel and the reference potential in V, respectively; \(b\) is the Tafel slope in V/decade. \(i_{\text{lim(H}^+\text{)}}\), \(i_{\text{lim(H}_2\text{CO}_3\text{)}}\), and \(i_{\text{lim(H}_2\text{S)}}\) are limiting currents for Eq. (2-4), respectively; \(k_m(\text{H}^+)\) is the mass transfer coefficient of hydrogen ions in m/s; \(F\) is Faraday constant (≈96500 C/mol); \(C_{\text{H}^+}\) is the concentration of hydrogen ions in the bulk solution in mol/m³; \(C_{\text{CO}_2}\) is the concentration of carbon dioxide in the bulk solution in mol/m³; \(f_{\text{H}_2\text{CO}_3}\) is the flow factor carbonic acid; \(D_{\text{H}_2\text{CO}_3}\) is the diffusion coefficient of aqueous carbonic acid in m²/s; \(K_{\text{hyd}}\) is equilibrium hydration constant for carbon dioxide (=2.58×10⁻³); \(k_{\text{hyd}}^f\) is the forward reaction rate for carbon dioxide hydration in s⁻¹. It should be noted that the dissolution of iron and the direct H₂O reduction are charge transfer controlled only, while the reduction of hydrogen ion, direct reduction of aqueous H₂S, and direct H₂CO₃ reduction are both charge transfer and mass transfer controlled under certain conditions.

Both the charge transfer current density and the limiting current density contribute to the overall current density (i) in A/m² in a parallel form:
\[i = \frac{1}{1/i_a+i_{\text{lim}}}\]

The unknown corrosion potential (E) can be obtained by applying the mixed potential theory in which the sum of the anodic overall current density equals to the sum of the cathodic overall current density. Once the corrosion potential is obtained, by applying it to Eq. (6), the corrosion current density (\(i_{\text{corr}}\)) is the charge transfer current density in A/m² at the corrosion potential for the anodic reaction. The corrosion rate, (CR, further correction is needed for corrosion rate unit mm/y), can be calculated by:
CR = \frac{i_{\text{corr}} M_{\text{Fe}}}{\rho_{\text{Fe}} 2F} \quad (11)

M_{\text{Fe}} \text{ is the molar mass of iron } (= 55.85 \text{ g/mol}); \rho_{\text{Fe}} \text{ is the density of iron } (= 7.86 \text{ g/cm}^3).

Stage II is assumed to be under mass transfer control in the presence of corrosion protective layers (i.e., mackinawite layers). Mackinawite layers grow over time by a direct and fast heterogeneous solid-state reaction as diffusion barriers according to Sun and Nešić [15], thus the corrosion rate is a function of time in this stage. For the details of corrosion modelling in Stage II, readers are referred to authors’ paper (Wu and Mosleh 2018, submitted to International Conference on Probabilistic Safety Assessment and Management, PSAM14, Los Angeles).

2.2. Effect of Parameter Uncertainty and Time Variability on the Corrosion Rate and Depth Estimation

The corrosion rate as a function of time is calculated by randomly selecting a value from the specified probability density function of each operating parameter (i.e., temperature, pH value, flow velocity, partial pressure of CO$_2$ and H$_2$S) and putting them into the corrosion rate predictive model at every time step (i.e., day). The corrosion depth is a direct reflection of the corrosion rate and is a cumulative degradation caused by the daily corrosion at a certain segment of the pipeline. It should be noted that the calculated corrosion depth here considers only temporal variability but not positional variability; therefore, it can’t represent the whole pipeline. The corrosion depth for a specific operating time can be expressed as:

\[ d(t) = \frac{\sum_{i=1}^{N} CR_i(t)}{365} \quad (12) \]

\(d\) is the corrosion depth in mm; \(CR(t)\) is the corrosion rate in mm/y; \(t\) is the time in days; \(N\) is the number of days.

3. RESULTS AND DISCUSSION

In this paper, a set of field data from a wet gas gathering pipeline in Sichuan Province, China, was used as an example to study the influence of time-varying operating parameters on the corrosion rate and depth. The probabilistic operating variables relevant to this pipeline are given in Table 1. As the original data provided in the paper [12] is in the deterministic framework, in order to consider the uncertainties of operating parameters a coefficient of the variable (COV) and a probability distribution are assigned to each variable based on the suggestions of several studies [11, 16].

<table>
<thead>
<tr>
<th>Variables</th>
<th>T (K)</th>
<th>P (Pa)</th>
<th>pH$_2$S (Pa)</th>
<th>pCO$_2$ (Pa)</th>
<th>V (m/s)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Lognormal</td>
<td>Lognormal</td>
<td>Lognormal</td>
<td>Lognormal</td>
<td>Lognormal</td>
<td>Lognormal</td>
</tr>
<tr>
<td>Mean</td>
<td>299.5</td>
<td>1950000</td>
<td>33540</td>
<td>11505</td>
<td>2</td>
<td>6.58</td>
</tr>
<tr>
<td>COV</td>
<td>0.10</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.10</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*\(T\) is the temperature; \(P\) is the operating pressure; \(pH_2S\) is the partial pressure of H$_2$S; \(pCO_2\) is the partial pressure of CO$_2$; \(V\) is the flow velocity; \(pH\) is the pH value.*
Two simulations were implemented for comparison in which Group A took operating parameters as mean values while Group B took operating parameters as probability distributions. Firstly, the corrosion rate at Stage I was calculated by the electrochemical approach. According to the study by Zheng et al. [17], the time period during which there is no presence of sulfide layers in an aqueous CO₂/H₂S environment is about several hours. Therefore, the uncertainties of operating parameters were assumed to have less impact on the corrosion rate and the corresponding accumulated corrosion depth at Stage I compared to Stage II and the corrosion rate calculation of Stage I was done in the deterministic framework which should yield the same result for both groups. Fig. 2 shows the polarization curves of every electrochemical reactions involved in the corrosion process of the studied pipeline.

![Polarization Curves](image_url)

**Fig. 2.** Polarization curves of the studied pipeline by the electrochemical approach at Stage I.

The result shows that the hydrogen sulfide reduction contributes the most to the cathodic current densities among all cathodic reactions in this case. The corrosion current density and the corrosion potential are found to be 0.634 A/m² and -0.489 V, respectively. The time-dependent corrosion rate at Stage I was then calculated and found to be around 0.734 mm/y.

The corrosion rate as a function of time including both Stage I and Stage II for Group A when the operating time is 1 year was shown in Fig. 3. The result shows that although the initial corrosion rate of Stage I is as high as 0.734 mm/y, it only exists for a short time (less than 1 day) and the corrosion rate then drops drastically after Stage II is entered. The corrosion rate then gradually decreases as the growth of the mackinawite layers continues over time. After 365 days of operation, the corrosion rate is reduced to below 0.070 mm/y. As the operating condition stays constant over time, the growth of protective layers follows the parabolic pattern and the decrease of corrosion rate slow down with increasing time. However, although the result in Group A is easily attainable in a laboratory setup, it is far from real for an operating pipeline. Understandably, it is not an easy task to control operating conditions along a few kilometer-long pipeline and the consideration of uncertainty is definitely needed.
Fig. 3. The corrosion rate as a function of time using mean values for operating variables (Group A). Operating time is limited to 1 year.

Considering the uncertainties of operating conditions on a daily basis, the time-varying operating parameters as a function of time and the corresponding corrosion rate as a function of time for Group B are illustrated in Fig. 5 and Fig. 5, respectively. From Fig. 4 it can be seen that the values of every operating parameter fluctuate with different extent of variations based on their probability distributions. Some extremely large or small values randomly happen over operating time corresponding to the nature of lognormal distributions in a reflection of real situations that the system may encounter a huge change of operating conditions more or less during the operation.

The corrosion rate in Fig. 5 also shows a sudden drop after Stage II is entered like Group A, however, the corrosion rate fluctuates instead of steadily decreasing over operating time. It indicates the fact that the growth of sulfide layers has much to do with the operating parameters and the remaining thickness of them is the consequence of the tradeoff between growth and annihilation. The effects of several operating parameters on the corrosion rate in the CO₂/H₂S aqueous environment have been studied elsewhere. According to Cui et al.’s study [18], the corrosion rate tends to increase with increasing temperature in the range between 15 to 55°C and decreases with increasing temperature in the range between 55 to 80°C. Meanwhile, the corrosion rate is likely to increase with increasing partial pressure of H₂S up to 0.3 bar, but it shows decreasing trend after that. Moreover, the increasing pH value in the range between 4 to 6 results in the decrease of corrosion rate, whereas the rising flow velocity in the range between 60 to 600 rpm leads to the increase of corrosion rate as reported by Zheng et al. [19]. The predicted corrosion rate is, therefore, the outcome of the combined effects among these operating parameters. This result indicates that the severity of operating conditions on a daily basis has a direct influence on the corrosion rate; namely the more extreme the operating conditions are; the higher the corresponding corrosion rates are expected to be. Interestingly, the lower bound of the corrosion rate slows down in decreasing as time proceeds, which is due to the fact that every time when protective layers are broken, the formation of new layers follows up.
Fig. 4. The time-varying operating parameters as a function of time. Operating time is limited to 1 year.
According to Eq. (12), the corrosion depth is attributed to the contribution of daily corrosion rate. After calculations, it is found that the corrosion depths for Group A and B are 0.076 mm and 0.131 mm after 1 year of operation, respectively. In addition, the results in Fig. 6, which illustrates the corrosion depths as a function of time for Group A and Group B when the operating time is 1 year, shows that the growth of corrosion depth can be represented as a nearly-straight line for Group A, whereas that for Group B is not.

This finding shows that the influence of time-varying operating parameters on the corrosion rate can lead to a large deviation on the corrosion depth calculation in the long-term prediction. Using mean values for operating parameters to calculate the corrosion rate is likely to underestimate the corrosion depth, which eventually exposes the pipeline to the potential risk of leaking and bursting faster than expected. To find the probability distribution of corrosion depth, Monte Carlo sampling was done and the results were analyzed by Easyfit 5.6 [20]. Fig. 7 shows the probability density function for the corrosion depth when the operating time is 1 year. As Fig. 7 illustrates the Weibull distribution is a better fit for the corrosion depth in which the mode value (i.e., most likely corrosion depth) is larger than the corrosion depth of Group A by a factor of 1.6. The largest deviation of corrosion rate can be as large as a factor of almost 2. In other words, the operating parameters should not be viewed as constant over time as they have been proved to have a large influence on the corrosion rate and depth.
4. CONCLUSION

In this research, a physics-based corrosion rate predictive model of internal uniform corrosion has been demonstrated to study the influence of time-varying operating parameters on the corrosion rate and depth. The model is capable of predicting instantaneous corrosion rate corresponding to the fluctuation of operating parameters on a daily basis. The simulation results of a set of field data from a wet gas gathering pipelines in Sichuan Province, China, show that time-varying parameters not only has a large influence on the corrosion rate but also result in a non-negligible deviation on corrosion depth estimation. The corrosion rate as a function of time shows fluctuated characteristic, which makes the growth of corrosion depth far from linear. Finally, it is indicated that using mean values for operating parameters to calculate the corrosion rate can significantly underestimate the corrosion depth around a factor of 2.

Acknowledgements

The research leading to the development of this paper was supported by Pipeline System Integrity Management research project sponsored by the Petroleum Institute, Abu Dhabi, UAE through a subaward from the University of Maryland Department of Mechanical Engineering.

References


