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A FREE OPEN SOURCE MECHANISITC MODEL FOR PREDICTION OF MILD STEEL CORROSION

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ABSTRACT

A mechanistic model is developed based on the general understanding of corrosion kinetics. The model is capable of predicting the uniform corrosion rate of mild steel in aqueous environments containing dissolved carbon dioxide, hydrogen sulfide and organic acids. The contribution of various corrosive species to the corrosion rate and the dominant corrosion mechanism can be explored by using the model. The protective film growth on the metal surface is simulated in a simple manner to make the corrosion rate prediction more realistic. Furthermore, the interface allows for the polarization curves to be displayed during analysis.

This project is initiated with the aim of offering the corrosion community a freely available, transparent and reliable corrosion prediction model firmly rooted in theory. The source code, and all the background information, such as theories, assumptions, data used for calibration, known problems, limitations etc., are shared with the users. The source code behind the model is written in such a way that various modules can be easily accessed and modified by third parties to encourage further development as well as building of derivative works and add-on modules.

Keywords: mechanistic model, open source, carbon dioxide, hydrogen sulfide, organic acid

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INTRODUCTION

Corrosion of mild steel in aqueous corrosive environments has been a long standing concern in the oil and gas industry. Various dissolved corrosive species, such as hydrogen sulfide, carbon dioxide, and organic acids, are present in the water flowing through the oil and gas pipelines, leading to internal corrosion which is a significant threat to normal operation of facilities, personnel safety as well as a serious environmental concern. Extensive research efforts have been made in the past two decades in order to understand the corrosion mechanism of mild steel induced by the different corrosives species and how the process is affected by various environmental factors, such as flow velocity, temperature, pressure, pH and formation of corrosion product layers. It appears that sufficient public knowledge is available at this point in time to enable development of a mechanistic model which can be used by the corrosion engineers to predict the corrosion rate while enhancing the further understanding of the corrosion process.

Various models have been developed in the past for CO_2 corrosion prediction as encountered in oil and gas industry[1]. Most of them are proprietary and unavailable to the public. Furthermore, the wide scatter of predictions they produce results primarily from the disparity of assumptions they are based on as well as very different modeling approaches. The problem is compounded by the lack of transparency with most of the models, all leading to a significant level of confusion currently existing in the field. When other corrosive species are present, such as organic acids and H_2S, the picture painted above is even bleaker. Therefore the goal of the present project is to provide the corrosion engineers and the broader corrosion community with a public, transparent, theoretically sound, simple and effective model for predicting internal corrosion of mild steel in the environment containing carbon dioxide, hydrogen sulfide and organic acids. The model was developed exclusively based on public information. All the background information, including theories behind the various modules, assumptions, data used for calibration and model limitations are shared with the users. More importantly, this model is freely available and can be easily accessed via the internet. To ensure the transparency of theories and numerical solutions used in the model, the source code is also shared. The application of object-oriented programming in constructing the model enables easy access to various modules. Further development of the model can be achieved by modifying existing modules or adding additional modules by third parties.

By offering this model free to the corrosion community, it is hoped that this will:

- Elevate the level of understanding and the prediction capability of mild steel corrosion as related to the oil and gas industry.

- Ensure that best available science and technology is available to the corrosion engineers, implemented by using a transparent approach which is open for further development and improvement.

- Increase the level of involvement of the broader corrosion community in developing better and more flexible tools fit for their intended purposes, an approach which will hopefully be mimicked in the future in other fields of corrosion.

- Fulfill one of the key missions of ICMT[*] and Ohio University as a public institution: to educate the wider professional community and extend its reach beyond the pool of the current research sponsors in order to enable more effective dissemination of the already published knowledge and technology.

With the model described below, one can predict the uniform corrosion rate of mild steel in environments containing carbon dioxide, hydrogen sulfide and organic acids. Respective contributions from various species to the overall corrosion process are calculated and reported quantitatively which enables the identification of the dominant corrosive species. A more in-depth study of the corrosion mechanism can be achieved by taking advantage of the polarization curves and species concentration profiles which can be easily displayed.

In the text below, the basic theories behind the corrosion mechanisms associated with aqueous carbon dioxide, hydrogen sulfide, organic acids, are first reviewed, followed by the description of the model implementation in terms of mathematical treatment and model functionality. The model predictions are then compared with experimental results under various conditions. In the final section, the limitations associated with the current version of the model are stated and the directions for future development are suggested.

THEORIES BEHIND THE MODELS

Most of the theories that serve as the basis of the present models are taken from three key papers[2,3,4]. A detailed description of the theoretical background as well as the relevant corrosion mechanisms can be found in the original publications. However, to facilitate the understanding of the present model, a brief introduction of the theories presented in those publications papers is given below.

Carbon Dioxide Corrosion

Carbon dioxide corrosion of mild steel is a process in which a number of chemical reactions, electrochemical reactions and transport process take place simultaneously. [2]

Chemical reactions. Carbon dioxide is predominantly a problem in internal corrosion of oil and gas pipelines when water is present. CO_2 is sparingly soluble in water:

$$CO_{2(g)} \Leftrightarrow CO_{2(w)} \qquad (1)$$

producing a hydration a weak acid, known as carbonic acid, H_2CO_3.:

$$CO_{2(w)} + H_2O \Leftrightarrow H_2CO_3 \qquad (2)$$

Carbonic acid partially dissociates in two steps to form bicarbonate and carbonate ions:

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$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (3)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (4)$$

Homogenous dissociation reactions (3) and (4) proceed much faster than the other simultaneously occurring processes in the system. Reactions (1) and particularly (2) have been known to be much slower (rate controlling) and could lead to local non-equilibrium in the solution.

Another important chemical reaction often seen in aqueous CO_2 solutions is the formation of solid iron carbonate as shown by reaction (5):

$$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_{3(s)} \quad (5)$$

$FeCO_{3(s)}$ will precipitate (predominantly on the steel surface) only when the local concentrations of Fe^{2+} and CO_3^{2-} exceed the solubility limit of $FeCO_{3(s)}$. The precipitation of $FeCO_{3(s)}$ often plays a significant role in the corrosion process because the $FeCO_{3(s)}$ layer may increases the mass transfer resistance for the corrosive species as well as reduces the available steel surface exposed to the corrosive solution. In fact, in many cases, the CO_2 corrosion rate is largely controlled by the presence of the $FeCO_{3(s)}$ layer. The protectiveness of the $FeCO_{3(s)\ (s)}$ layer depends primarily on the relative magnitude of the precipitation rate as compared to the underlying corrosion rate. High precipitation rate and low corrosion rate will lead to a dense and a protective $FeCO_{3(s)}$ layer, while low precipitation rate and high corrosion rate results in a porous, poorly protective layer on the steel surface.

Electrochemical reactions. There are a number of electrochemical reactions that have been found to contribute to the overall CO_2 corrosion process of mild steel. Hydrogen ion, H^+, reduction is one of the key cathodic processes:

$$2H^+ + 2e^- \rightarrow H_2 \quad (6)$$

This reaction is often limited by how fast the H^+ can be transported from the bulk solution to the steel surface through the mass transfer boundary layer (and the $FeCO_{3(s)}$ layer if in place). The presence of H_2CO_3 provides an additional reservoir for H^+ ions as any rapid consumption of H^+ can be readily replenished by reactions (3) and (4). Therefore, the presence of CO_2 enables higher rates of H^+ reduction, leading to higher corrosion rates. At a given pH, the CO_2 solutions are more corrosive than most mineral acids (e.g. HCl).

When the H_2CO_3 adsorbs at the steels surface first followed by reduction of the H^+ ion, this is referred to as “direct reduction of carbonic acid”. This reaction is in essence just an alternative pathway for the same cathodic reaction - hydrogen evolution (6):

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \quad (7)$$

The rate of this additional hydrogen evolution due to the presence of CO_2 is mainly controlled by slow CO_2 hydration step (2) and is a strong function of H_2CO_3 concentration which directly depends on partial pressure of CO_2.

Using a similar line of reasoning, it has been argued that additional hydrogen evolution in CO_2 saturated solutions can also happen via heterogeneous reduction of the adsorbed HCO_3^- (bicarbonate ion):

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \tag{8}$$

and that this reaction is particularly significant at pH>5 when the concentration HCO_3^- is elevated. However, no direct evidence has been found to support the significance of reaction (8), partially due to the fact that it is difficult to distinguish this pathway for hydrogen evolution from the other two described above. From pure kinetic arguments, it is also suspected that the rate of reaction (8) would be much slower than that of reactions (6) and (7). Therefore, direct reduction of bicarbonate (8) is considered insignificant and has been disregarded in the present version of the model.

Another possible pathway for hydrogen evolution is direct reduction of water:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{9}$$

Compared to the cathodic reactions described above, this pathway is very slow and often can be neglected in practical CO_2 corrosion environments. However, under peculiar conditions, such as very low partial pressure of CO_2 ($P_{CO2} << 0.1$ bar) and high pH (pH >6), this reaction may become significant and contribute to the overall corrosion process. Therefore, even if rarely relevant, this reaction has been included in the model for completeness.

Usually, at the corrosion potential, there is only one dominant anodic reaction involved in the CO_2 corrosion process. For mild steel, it is the iron oxidation:

$$Fe \rightarrow Fe^{2+} + 2e \tag{10}$$

This reaction proceeds via a multi-step mechanism which is mildly affected by pH and CO_2 concentration.

Transport. Due to evolution or consumption of certain species at the steel surface, concentration gradients are established between bulk solution and steel surface, which leads to molecular diffusion. In practical systems, pipelines are often subject to turbulent flow. Turbulent eddies can penetrate deep into the boundary layer i.e. get very close to the steel surface and therefore greatly enhance the abovementioned diffusional transport of species. Compared to some fast electrochemical reactions, such as hydrogen evolution (6), mass transfer of H^+ proceeds much slower, and therefore the rates of the overall reaction will be limited by transport, i.e. how fast the species can move through the mass transfer layer and any solid corrosion product layer. It is therefore essential to incorporate transport issues into the overall model in order to give an accurate description of the overall corrosion process.

Hydrogen Sulfide Corrosion

In contrast with CO_2 corrosion, which is electrochemical in nature, H_2S corrosion of mild steel is considered to proceed predominantly via a *solid state, chemical* reaction:

$$Fe + H_2S \Leftrightarrow FeS_{(s)} + H_2 \tag{11}$$

The term *chemical* reaction emphasizes the fact that due to the speed of formation of solid $FeS_{(s)}$ there is no significant spatial separation of the oxidation and reduction reactions at the steel surface, i.e. no electrical current flowing between the anodic and cathodic sites; while *solid state* reaction refers to the fact that both initial and final state of iron are solid.

Sun et. al.[3] proposed a plausible mechanism for H_2S corrosion of mild steel based on laboratory experiments. H_2S initially absorbed onto the steel surface reacts very fast with iron to form a very thin (<<1 μm) dense and protective non-stoichiometric iron sulfide film – mackinawite. Due to its compactness, this film acts as a solid state diffusion barrier for species involved in the corrosion process which leads to a significant and rapid reduction of the corrosion rate. However, the diffusion of the corrosive species through this mackinawite film does not stop altogether and the continuing corrosion at the steel surface keeps on generating more mackinawite. This gradually leads to the growth of internal stressing in the mackinawite film due to epitaxial stresses and the Pilling-Bedford ratio (much larger volume of the mackinawite when compared to the originating *Fe*). These stresses lead to microcracking and eventually delamination of the mackinawite film. A cyclic process of growth, cracking and delaminating of mackinawite eventually leads to formation of an outer mackinawite layer which is much thicker, more porous and less protective. The mackinawite might transform over time into other forms of sulfide such as pyrhotite. In addition pyrhotite might precipitate from the solution, however this effect is not included in the present version of the model. The same is true for formation of pyrite and elemental sulfur which are not considered in the present version of the model.

It is clear that, according to the above scenario, H_2S corrosion is largely limited by how fast corrosive species can move through the iron sulfide layers inevitably present on the steel surface. Therefore, in the present model, H_2S corrosion is always considered to be under mass transfer control. In addition, it is assumed that the presence of the mackinawite layers acts as a diffusion barriers for other species as well and that they affect any accompanying CO_2 and/or organic acid corrosion in a similar fashion.

Organic Acid Corrosion

There are several forms of water soluble organic acids that are typically seen in the water phase accompanying oil and gas production, such as formic, acetic and propionic acids, among which acetic acid is the most common one. Furthermore it has been shown that there is no significant difference in the corrosiveness of these three acids, therefore, acetic acid is often used in corrosion analysis to represent the whole group.

Acetic acid, CH_3COOH, or in shorthand: *HAc*, is a small molecular length water soluble organic acid which is rather volatile – a property that makes it a major concern in top-of-line corrosion (TLC). Similarly to carbonic acid, acetic acid is a *weak* – only partially dissociated acid. In the temperature range of interest, *HAc* is mainly found in the aqueous phase and therefore corrosion caused by *HAc* is not strongly affected by presence of *HAc* vapors (other than in the case of TLC). This is different from CO_2 corrosion where gaseous CO_2 controls the amount of H_2CO_3 in the aqueous phase and therefore determines the rate of CO_2 corrosion.

Partial dissociation of acetic *HAc* provides an additional source of hydrogen which can be reduced:

$$HAc \Leftrightarrow H^+ + Ac^- \tag{12}$$

Experiments have confirmed that other than being an extra reservoir of hydrogen ion, the undissociated *HAc* can be "directly" reduced after adsorbing at the steel surface.

$$2HAc + 2e^{-} \rightarrow H_2 + 2Ac^{-} \qquad (13)$$

Therefore, the presence of "free" acetic acid becomes a major concern especially at lower pH when the equilibrium of the dissociation reaction (12) is shifted to the left. Direct reduction of *HAc* has been found to be strongly affected by velocity indicating that this reaction is a mass transfer controlled process i.e. the rate of corrosion depends primarily on the concentration of *HAc* and how fast *HAc* can transport to the steel surface.

MODEL IMPLEMENTATION

Numerical Calculation

Calculation of CO_2/ HAc corrosion rate. CO_2 and HAc corrosion are both electrochemical in nature. The corrosion rate can therefore be calculated based on total current density of the anodic reaction (or the sum of cathodic reactions).

$$CR = \frac{i_a M_{w,Fe}}{\rho_{Fe} nF} \times 1000 \times 3600 \times 24 \times 365 = 1.159 \times i_a \qquad (14)$$

Where,

CR: corrosion rate, mm/a;
ia: anodic current density, A/m^2;
$M_{w,Fe}$: atomic mass of iron;
ρ_{Fe} : density of iron;
n: number of moles of electrons involved in iron oxidation, 2 mole/mol;
F: Faraday's constant.

The anodic current density of iron oxidation is obtained by,

$$i_{a,Fe} = i_{o,Fe} \times 10^{\frac{E_{corr} - E_{rev,Fe}}{b_{Fe}}} \qquad (15)$$

Where,

$i_{a,Fe}$: current density of iron oxidation, A/m^2;
$i_{o,Fe}$: exchange current density of iron oxidation, A/m^2;
E: corrosion potential, V;
$E_{rev,Fe}$: reversible potential of iron oxidation;
b_{Fe}: Tafel slope of iron oxidation.

The current density of individual cathodic reaction is given by,

$$\frac{1}{i_c} = \frac{1}{i_{ct}} + \frac{1}{i_{\lim}} \qquad (16)$$

Where,

i_c: current density of any cathodic reaction,A/m^2;

i_{ct}: component of charge transfer current density, A/m^2;

$i_{\lim}$: component of limiting current density , A/m^2;

The charge transfer current density of cathodic reactions can be calculated by,

$$i_{ct} = i_o \times 10^{\frac{E_{rev}-E}{b}} \cdot \eta_{FeCO_3} \cdot \eta_{FeS} \tag{17}$$

Where,

i_O: exchange current density of cathodic reactions, A/m^2;

E_{rev}: reversible potential of cathodic reactions, V;

b : Tafel slope of cathodic reactions;

$\eta_{FeCO_3}, \eta_{FeS}$: scale factors due to formation of $FeCO_3$ and FeS film, respectively.

Most of cathodic reactions are mass transfer limited. Therefore, the limiting current density can be calculated as,

$$i_{\lim}^{d} = \eta_{FeCO_3} \cdot \eta_{FeS} \cdot k_m F c_j \tag{18}$$

Where,

k_m: mass transfer coefficient of corrosive species, m/s;

c_j: bulk concentration of corrosive species, mol/m^3;

However, carbonic acid reduction is limited by slow reaction rate of CO_2 hydration, as shown in reaction 2. The limiting current density of this reaction is calculated in a different fashion, as shown below,

$$i_{\lim,H_2CO_3}^{r} = Fc_{CO_2}\left(\eta_{FeCO_3} \cdot \eta_{FeS} \cdot D_{H_2CO_3} K_{hyd} k_{hyd}^{f}\right)^{0.5} f \tag{19}$$

Where,

c_{CO_2} : concentration of CO_2 in bulk solution, mol/m^3;

$D_{H_2CO_3}$: diffusion coefficient of H_2CO_3 in water, m^2/s;

k_{m,H_2CO_3} : mass transfer coefficient of H_2CO_3, m/s;

K_{hyd}: equilibrium constant for CO_2 hydration reaction;

k_{hyd}^{d} : forward reaction rate constant for CO_2 hydration reaction;

f: flow factor affecting CO_2 hydration, which is given by,

$$f = \frac{1+e^{-2\delta_m/\delta_r}}{1-e^{-2\delta_m/\delta_r}} \tag{20}$$

Where δ_m and δ_r are defined as mass transfer and reaction layer thickness, respectively, and can be calculated as,

$$\delta_m = \frac{D_{H_2CO_3}}{k_{m,H_2CO_3}} \tag{21}$$

$$\delta_r = \sqrt{\frac{D_{H_2CO_3} K_{hyd}}{k_{hyd}^f}} \tag{22}$$

The unknown corrosion potential, E_{corr}, can be found based on charge balance on the steel surface.

$$\sum_1^{na} i_a = \sum_1^{nc} i_c \tag{23}$$

Where,

i_a, i_c: anodic and cathodic current density, respectively, A/m^2;
n_a, n_c: total numbers of anodic and cathodic reactions, respectively.

Normally, only one anodic reaction (iron oxidation) is involved in the model, while the number of cathodic reactions is variable depending on the corrosive environment.

Calculation of H_2S corrosion rate. Corrosion by H_2S is assumed to be under pure mass transfer control due to the presence of makinawite layers and the mass transfer boundary layer. At steady state, the corrosion rate caused by H_2S can be obtained by equating the flux of H_2S through three layers existing on steel surface. The corrosion rate of H_2S is given by[4]:

$$CR_{H_2S} = A_{H_2S} \ln \frac{c_{b,H_2S} - Flux_{H_2S}\left(\frac{\delta_{OS}}{D_{H_2S}\varepsilon\psi} + \frac{1}{k_{m,H_2S}}\right)}{c_{s,H_2S}} \tag{24}$$

Where,

CR_{H_2S} : corrosion rate caused by H_2S expressed in mol/(m^{2}s);
k_{m,H_2S} : mass transfer coefficient of H_2S in liquid boundary layer, m/s;
D_{H_2S} : diffusion coefficient of H_2S in water;
ε, ψ : porosity and tortuosity of outer mackinawite scale;
δ_{os} : thickness of the outer scale, m;
c_{b,H_2S}, c_{s,H_2S} : concentration of H_2S in bulk solution and at steel surface, respectively, mol/m^3;
A_{H_2S} : constant for solid state diffusion.

In the presence of H_2S the corrosion by other species such as H^+, H_2CO_3, etc., is also assumed to be under mass transfer control due to the protectiveness of the mackinawite layers. Therefore, the corrosion rates caused by these other species are calculated in a similar fashion as that for H_2S by using different physical properties as appropriate.

Model Construction

The model* was developed as an Excel add-in, which does not require any special software on users' computers other than Microsoft Excel®. Once the model has been added into the Excel add-in list

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[*] The model is available for download from http://www.corrosioncenter.ohiou.edu/freecorp

for the first time, it can be accessed from every Excel file without duplicating the code. The object-oriented programming (OOP) concepts[5] are employed while developing the code, which makes the program highly modular. For CO_2 corrosion, the major calculation processes are treated as individual objects, which are separated from the graphic user interface (GUI) of the program and can be integrated into any other programs that users might need. In the current version of the code, the H_2S corrosion model has not been modularized to the same extent, a feature which will be improved in the near future. The architecture of the model is schematically shown in Figure 1.

Major Features of the Model

One of the major features of the model is that the advanced users are allowed to modify the calculation process by adding/ removing reactions, including adding new user-defined reactions into the electrochemical model. The latter feature enables the users to explore how one or more reactions, including user-defined reactions, affect the corrosion process. A maximum of 10 anodic reactions and 10 cathodic reactions are allowed to participate in any corrosion calculation. The same flexibility is not built into the H_2S module in the present version of the code.

Another important feature is the so called “Corrosion Details”. This feature gives a tabulation of all involved corrosive species in terms of their contributions to the overall corrosion rate expressed in percents. For CO_2 corrosion, the contributions are obtained based on individual cathodic current density of corrosive species, while for H_2S corrosion, the contributions are calculated based on fluxes of corrosive species. This feature gives a quantitative measure of how much each corrosive species contributes to the overall corrosion rate and facilitates the exploration of major corrosion mechanism.

In-depth investigation of corrosion mechanism can be furthered by studying the various plots that can be produced by the model. If the corrosion process is CO_2/HAc dominated, the polarization curves, which relate potential with current density, are given for all individual electrochemical reaction involved in the corrosion process. In addition, the net anodic and cathodic reaction as well as the potentiodynamic sweep can also be displayed. Each of these curves can be made visible or hidden. An example of the polarization curves is illustrated in Figure 6. When corrosion process is H_2S dominated, a different type of plot is shown which gives the concentration profile of H_2S through the layers existing on steel surface. An example of H_2S concentration profile is shown in Figure 8.

MODEL VERIFICATION AND DEMONSTRATION

The model has been extensively tested against experimental data under various conditions. Experimental data was obtained from both the open publications and the ICMT database at Ohio University which contains over 700 unique cases. As an example, Figure 2 shows the predicted corrosion rate vs. experimental corrosion rate for cases of CO_2 corrosion. It can be seen that predicted corrosion rates increase with increasing temperatures and decrease with increasing pHs, which matches the trends seen in the experiments. Clearly, fairly good agreements between model predictions and experiments are obtained at various temperatures and pHs.

Figure 3 shows an example of a comparison of the model with the experimental results for the case of combined CO_2/HAc corrosion. It is clear that under these test conditions, model predictions match well with both LPR and weight loss test results for different concentrations of HAc. With increasing HAc concentration, the model gives an increasing corrosion rate as expected.

Figure 4 shows comparison between predicted and measured corrosion rates for three different cases. Experimental data was obtained by IFE[*]. The test conditions are tabulated in Table 1. It can be seen that these cases reflect a range of physical and chemical conditions in terms of some critical factors affecting corrosion, such as temperature, partial pressures of CO_2 and H_2S. Clearly, the model was able to accurately predict the corrosion rate under various conditions thanks to the good theoretical base of the model.

Figure 5 compares the experimental and predicted potentiodynamic sweeps. It is evident that the model is in good agreement with the experimental data under test conditions.

An example of deploying a user-defined reaction is demonstrated in Figure 6 and 7. Figure 6 shows the polarization curves with 3 pre-defined (default) cathodic reactions, H_2CO_3 reduction, H^+ reduction and H_2O reduction; the corrosion rate given by the model is 1.6 mm/y. An arbitrary user-defined cathodic reaction is then added into the system by defining the necessary parameters, such as reversible potential, exchange current density, Tafel slope and limiting current density. For real cases, these parameters can be obtained either by experimentation or from the literature. The new polarization curves which included the additional user-defined cathodic reaction are shown in Figure 7. It can be seen that due to the participation of the additional cathodic reaction, the net cathodic reaction rate significantly increased leading to a higher corrosion current density. The corrosion rate predicted by the model is now 3 mm/y. Other user-defined reactions, both cathodic and anodic, can also be added into the model. This feature of the electrochemical model offers user the flexibility to smoothly explore how a customized reaction affects corrosion process.

Figure 8 illustrates a plot of H_2S concentration vs. distance from steel surface given by the model for a case of H_2S dominated corrosion. It can be seen that concentration gradient of H_2S was established across the three layers on the steel surface, which are called here: inner mackinawite film, porous outer scale and mass transfer boundary layer. In this case, the porous outer scale caused a major concentration gradient of H_2S due to its torturous pathway available for species to travel through. The mass transfer boundary layer, although is the thickest, contributed very little to the mass transfer resistance.

MODEL LIMITATIONS

In this initial version of model, a few factors have not yet been taken into consideration. These factors limit the use of this model under certain circumstances. Major limitations associated with current version of the model are listed below,

- This model is a so-called “point model”, corrosion rates are predicted based on conditions for a single point on the metal surface, e.g. somewhere along the pipeline where the operating conditions are known. The accuracy of the prediction heavily depends on the reliability of the parameters provided to the model.
- This model is developed currently to only take into account the effect of single-phase flow; multiphase flow module is not available at present; however object-oriented programming of this model enables existing corrosion modules to be readily coupled with external flow simulators such as OLGA, FLUENT, etc.

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- This model predicts uniform corrosion; no localized corrosion module has been included at present.

- This model assumes simple water chemistry, i.e. the infinite solution theory is invoked and an ideal solution is assumed; furthermore the interaction between the chemical and diffusional processes is ignored meaning that the species independently diffuse through the boundary layer without interacting with each other.

- This model employs a simple empirical correlation based on supersaturation of iron carbonate to simulate iron carbonate film growth which is subject to further development.

- This model does not take into account the effect of high solution salinity on corrosion process.

- A simple criterion is used to determine the transition between CO_2 dominated and H_2S dominated corrosion. When CO_2 and H_2S coexist, corrosion rates are calculated based on both CO_2 and H_2S corrosion mechanism as described earlier, the corrosion rates are then compared with each other. The mechanism that gives the higher corrosion rate is considered as the dominated mechanism.

- No data post processing is available in this model.

Most of the limitations listed above will be overcome in the near future as work on the model continues and as the involvement from the broader corrosion community initiates.

CONCLUSIONS

- A free open-source mechanistic corrosion predictive model has been developed and described in this work. At present the default version of the model can be used to predict the uniform corrosion rate of mild steel caused by CO_2, H_2S and HAc.

- Corrosion calculations can be easily modified by users by adding or removing electrochemical reactions to/from the system.

- The default version of the model has been carefully calibrated and is in good agreement with experimental results under various test conditions.

REFERENCES

1. Rolf Nyborg, “Overview of CO_2 Corrosion Models for Wells and Pipelines”, Corrosion/2003, Paper No. 02233. (Houston, TX: NACE 2003)

2. S. Nesic, J.Postlethwaite and S. Olsen, Corrosion Science, “An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions”, Vol. 52, No.4, 1996, p.280-294.

3. Keith George and Srdjan Nesic, “Electrochemical Investigation and Modeling of Carbon Dioxide Corrosion of Carbon Steel in the Presence of Acetic Acid”, Corrosion/2004, Paper No. 04379. (Houston, TX: NACE 2004)

4. Wei Sun and Srdjan Nesic, “A Mechanistic Model of H_2S Corrosion of Mild Steel”, Corrosion/2007, Paper No. 07655. (Houston, TX: NACE 2007)

5. James Rumbaugh, Michael Blaha, Frederick Eddy, William Lorensen and William Premerlani, Object-oriented Modeling and Design, Prentice Hall,1991.

TABLE 1 THREE CASES OF TEST CONDITIONS

Parameters	Case 1	Case 2	Case 3
Temperature, °C	80	25	80
pCO_2, bar	3.3	3.3	10.0
pH_2S, bar	10	10	30
Solution pH	3.10	3.20	2.90
Pipe diameter, m	0.015	0.015	0.015
Velocity, m/s	1	1	1
Duration, days	19	21	15

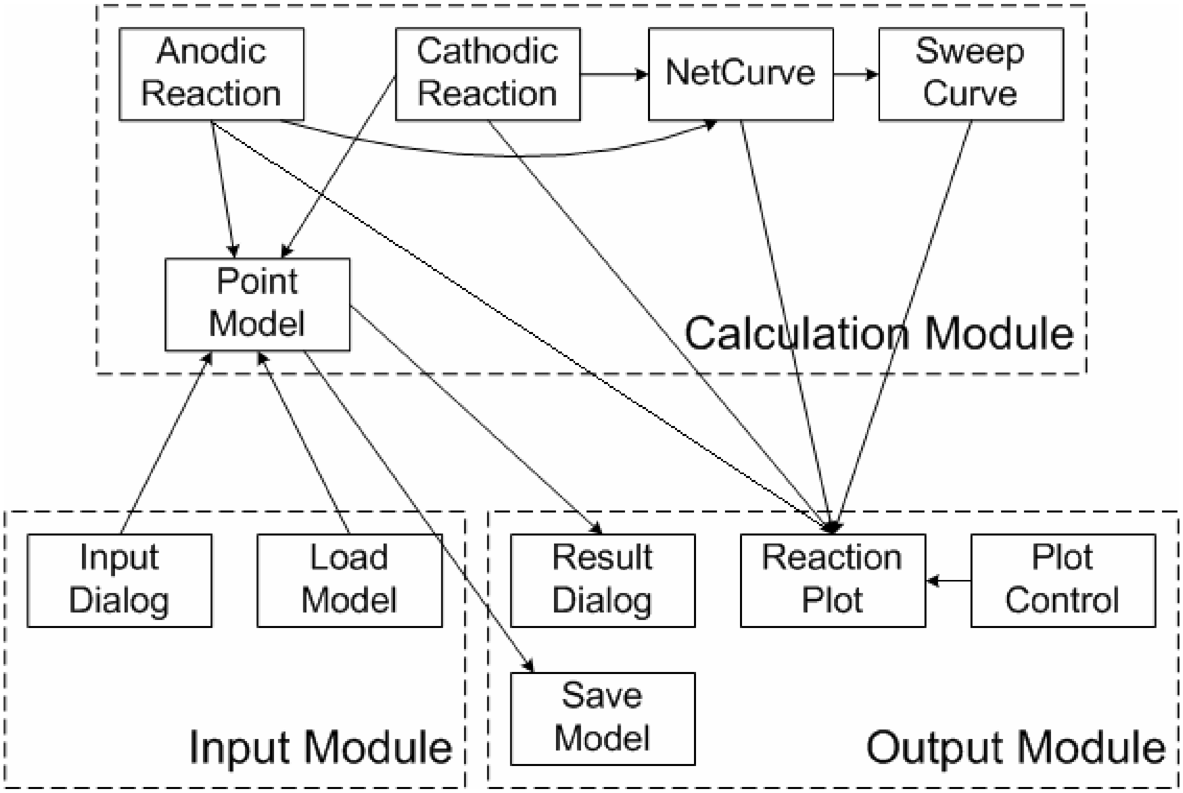

Figure 1. Architecture of the Model

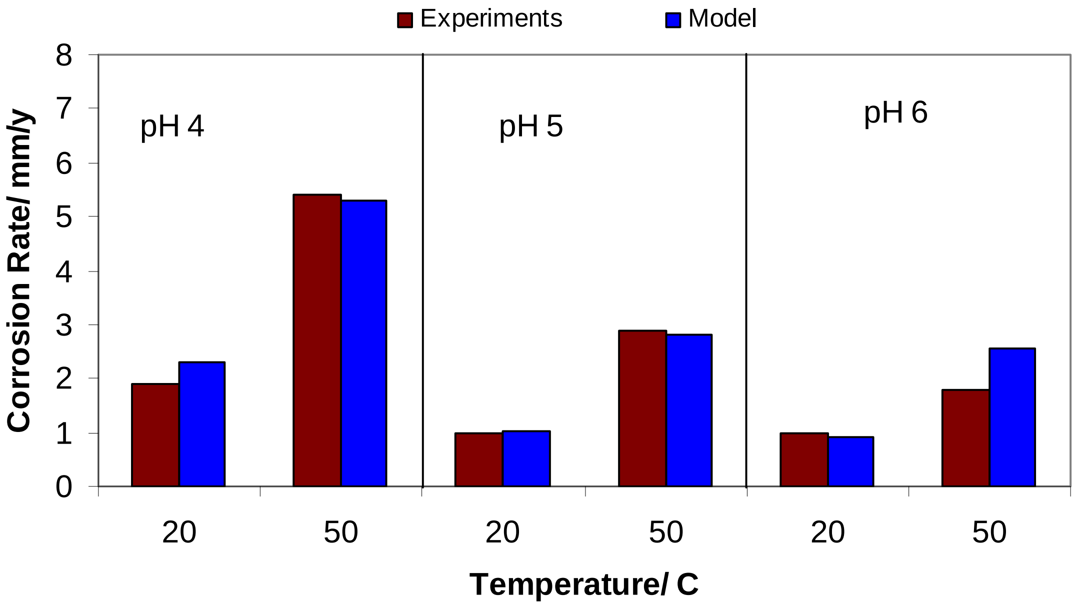

Figure 2. The comparison of experimental and predicted corrosion rate; conditions: partial pressure of CO_2 1bar, liquid velocity 2 m/s, pipe diameter 0.015 m.

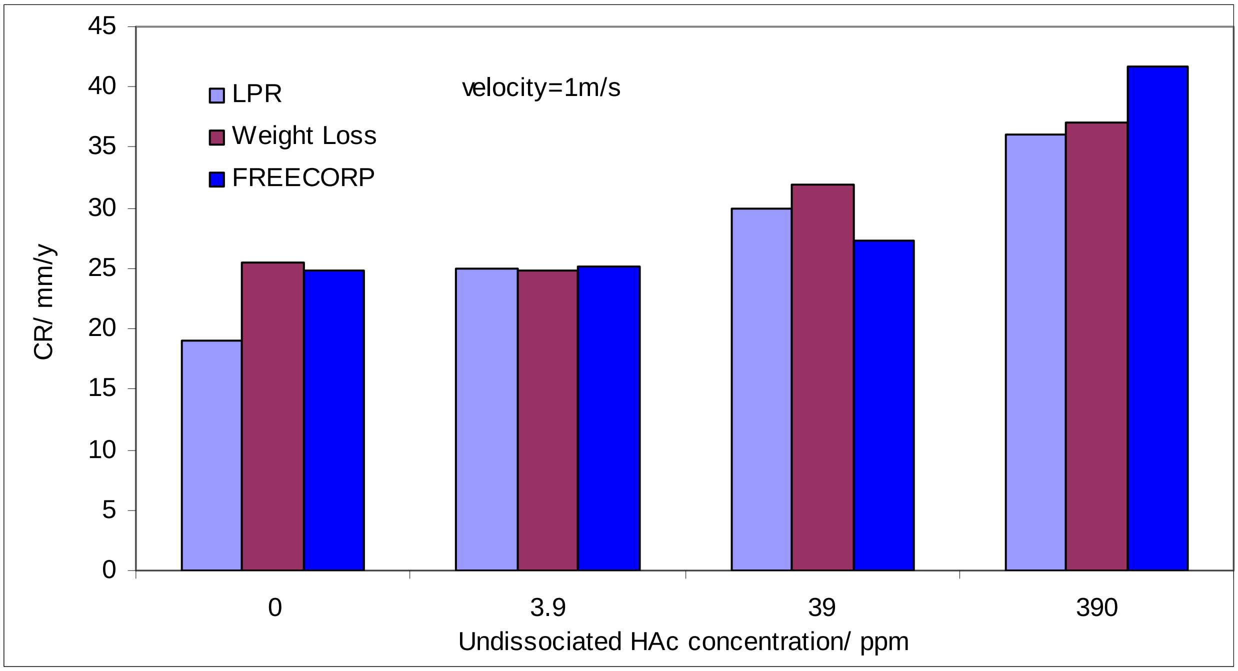

Figure 3. The comparison of experimental and predicted corrosion rate; conditions: temperature 60° C, pH 5, liquid velocity 1 m/s, partial pressure of CO_2 10 bar, pipe diameter 0.1m.

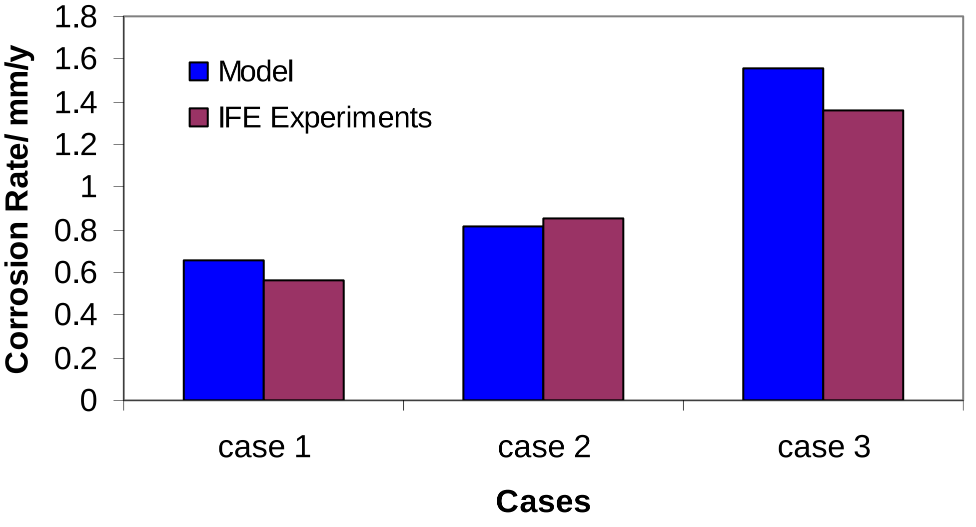

Figure 4. The comparison of experimental and predicted corrosion rate under the conditions listed in Table 1.

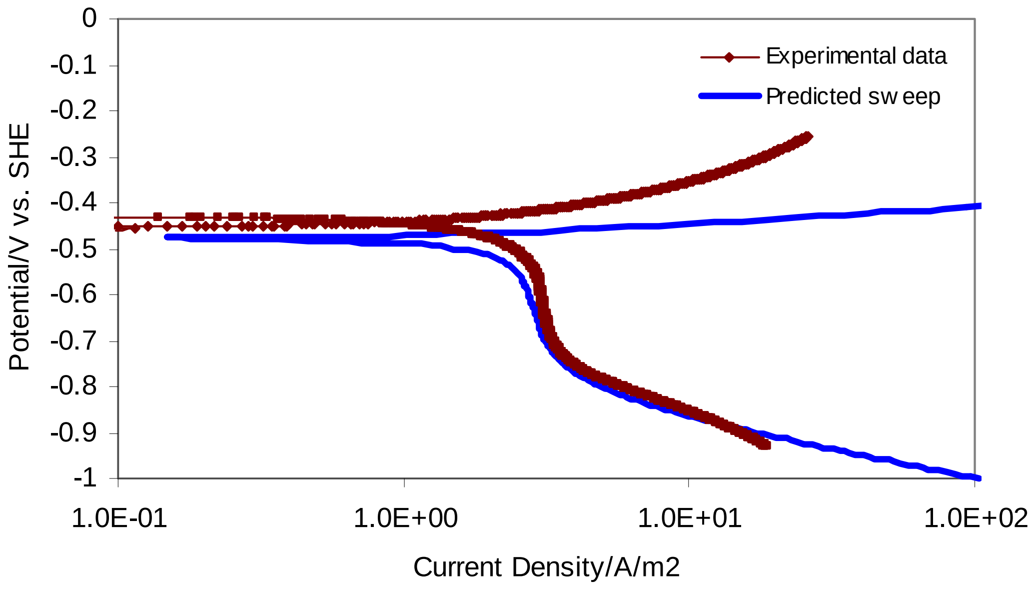

Figure 5. The comparison of experimental and predicted potentiodynamic under the conditions of for a case of temperature 25° C , partial pressure of CO_2 1bar, solution pH 4 and rotation speed 1000rpm.

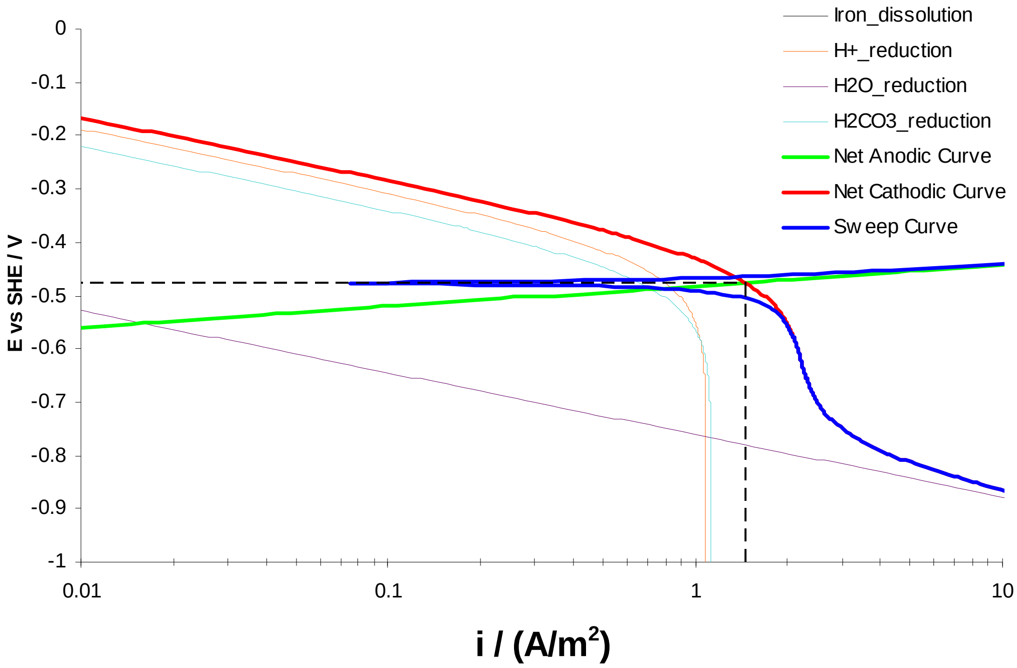

Figure 6. Polarization curves without user-defined reactions

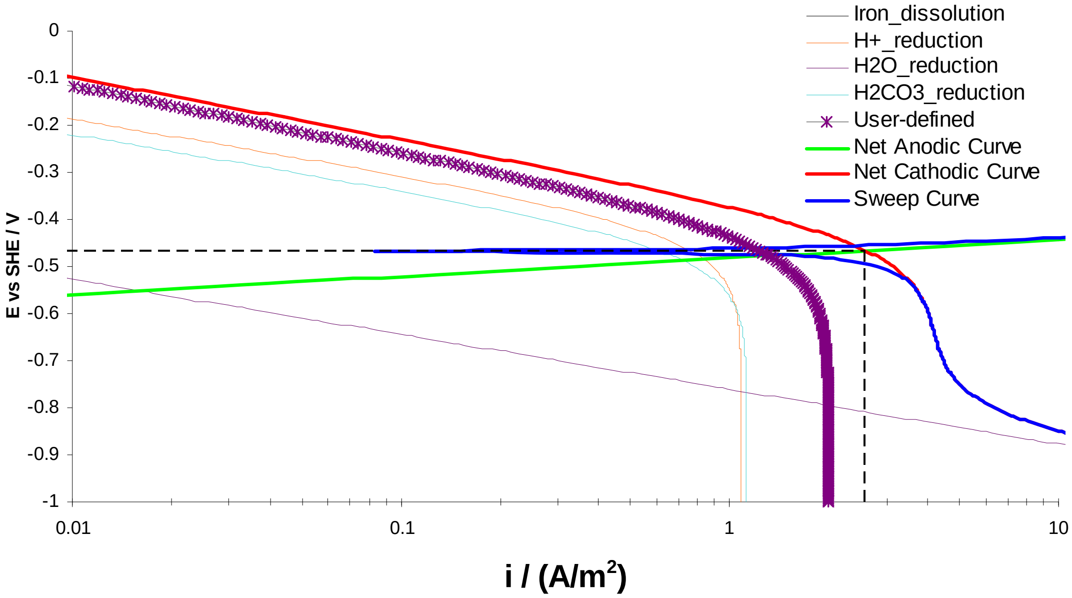

Figure 7. Polarization curves with a user-defined reaction

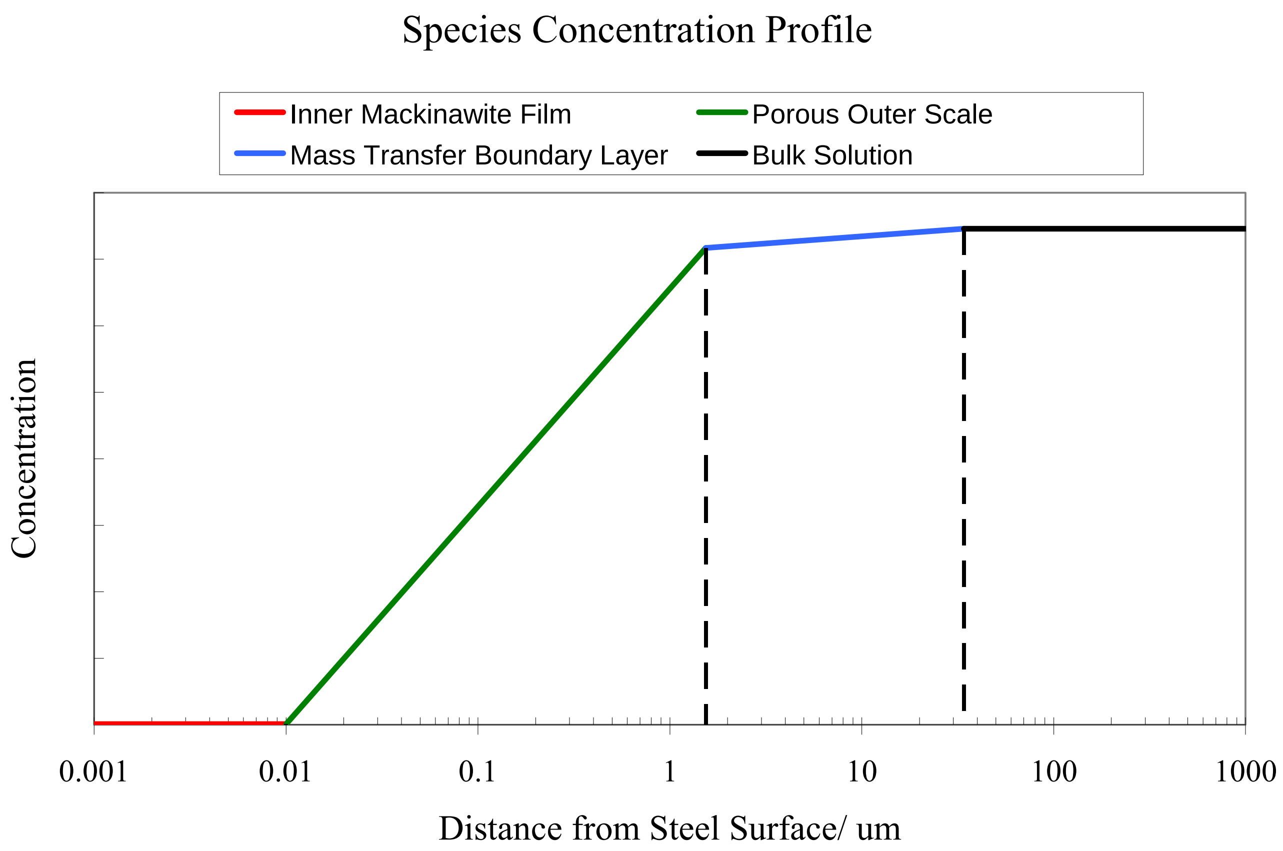

Figure 8. Predicted H_2S concentration profile as a function of distance from steel surface; conditions temperature 20° C, partial pressure of CO_2 1bar, pipe diameter 0.1m, liquid velocity 1m/s, solution pH 4 and H_2S concentration 50ppm in gas phase.