

Calculation of Surface Speciation on Mild Steel under Applied Polarization

Zheng Ma, Bruce Brown, Srdjan Nescic, and Marc Singer
Institute for Corrosion and Multiphase Technology (ICMT), Ohio University
342 West State Street
Athens, OH, 45701
USA

ABSTRACT

The rates of electrochemical and precipitation reactions taking place on the steel surface are dependent on the chemistry of the aqueous phase in contact with the substrate. While the bulk speciation is often used to characterize the severity of the environment, large differences can exist between bulk and surface chemistries, leading to inaccurate representation of the corrosion phenomena. This issue requires a better understanding of the surface speciation. Given the fact that directly measuring surface speciation is a very challenging task, corrosion models must be employed to calculate these surface parameters based on the bulk chemistry. In the present work, an electrochemical model was developed for that exact purpose and used to predict corrosion behavior not only at the corrosion potential, but also under applied polarization, where surface and bulk chemistries differ greatly. This model has been extensively calibrated against experimental results in both corrosion product free conditions as well as in conditions where corrosion product layers form.

Keywords: carbon steel, corrosion rate, modeling, uniform corrosion, carbon dioxide, hydrogen sulfide

INTRODUCTION

It has been well understood that corrosion product layers can precipitate on the surface of mild steel in both sweet corrosion (CO_2 dominated) and sour corrosion (H_2S dominated) environments. However, all the current kinetics models focused on corrosion product layer formation are proposed based on bulk speciation¹⁻⁵. This situation is understandable: most of kinetics related parameters used in these models can either be measured directly from the bulk solution, or can be estimated through a simple bulk water chemistry model; not to mention the fact that the predictions from some of the bulk speciation-based kinetics models have been proven accurate within an acceptable range.

To separate the effects from “precipitation” and “corrosion”, the two processes that normally occur simultaneously during corrosion product formation, a cathodically protected iron substrate and an actively corroding iron substrate were used for corrosion product layer precipitation in the authors

previous study⁴⁻⁶. For experiments using the cathodically protected substrate, a cathodic polarization (-50~-100 mV vs. OCP) was applied to ensure that substrate corrosion was minimized and the precipitation of corrosion product layer was the dominant process during measurement; for experiments using the actively corroding substrate, both the precipitation and spontaneous iron corrosion were taking place at the substrate surface. Figure 1 compares predictions and measured data at 50°C (the lowest experiment temperature) on the left and 80°C (the highest experiment temperature) on the right. The results from two different substrates do not completely overlap with each other, yet they are similar in magnitude, and most of the results from the actively corroding surface are lower than the results from the cathodically protected surface within a factor of two. This means the surface speciation did not affect FeCO_3 precipitation kinetics significantly, at least in these tested conditions.

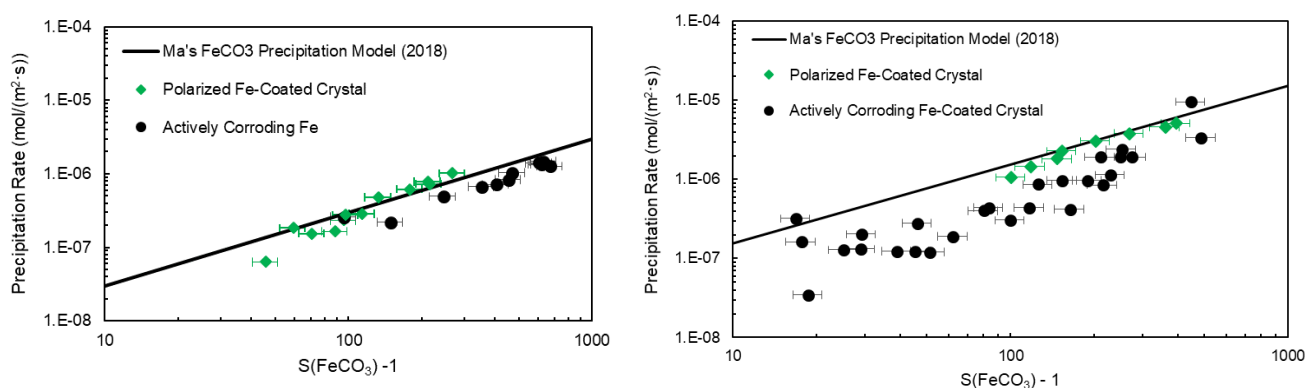


Figure 1. Comparison between model predictions and experimental results for FeCO_3 precipitation rate on different substrates at 50°C (left) and 80°C (right), 1 wt% NaCl, 1 bar total pressure.

Different phenomena, however, have been observed when a similar study was performed for mackinawite precipitation kinetics in a solution with a much lower FeS saturation value. Part of the experimental results are shown in Figure 2. It can be seen from the experimental results obtained at 80°C, that the precipitation rate, PR_{FeS} , measured on an actively corroding substrate was slightly lower than on a cathodically protected specimen by a factor of two when the S_{FeS} was higher than 10, similar to what had been observed in FeCO_3 precipitation measurements. However, the discrepancy between the PR_{FeS} of these two surfaces became larger with the decrease of the bulk S_{FeS} value. It was also noticed that the PR_{FeS} was less dependent on S_{FeS} when using the cathodically protected specimen, i.e., the PR_{FeS} was only reduced by 3-4 times when the measured S_{FeS} was changed by about three orders of magnitude. In addition to that, according to recorded PR_{FeS} , FeS was continuously precipitating on the electrically polarized surface even when the bulk $S_{\text{FeS}} < 1$. The results for cathodically protected specimen were examined at different temperatures and it was found that the FeS precipitation continued even when the solution was highly under saturated in all tested cases, as illustrated in Figure 2 (right).

Based on these observations, it can be concluded that the speciation difference between bulk conditions and surface conditions might be small enough to be ignored for CO_2 corrosion, as in the cases for FeCO_3 precipitation. However, the examples of FeS precipitation point out that the speciation difference could be significantly large in sour conditions, and bulk speciation calculations may no longer accurately describe the speciation on the substrate surface, where the precipitation takes place. This requires a better understanding of the surface speciation, especially for those obtained from the

electrically polarized substrates. Given the fact that “directly” measuring surface speciation is an impossible task, corrosion models must be employed to estimate these parameters. Three currently available in-house corrosion models will be briefly discussed.

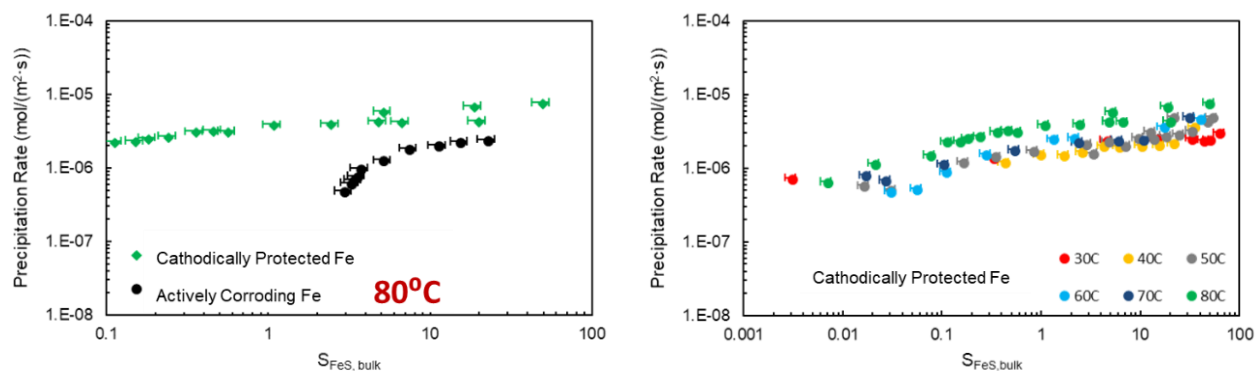


Figure 2. Comparison of experimental results for FeS precipitation kinetics. 1 wt% NaCl, 1 bar total pressure. Left: PR_{FeS} on different substrates at 80°C; right, PR_{FeS} on cathodically protected specimens at different temperatures.

FREECORP 1.0 is a steady-state electrochemical corrosion prediction model, strongly rooted in theory, and all the parameters in which are calculated based on the bulk solution parameters. This model will be referred to as a “*steady-state*” model. All the related chemical reactions are assumed to be in equilibrium, so that the kinetics of chemical reactions can be ignored. The formation of $FeCO_3$ and FeS in the *steady-state* model is calculated using empirical correlations in order to improve the accuracy of corrosion rate prediction. This model is simple and easy to be understood. It can provide reasonable predictions for many different conditions⁷. However, due to the lack of surface speciation information in the *steady-state* model, this model cannot be used to interpret the FeS results as showed previously.

MULTICORP™, on the other hand, is and will be referred to as a “*fully mechanistic*” corrosion prediction model. Almost all the missing pieces from the *steady-state* model have been accounted for in the *fully mechanistic* model. This model discretizes the domain from the bulk solution to the metal surface into hundreds of small control volumes, called nodes, and calculates all the interactions of the species at each node throughout the liquid boundary layer. This model solves 2nd order non-linear partial differential equations, which were derived from fundamental physico-chemical relationships, for each single node. Accurate predictions for speciation on the steel surface can be obtained from this *fully mechanistic* model; however, the model is more complicated and requires more computing power.

Zheng’s *Two Nodes Model*⁸ has more detailed computations than the *steady-state* model, but is not as complicated as the *fully mechanistic* model. This model has one node at the bulk solution interface and another node on the steel surface. The fundamental physico-chemical laws are applied to both nodes, which is similar to the *fully mechanistic* model. However, this model eliminates the process calculations in the boundary layer between the two nodes, which is similar to the *steady-state* model, and assumes the concentration gradient within the boundary layer to be linear. Another simplification that has been made for this model is that all the chemical reactions are assumed to be in equilibrium on the steel surface except for CO_2 hydration. Prior to this research, neither the *fully mechanistic* model nor the *Two Nodes Model* could calculate conditions at an electrically polarized metal surface in solution, a condition that needed to be addressed in order to explain the FeS precipitation results as shown in Figure 2. To

solve this, the *Two Nodes Model* was modified to calculate surface speciation at a cathodically protected metal surface because this model has a good balance of accuracy and simplicity.

DESCRIPTION OF SURFACE SPECIATION CALCULATION WITH APPLIED POLARIZATION

The *Two Nodes Model* used in this research has three main parts to describe H₂S/CO₂ corrosion⁸:

1. A water chemistry model to calculate speciation in the bulk solution.
2. An electrochemical corrosion model including the process of mass transfer from bulk to surface to calculate surface speciation and corrosion rate under an applied potential. The effect of corrosion product layer precipitation on surface speciation was not considered.
3. A corrosion product precipitation and growth model for both FeCO₃ and FeS. Parameters related to surface speciation and corrosion rate under applied potential were calculated in a condition of corrosion product layer precipitation.

The methodology of calculating bulk speciation has been addressed in the literature related to both CO₂⁹ and H₂S corrosion¹⁰ and will not be repeated here. The principles of the latter two models will be briefly covered in this section since modifications have been made to enable the surface speciation calculation under applied polarization. This modified version of the *Two Nodes Model* will be referred to as the *Polarization Model*.

Electrochemical Corrosion Model

The *Two Nodes Model* considers one node on the steel surface and another node in the bulk solution as shown in Figure 3. The calculation of species concentration starts with a mass conservation on the steel surface:

$$\frac{\partial c_{surface,j}}{\partial t} = \frac{N_{in,j} - N_{out,j}}{\Delta x} + R_j \quad (1)$$

where $N_{in,j} - N_{out,j}$ calculates the net flux caused by mass transfer from bulk to surface as well as heterogeneous electrochemical reactions; R_j is the production of homogeneous chemical reactions, and Δx represents the thickness of the boundary layer between the steel surface and bulk solution. In this model, the species concentration in the bulk solution, $c_{bulk,j}$, is calculated using the *steady-state* model's bulk water chemistry calculations.

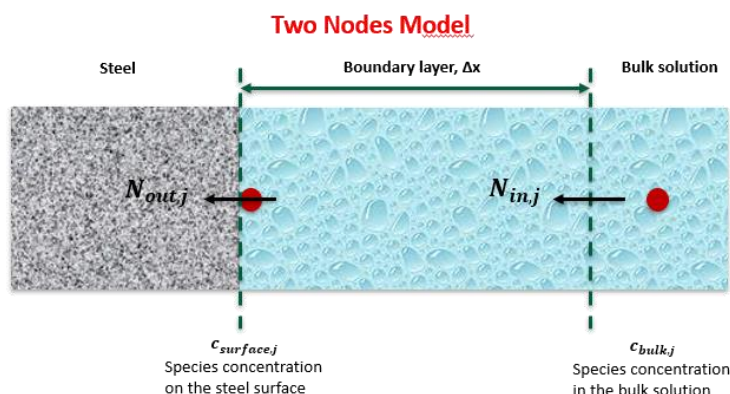


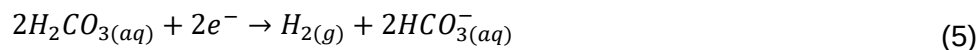
Figure 3. Illustration for the mass transport governing equation and computation domain of the Two Nodes Model.

To calculate the flux of mass transfer, the diffusion due to concentration gradient (considered for all species) and the electromigration due to potential gradient (only considered for Na^+ and Cl^- because of their much higher concentrations as compared to the rest) are both included:

$$N_{in,j} = \underbrace{k_{m,j}(c_{bulk,j} - c_{surface,j})}_{\text{Diffusion due to concentration gradient}} + \underbrace{k_{m,j} \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi}_{\text{Electromigration due to potential gradient}} \quad (2)$$

Where $k_{m,j}$ is mass transfer coefficient; $c_{bulk,j}$ and $c_{surface,j}$ are species concentration in bulk solution and on steel surface respectively; z_j is the electric valency of the calculated species; $\Delta \Phi$ is electrical potential difference between the two nodes; F , R , and T are Faraday's constant, gas constant, and temperature, respectively.

Several heterogeneous electrochemical reaction terms are considered in this model, which include iron dissolution (Reaction (3)), proton reduction (Reaction (4)), H_2CO_3 reduction (Reaction (5)), H_2S reduction (Reaction (6)), and water reduction (Reaction (7)).



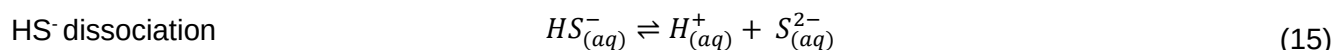
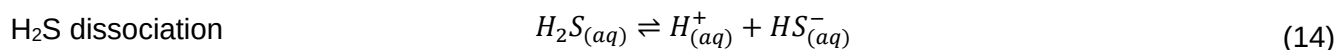
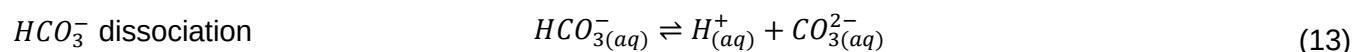
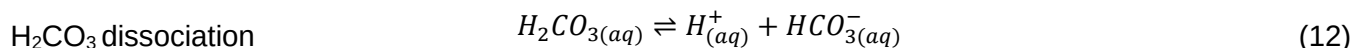
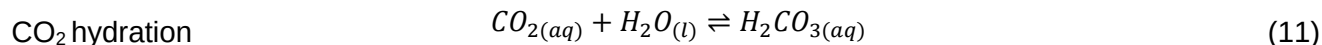
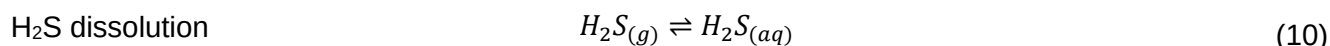
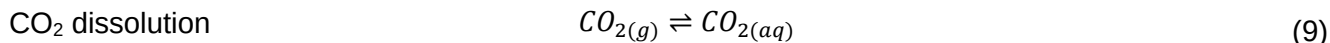
For each reaction, the flux at steel surface can be calculated through Equation (8):

$$N_{out,j} = \pm \frac{i_j}{n_j F} \quad (8)$$

Where i_j is current density for a given species, and n_j is the number of exchanged electrons per mol of the given species in the electrochemical reactions.

One should note that the direct electrochemical reductions of H_2CO_3 and H_2S are used in this model. According to current literature, the mechanisms for both CO_2 ^{11, 12} and H_2S ¹³ corrosion of mild steel are caused by their dissociation reactions and buffering effect to provide $[H^+]$ instead of directly reducing at the metal surface. However, it can be argued that the difference in calculated corrosion rates between the two possible mechanisms for CO_2 corrosion are minor until reaching a relatively high CO_2 partial pressure (at least 10 bar pCO_2)¹¹. Consequently, predictions based on the direct reduction of H_2CO_3 mechanism should be quantitatively correct under the tested conditions. It is also reasonable to assume that this argument holds true for the case of H_2S corrosion. Models based on these two different mechanisms have been shown to produce good agreement with corrosion rate results over their respective temperature and pressure ranges^{2, 13}.

The term $(\Delta x * R_j)$ is related to homogeneous chemical reactions, where CO_2 and H_2S dissolutions, CO_2 hydration, and H_2CO_3 and H_2S dissociations are included for Equation (1):



After these calculations, Equation (16) can be obtained for each participating species by substituting the flux of mass transfer, electrochemical reactions, and chemical reactions into the mass balance equation of Equation (1):

$$\Delta x \frac{\partial c_{surface,j}}{\partial t} = \pm \frac{i_j}{n_j F} + k_{m,j}(c_{bulk,j} - c_{surface,j}) + k_{m,j} \frac{z_j F}{RT} c_{bulk,j} \Delta \Phi + \Delta x * R_j \quad (16)$$