Modelling of carbon dioxide corrosion of steel with iron carbonate precipitation

M. Shayegani*[1,2], M. Ghorbani[1], A. Afshar[1] and M. Rahmaniyan[2]

Corrosion of mild steel in aqueous solutions containing carbon dioxide was modelled under condition that protective iron carbonate films formed on the steel surface. In this model, the film form on the steel surface due to precipitation of iron carbonate from saturated solution. The precipitation of iron carbonate produces a porous layer on the steel surface, reducing the diffusion of species toward the steel surface. If the precipitation rate is high, the porosity decreases and the mass transport becomes slower. Therefore, formation of protective layers on the steel surface reduces the corrosion rate. In this case, the corrosion processes are controlled with diffusion of species. The model was verified against published experimental data. The model can predict the thickness and the porosity of the film formed on the steel surface and also the corrosion rate of steel under deposited layer. The effects of some parameters such as Fe^{2+} concentration and temperature on film thickness and corrosion rate were investigated. The developed model is a solid approach for prediction of corrosion rate in conditions that precipitation of iron carbonate occurs on the steel surface.

Keywords: Carbon dioxide corrosion, Mild steel, Prediction, Precipitation, Protective layers

Introduction

The formation of iron carbonate on steel surface is one of the important factors influencing the rate of corrosion.[1–4] Therefore if it is not considered in a corrosion prediction model, the worse case corrosion rate is predicted. In the previous work,[5] a mechanistic model of carbon dioxide corrosion is developed. In that model, the electrochemical reactions at the steel surface, chemical reactions and transport of species between the steel surface and the bulk solution have been included. However, it cannot predict the thickness and morphology of the growing scales. Therefore, that model is suitable for condition that the iron carbonate layer does not precipitate on the steel surface or the precipitation rate is very low. In this research, the formation and the growth of iron carbonate layer on the steel surface is modelled. Therefore some changes took place in the model. First these changes describe briefly here and then the film growth model is proposed. Because the iron carbonate layer is formed on the steel surface (Fig. 1), the diffusion through the pores of the layer must be considered in the transport processes. A one-dimensional form of the mass balance equation[6] which describes transport for species j from the bulk solution to the steel surface through the liquid boundary layer and the porous film, is

$$\frac{\partial(\varepsilon c_j)}{\partial t} = \frac{\partial}{\partial x}\left[\varepsilon^{1\cdot5} D_j^{\mathrm{eff}} \frac{\partial c_j}{\partial x}\right] + \varepsilon R_j \qquad (1)$$

where c_j is the concentration of species j in kmol m^{-3}, ε is the porosity of the film, D_j^{eff} is the effective diffusivity coefficient of j in m^2 s^{-1}, R_j is the rate of consumption or production of species j due to all the chemical reactions in which a particular species is involved in kmol m^{-3} s^{-1}, t is time, x is the spatial coordinate in m.

D_j^{eff} obtained from

$$D_j^{\mathrm{eff}} = D_j^{\mathrm{m}} + D_j^{\mathrm{t}} \qquad (2)$$

where D_j^{m} is molecular diffusivity coefficient and D_j^{t} is turbulent diffusivity coefficient. The turbulent diffusivity coefficient D_j^{t} in porous layer is zero and in the liquid boundary layer is given by[7]

$$D_{\mathrm{t}} = 0\cdot18\left(\frac{x}{\delta}\right)^3 \frac{\mu}{\rho} \qquad (3)$$

where ρ is the liquid density, μ is dynamic viscosity, δ is the liquid boundary layer thickness and x is the distance from the iron carbonate layer.

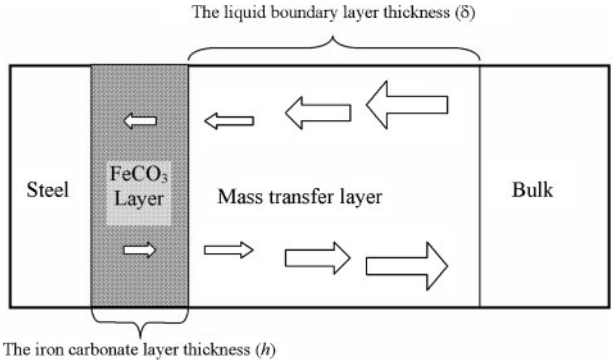
Other steps for determining the electrochemical currents and solving the transport equation (1) are described in previous work completely.[5] In this research, a simple model for formation of iron carbonate layer on the steel surface due to precipitation is proposed. Then the model is verified against the published experimental results.

---

[1] Department of Materials Science and Engineering, Sharif University of Technology, Azadi St., Tehran, Iran
[2] Corrosion research department of Research Institute of Petroleum Industry (RIPI), NIOC, Pazhooheshgah Boulevard, Old Qom Road, Tehran, Iran

*Corresponding author, email Shayeganim@ripi.ir

Published by Maney on behalf of the Institute
Received 21 July 2007; accepted 5 December 2007
DOI 10.1179/174327808X286338



1 Sketch of computational domain

Precipitation model

In the case of CO_2 corrosion, when the concentration of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, solid iron carbonate precipitates on the steel surface or on the surface of previous precipitated iron carbonate layer according to[4,8]

$$Fe^{2+}+CO_3^{2-}\rightarrow FeCO_3 \tag{4}$$

Iron carbonate scale growth depends on the precipitation kinetics. The rate of precipitation (R_{FeCO_3}) is a function of iron carbonate supersaturation (S), the solubility limit (K_{sp}), temperature and surface to volume ratio (S/V)[9]

$$R_{FeCO_3}\left(\mathrm{mol\ m^{-3}\ s^{-1}}\right)=\frac{S}{V}e^{28\cdot2-\frac{64851(\mathrm{J\ mol^{-1}})}{RT}}K_{sp}(S-1) \tag{5}$$

Supersaturation is defined as

$$S=\frac{C_{Fe^{2+}}C_{CO_3^{2-}}}{K_{sp}} \tag{6}$$

Iron carbonate solubility limit (K_{sp}) is a function of temperature T (K), and ionic strength I (mol L^{-1})[9]

$$\log(K_{sp})=-59.35-0.04138T-\frac{2.1963}{T}+24.5724\log(T)+2.518I^{0.5}-0.657I \tag{7}$$

The proposed equation describing the iron carbonate layer growth kinetics is

$$\frac{\partial c_{FeCO_{3(S)}}}{\partial t}=R_{FeCO_{3(S)}} \tag{8}$$

As $FeCO_{3(S)}$ is a solid, its diffusion and convection can be neglected. Therefore, if precipitation occurs the amount of $FeCO_{3(S)}$ will increase over time in any mesh. The morphology of iron carbonate layer can be expressed in terms of thickness and porosity. The proposed equation describing the film thickness growth is

$$\frac{\partial h}{\partial t}=\frac{dxM_{FeCO_3}}{\rho_{FeCO_3}(1-\varepsilon_{in})}R_{FeCO_3} \tag{9}$$

where $M_{FeCO_3}\left(=115\cdot847\ \mathrm{kg\ mol^{-1}}\right)$ is the molecular mass and $\rho_{FeCO_3}\left(=3900\ \mathrm{kg\ m^{-3}}\right)$ is the density of iron carbonate. dx is the mesh thickness and ε_{in} is the initial porosity. A one-dimensional transport model has been used in the pervious work to describe the mass transport process.[5] It can be used to describe the film thickness growth as expressed by equation (9). The precipitation rate is calculated for each mesh separately. Therefore with respect to the method that the equation (5) has been obtained from it, the S/V equal to $1/dx$. If the precipitation occurs simultaneously in more than one mesh, the precipitation rate in each mesh will be obtained simply from

$$(R_{FeCO_3})_{mesh}=R_{FeCO_3}\frac{1}{n} \tag{10}$$

where n is the number of the mesh which precipitation occurs in, simultaneously. At the beginning stage of precipitation, it occurs in each mesh with initial porosity and the scale thickness calculated from equation (9) after each time step. This procedure continues until the thickness of the scale formed in the mesh, being equal to the mesh thickness, dx. After that, if precipitation continues in that mesh, the initial porosity of formed scale will be decreased. The changes of the porosity of scale are obtained from

$$\frac{\partial\varepsilon}{\partial t}=-\frac{M_{FeCO_3}}{\rho_{FeCO_3}}R_{FeCO_3} \tag{11}$$

Initial and boundary conditions

The initial conditions for the equation (1) are considered to be bulk concentrations, which are calculated from a prior chemical equilibrium calculation.[5] These equilibrium concentrations are also used as boundary condition at the bulk mass transfer boundary layer interface.

At the metal surface, flux of the species not involved in electrochemical reactions, is assumed to be zero. For species j involved in an electrochemical reaction, the flux at the metal surface is determined from the rate of the electrochemical reaction as described elsewhere.[5]

The initial condition for the equation (9) was $h=0$ for all mesh and that of for the equation (11) was $\varepsilon=1$ for all mesh.

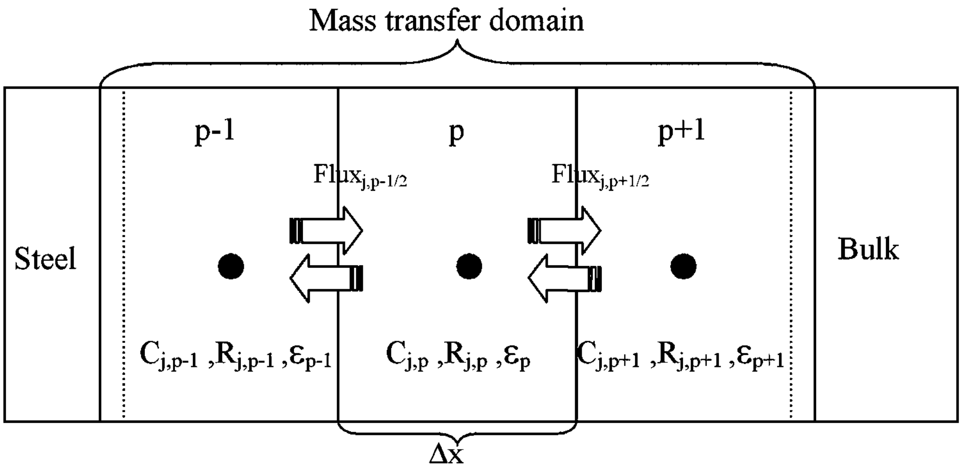
Computational techniques

Concentration profile of species can be determined by solving a set of equations simultaneously in space and time. Therefore equation (1) is written for each species in the solution. There are n equations for n species in the solution, because there is a transport equation (1) for each species. Note that the concentration profile of solid iron carbonate obtains from equations (9) and (11) as thickness and porosity. The differential transport equation (1) was discretised using a finite difference method and a uniform grid as shown in Fig. 2.

The finite difference approximation of the transport equations for species j in node p is given by

$$\varepsilon_p\frac{c_p^{n+1}-c_p^{n}}{\Delta t}=\varepsilon_{p+1/2}^{1.5}D_{j,p+1/2}\frac{c_{p+1}^{n+1}-c_p^{n+1}}{(\Delta x)^2}-\varepsilon_{p-1/2}^{1.5}D_{j,p-1/2}\frac{c_p^{n+1}-c_{p-1}^{n+1}}{(\Delta x)^2}+\varepsilon_pR_{j,p}^{n+1} \tag{12}$$

Superscripts $n+1$ and n denote new and old points in time respectively; Δx is the mesh thickness on the order of 10^{-7} m. A fully implicit time discretisation scheme is used here for this purpose that larger time step can be used without having instability. Although fully implicit



2 Sketch of finite difference uniform grid used for implementation of model

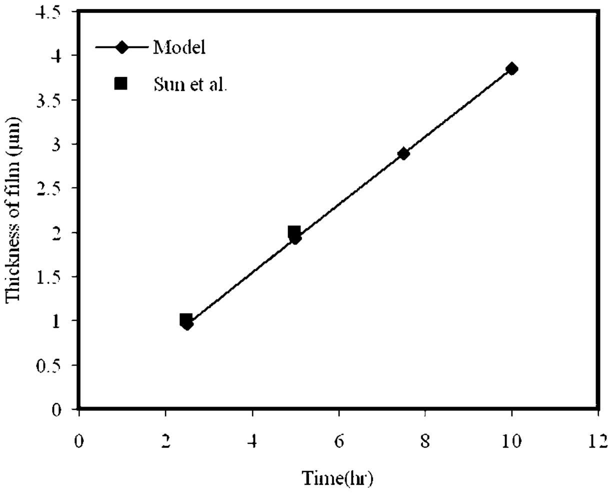
scheme is unconditionally stable, to start the simulation, time step on the order of 10^{-4} s was used. After some steps, time step was changed to 10^{-2} s. The mass transfer layer consisted of 100 nodes. All the terms are evaluated in the centre of the node, except the fluxes, which are evaluated at the node boundaries. More information about calculating the chemical reaction rate and the electrochemical reaction rate, is given in previous work.[5]

The film thickness growth and the film porosity equations were discretised using a finite difference method with an explicit time discretisation scheme. Because the film growth happens so slowly, an explicit method with time step 1 s can be used with good stability. When for each period of time the film thickness and its porosity were calculated, then the other processes such as the mass transport and the electrochemical reaction were handled as mentioned above. In the present study, to decrease the total calculating time of modelling, it is assumed that the film growth rate and the corrosion rate are constant values in each minute of the corrosion process. This assumption does not seem far from reality, because the film growth happens so slowly.[10] After solving the mass transport equations at the beginning of each minute of the process, these values are calculated as the constants of that minute.

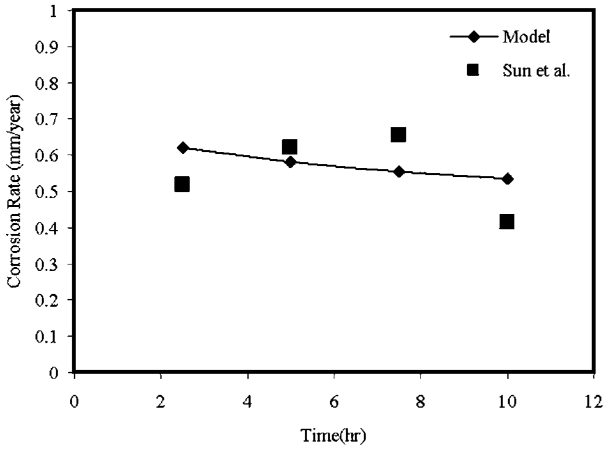
These steps are repeated until a desired time achieved. The model was implemented in Visual Basic programming language.

Verification

The CO_2 corrosion model was verified by comparing the prediction with published experimental values. The corrosion rate of X65 steel at pH 6·6, different temperatures and Fe^{2+} initial concentration 50 ppm were measured by Sun.[9] In Fig. 3, the measured and the predicted thickness of precipitated layer on the steel surface at T=60°C are shown. The predicted amounts are very close to the measured ones. The predicted and measured corrosion rates at T=60°C and for different periods of time are shown in Fig. 4. Because the iron carbonate precipitate on the steel surface, the thickness of it continuously increases and the porosity of it decreases. Therefore the predicted corrosion rates of steel decrease due to formation of a diffusion barrier on the steel surface. The experimental results first increase and then decrease. Sun[9] has obtained every point from one sample. It seems the increase in corrosion rates is related to the experimental method. Figure 5 shows the changes of iron carbonate layer thickness with time at a temperature of 70°C. The precipitation process is slower than the



3 Measured (Sun)[9] and predicted thickness of precipitated layer on steel surface at T=60°C, p_{CO_2}=0.8 bar, pH=6·6, Fe^{2+} concentration=50 ppm

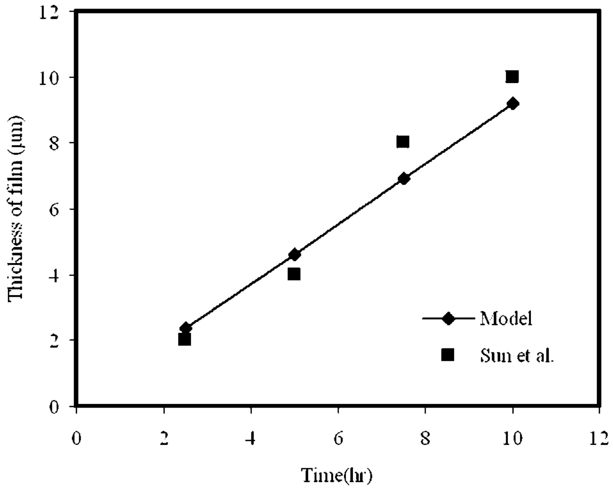


4 Measured (Sun)[9] and predicted corrosion rates of mild steel at T=60°C, p_{CO_2}=0.8 bar, pH=6·6, Fe^{2+} concentration=50 ppm

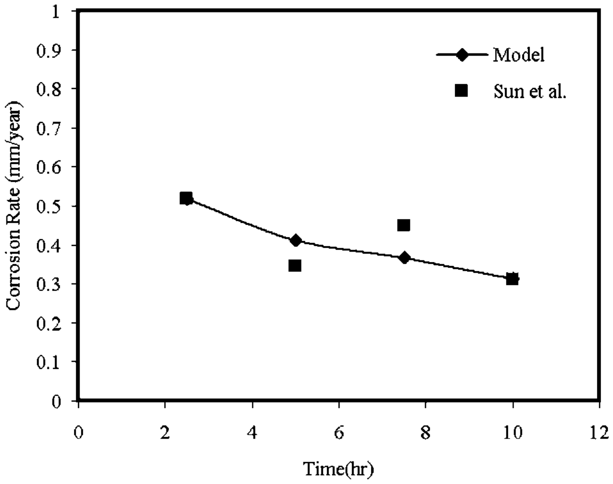
diffusion process. Therefore it seems that the concentration profiles of Fe^{2+} and CO_3^{2-} are constant in steady state condition. When iron carbonate layer forms on the metal surface, the diffusion of species is controlled by it. In this situation, the concentration of $Fe^{2+}$and CO_3^{2-} in front of the iron carbonate layer, approximately equal to the concentration of Fe^{2+} and CO_3^{2-} in the bulk of solution. According to equation (5), rate of precipitation depends on Fe^{2+} and CO_3^{2-} concentrations and temperature. Therefore the precipitation rate is constant if the concentration and temperature are constant. In this condition, the thickness of the iron carbonate layer increases linearly with respect to time. The predicted and measured corrosion rates at 70°C are shown in Fig. 6. The predicted corrosion rates are in very good agreement with the measured values.

The predictions of the model at 80°C are shown in Figs. 7 and 8. Agreement between the predicted amounts and the experimental results is very good at this temperature too.

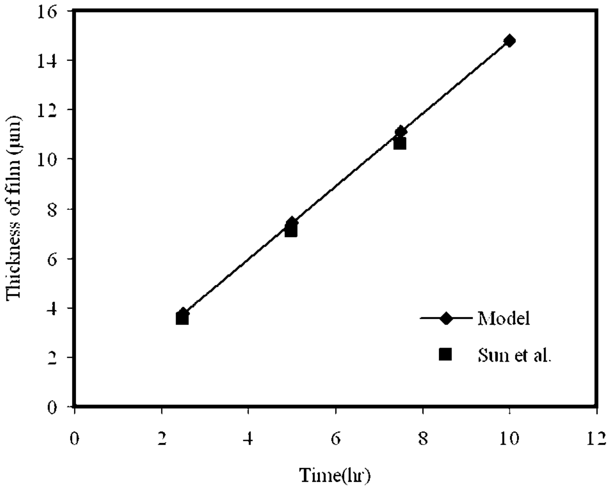
As mentioned, the precipitation of iron carbonate is influenced by concentrations of Fe^{2+} and CO_3^{2-} ions. Therefore, performance of the model was investigated at low concentration of Fe^{2+} ion. For this purpose, the experimental results of N?sić and Lee[10] were used. They investigated the corrosion of steel 1020 in aqueous solution saturated with CO_2 ($P_{CO_2}=0{\cdot}54$ bar). Other test conditions are: pH=6·6, temperature=80°C, ferrous ion concentration=5 ppm and velocity=1 m s^{-1}. The predicted corrosion rates and the measured amounts are shown in Fig. 9. The predicted rates are very close to measured values. At low Fe^{2+} concentration, the precipitation rate is negligible, so the formation of a layer with low porosity and full coverage of metal surface become impossible. As a result, the corrosion rate decrease a little after 48 h and the steel surface continuously is corroded. Therefore, the mechanical adhesion between the steel surface and the iron carbonate layer is very weak. Hence the probability of separation of the iron carbonate layer from the steel surface is high. Moreover the rate of corrosion in the aqueous solution with high concentration of Fe^{2+} ion was investigated. N?sić and Lee[10] have obtained some results showing the corrosion rate of the steel sample rapidly decreases to less than 0·03 mm y^{-1} after only 10 h due to formation of a dense iron carbonate layer on its surface. The experiments conducted at atmospheric pressure, T=80°C, pH 6·6, partial pressure of CO_2=0·54 bar, velocity=1 m s^{-1}, and Fe^{2+} concentration 250 ppm. The results of modelling under above condition are shown in Fig. 10. Becasue the concentration of Fe^{2+} ion is very high, according to equation (5), the precipitation rate of iron carbonate



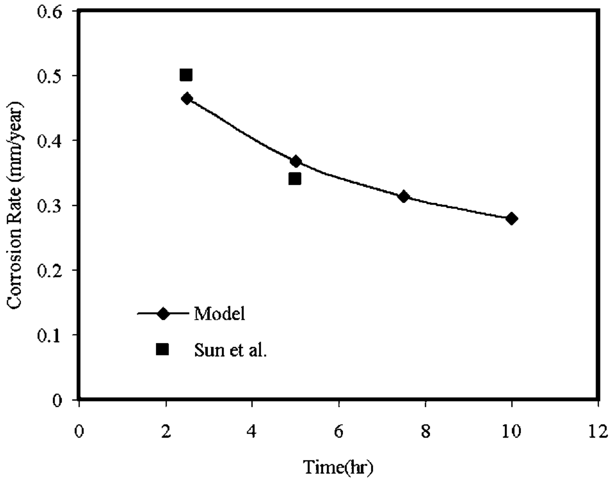
5 Measured (Sun)[9] and predicted thickness of precipitated layer on steel surface at T=70°C, p_{CO_2}=0.7 bar, pH=6·6, Fe^{2+} concentration=50 ppm



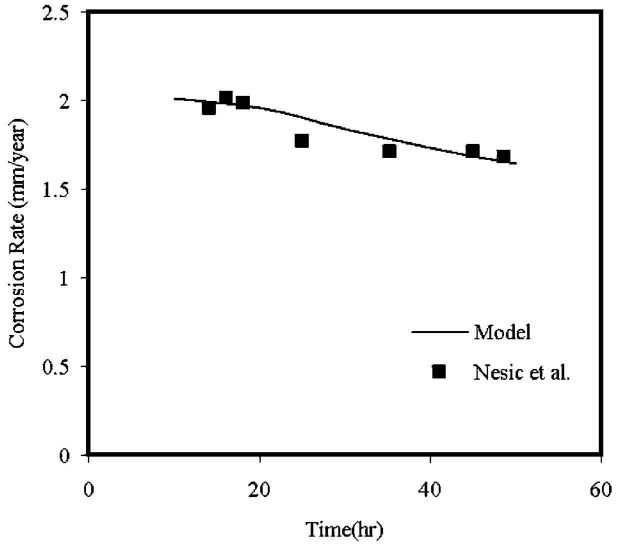
6 **Measured (Sun)[9] and predicted corrosion rates of mild steel at T=70°C, p_{CO_2}=0.7 bar, pH=6·6, Fe^{2+} concentration=50 ppm**



7 **Measured (Sun)[9] and predicted thickness of precipitated layer on steel surface at T=80°C, p_{CO_2}=0.5 bar, pH=6·6, Fe^{2+} concentration=50 ppm**



8 **Measured (Sun)[9] and predicted corrosion rates of mild steel at T=80°C, p_{CO_2}=0.5 bar, pH=6·6, Fe^{2+} concentration=50 ppm**



9 Measured (N?sić and Lee)[10] and predicted corrosion rates of mild steel at T=80°C, p_{CO_2}=0.54 bar, pH=6·6, velocity=1 m s^{-1}, Fe^{2+} concentration=5 ppm

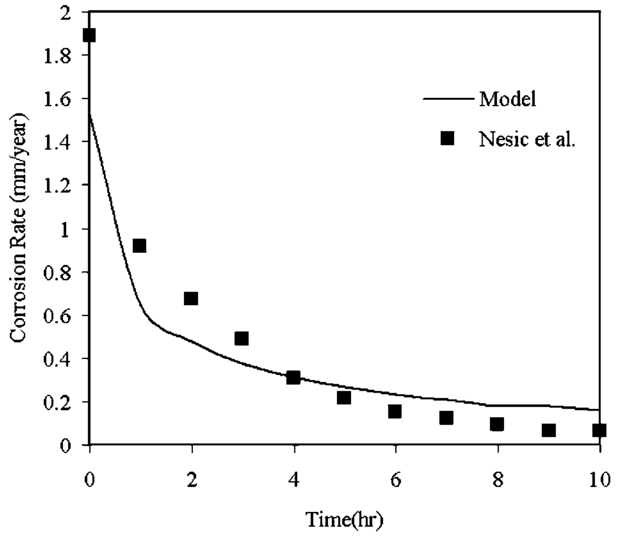
layer is high. Therefore a dense iron carbonate layer rapidly forms on the steel surface decreasing the corrosion rate. Ruzic *et al.*[11] investigated the formation of a protective iron carbonate layer on the 1020 steel surface. They measured the corrosion rate of steel at temperature 80°C, pH 6·9, P_{CO_2}=0·54 bar and velocity=0·13 m s^{-1}. Measured and predicted corrosion rates are compared as shown in Fig. 11. The maximum and minimum of Ruzic *et al.*'s results have been shown as points and the predicted corrosion rates have been shown as a line. It seems the predicted amounts are very close to the minimum values. Also, after 20 h, the difference between the maximum and minimum measured values is about 0·15 mm y^{-1}. Therefore the model predictions especially for long time are reliable.

The predicted and measured corrosion rates in different conditions showed in Figs. 4, 6, 8, 9, 10 and 11 are shown simultaneously in Fig. 12. The experiments were performed under conditions giving protective or non-protective iron carbonate layer. The results related to initial time when test conditions giving protective layer, have been not considered. The agreement between the predictions and the experiments is very good.

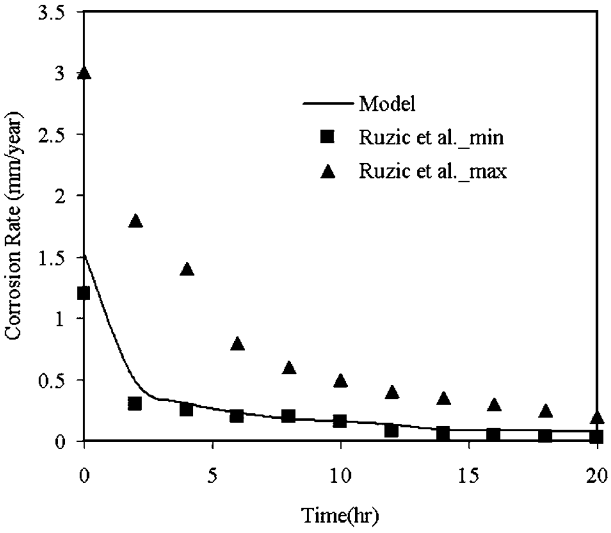
Parametric study

The effects of CO_2 pressure, pH, Fe^{2+} ion concentration and temperature on corrosion rate were investigated using the proposed model. The effect of Fe^{2+} ion concentration is shown in Fig. 13. Other conditions of modelling are pH=6·5, P_{CO_2}=0·54 bar, T=80°C, velocity=1 m s^{-1}. At 5 ppm Fe^{2+} ion concentration, the corrosion rate decreases so slowly. It seems the iron carbonate precipitation rate is insignificant in comparison with corrosion rate. As a result, no decrease is observed with respect to time because no protective layer is formed on steel surface. The formation of iron carbonate layer becomes more rapid when the Fe^{2+} ion concentration increases. Therefore at 100 ppm Fe^{2+}, the corrosion rate decreases in short time.

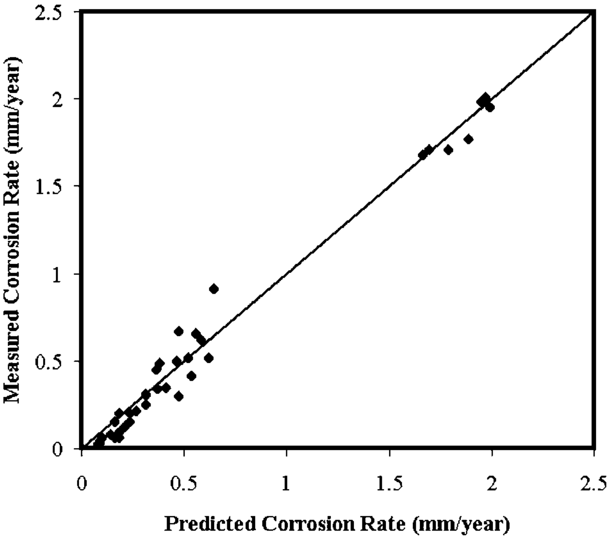
The effect of pH is shown in Fig. 14. Other conditions of modelling are P_{CO_2}=0·54 bar, T=80°C,



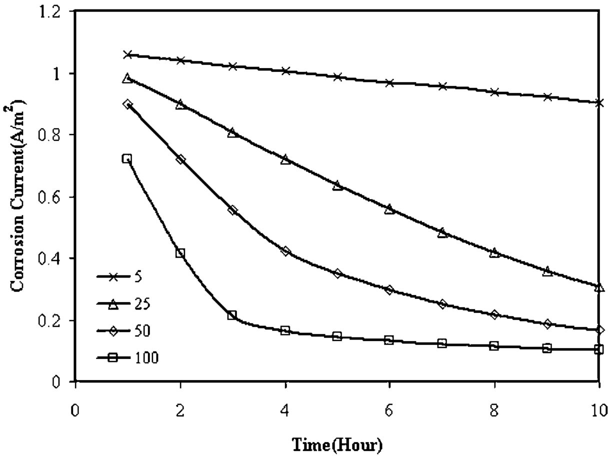
10 Measured (Nĕsić and Lee)[10] and predicted corrosion rates of mild steel at T=80°C, p_{CO_2}=0.54 bar, pH=6·6, velocity=1 m s^{-1}, Fe^{2+} concentration=250 ppm



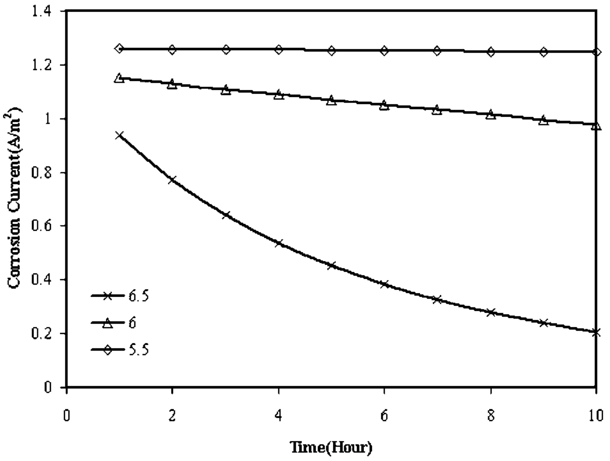
11 Measured (Ruzic *et al.*)[11] and predicted corrosion rates of mild steel at T=80°C, p_{CO_2}=0.54 bar, pH=6·9, velocity=0·13 m s^{-1}, Fe^{2+} concentration=250 ppm



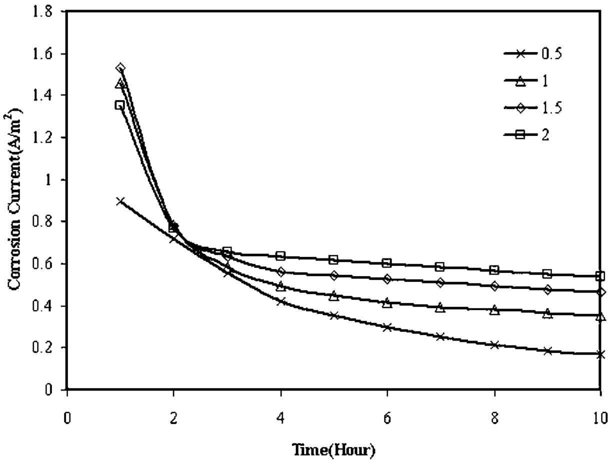
12 Comparison between measured and predicted corrosion rates of mild steel in aqueous phase at different conditions: experimental results are taken from Refs. 10–12



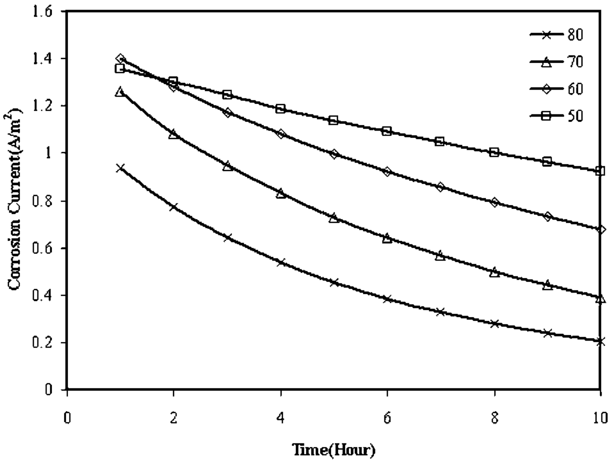
13 Effect of Fe^{2+} ion concentration (ppm) on corrosion rate: modelling condition are pH=6·5, p_{CO_2}=0.54 bar, T=80°C, velocity=1 m s^{-1}



14 Effect of pH on corrosion rate: modelling condition are Fe^{2+} concentration=50 ppm, p_{CO_2}=0.54 bar, T=80°C, velocity=1 m s^{-1}



15 Effect of CO$_2$ pressure (bar) on corrosion rate: modelling condition are Fe^{2+} concentration=50 ppm, pH=6·5, T=80°C, velocity=1 m s^{-1}



16 Effect of temperature (°C) on corrosion rate: modelling condition are Fe^{2+} concentration=50 ppm, p_{CO_2}=0.8 bar, pH=6·5, velocity=1 m s^{-1}

velocity=1 m s^{-1}, Fe^{2+} concentration=50 ppm. At lower pH values, the CO_3^{2-} concentration and so supersaturation are very small. The iron carbonate precipitation rate is related to supersaturation as it can be seen in equation (5). As a result, at lower pH values the precipitation rate is negligible and a protective layer is not form on steel surface. But at higher pH values, the precipitation rate increases, hence a protective layer gradually forms on the steel surface. Therefore the corrosion rate decreases with respect to time.

The effect of CO$_2$ pressure on corrosion rate is shown in Fig. 15. Other conditions of modelling are pH=6·5,

T=80°C, velocity=1 m s^{-1}, Fe^{2+} concentration=50 ppm. The initial corrosion rate is higher at the more elevated CO$_2$ pressure because the equilibrium concentration of carbonic acid is greater. It can be seen the corrosion rate decreases at each pressure after approximately 4 h but it is higher at elevated pressures.

The effect of temperature on corrosion rate is shown in Fig. 16. Other conditions of modelling are pH=6·5, P_{CO_2}=0·54 bar, velocity=1 m s^{-1}, Fe^{2+} concentration=50 ppm. The protective iron carbonate layer forms more rapidly at higher temperature, as a result the corrosion rates become smaller. At 50°C, the corrosion rate after 1 h is lower than similar point at 60°C. The temperature affects the corrosion rate in two ways. First, in condition that the protective layer is not formed on the steel surface, temperature raising leads to corrosion rate increasing. Second, when there is suitable condition for iron carbonate precipitation, the temperature rise increases the precipitation rate. Therefore, in constant times, the protective layer forms more quickly at higher temperatures than at lower ones. Hence, the corrosion rate at higher temperatures becomes lower because a good protective layer forms on the steel surface.

Conclusion

The iron carbonate layer growth model was developed and its performance was verified against the published experimental results. The model predictions are very close to the experimental results.

A dense and protective iron carbonate layer is formed on the steel surface when the concentration of Fe^{2+} ion is high, leading to a decrease in the corrosion rate.

If the concentration of Fe^{2+} and CO$_3^{2-}$ ions are constant, the precipitation rate of iron carbonate will be constant at each temperature. Therefore the thickness of layer increases linearly with respect to time.

Acknowledgements

The support on this work by Research Institute of Petroleum Industry (RIPI) is gratefully acknowledged. Also the authors wish to thank Dr H. R. Faridi for reviewing this paper.

References

1. A. Dugstad: Proc. CORROSION '92, Houston, TX, USA, 1992, NACE International, paper no. 92014.
2. J. L. Crolet, N. Thevenot and S. Nesic: Proc. CORROSION '96, Houston, TX, USA, 1996, NACE International, paper no. 96004.
3. E. W. J. van Hunnik, B. F. M. Pots and E. L. J. A. Hendriksen: Proc. CORROSION '96, Houston, TX, USA, 1996, NACE International, paper no. 96006.
4. A. Dugstad: Proc. CORROSION '98, Houston, TX, USA, 1998, NACE International, paper no. 98031.
5. M. Shayegani: *Corros. Eng. Sci. Technol.*
6. J. S. Newman: 'Electrochemical systems', 2nd edn; 1991, Englewood Cliffs, NJ, Prentice Hall.
7. J. T. Davies: 'Turbulence phenomena'; 1972, London, Academic Press.
8. A. Dugstad: Eurocorr '97, Vol. 1, pp. 15–20, Trondheim, Norway, 22–25 September 1997.
9. W. Sun: 'Kinetics of iron carbonate and iron sulfide scale formation in CO$_2$/H$_2$S corrosion', PhD thesis, Ohio University, USA, 2006.
10. S. N?sić and K.-L. J. Lee: *Corrosion*, 2003, **59**, 616–628.
11. V. Ruzic, M. Veidt and S. N?sić: *Corrosion*, 2006, **62**, 419–432.
12. W. Sun and S. N?sić: Proc. CORROSION 2006, Houston, TX, USA, 2006, NACE International, paper no. 06365.