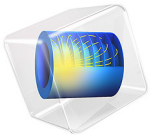

Carbon Dioxide Corrosion in Steel Pipes

Introduction

A flow mixture of water and carbon dioxide (CO_2) passing through a steel pipe can cause significant steel corrosion. Properties such as partial pressure of CO_2 and temperature affect the corrosion rate.

This model simulates the corrosion taking place on the steel surface of a pipe carrying CO_2 and water mixture. The model is based on several journal papers (Ref. 1–Ref. 3).

Model Definition

The corrosion is investigated at an arbitrary position within a steel pipe through which a flow of dissolved CO_2 in water passes. A 1D model is used. No variations along the length of the pipe are considered and the interaction of the mixture with the steel is confined to the boundary layer near the steel surface. The boundary layer thickness is considered to be 50 μm. The model geometry is shown in Figure 1.

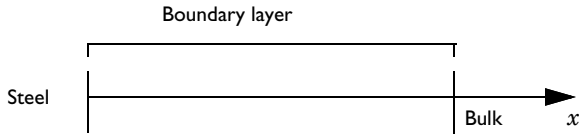

Figure 1: The model geometry comprising of the boundary layer adjacent to the steel surface.

All species are assumed to be diluted in water and the mass transport is modeled by diffusion and migration. The Tertiary Current Distribution, Nernst–Planck interface with water-based charge electroneutrality is used in the model. Carbon dioxide hydration, water dissociation, proton reduction reaction, and iron dissolution reaction are accounted for; resulting in four species (in addition to H^+ and OH^- ions) in the model. The species and diffusion coefficients are tabulated in Table 1

TABLE 1: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS.

Species	**D (m^2/s)·10^{-9}**
CO_2	1.96
H_2CO_3	2.00
HCO_3^-	1.11
H^+	9.31
OH^-	5.26
Fe^{2+}	0.72

The Electrode Surface boundary feature is used to calculate the corrosion potential at the steel surface. The electric potential is set to 0 at the steel surface which will result in a mixed potential condition since the electrolyte potential is left to float. The initial value of the electrolyte potential is set to –0.5 V around the free corrosion potential (Ref. 2).

Fluxes of species converted in the electrochemical reactions, i_j/F (Faraday's constant = 96,485 C/mol), are applied on the steel surface where i (SI unit: A/m^2) is the current density of j number of electrochemical reactions.

For all species, uniform concentrations of species in chemical equilibrium are used as initial values for concentration (Ref. 1). Concentration of CO_2 is set to its initial value at the outer point of the boundary layer.

EQUILIBRIUM REACTIONS

The following equilibrium reactions are present in the electrolyte:

$$H_2O(l) \Leftrightarrow H^+(aq) + OH^-(aq) \qquad K_1 = 6.418 \cdot 10^{-15}$$

$$CO_2(aq) + H_2O(aq) \Leftrightarrow H_2CO_3(aq) \qquad K_2 = 2.580 \cdot 10^{-3}$$

$$H_2CO_3(aq) \Leftrightarrow H^+(aq) + HCO_3^-(aq) \qquad K_3 = 1.251 \cdot 10^{-4}$$

where K_1 through K_3 are the equilibrium constants at 293.15 K (Ref. 1).

The water dissociation equilibrium reaction is in-built for the Tertiary Current Distribution, Nernst–Planck interface with water-based charge electroneutrality charge transport. The other two reactions are modeled using the Equilibrium Reaction domain node; one for each reaction. The Equilibrium Reaction nodes solve for one additional degree of freedom each, where the additional degree of freedom represents the local reaction rate required in order to fulfill the equilibrium expression. The equilibrium expressions are based on the reaction stoichiometry and equilibrium constant K_k according to

$$K_k = \prod_i a(c_i)^{v_{ik}}$$

where c_i (SI unit: mol/m^3) is the concentration of species i, v_{ik} the stoichiometric coefficient of species i in reaction k. The activity of a species, $a(c_i)$ is given by dividing the concentration with 1 M.

ELECTROCHEMICAL REACTIONS

The following electrochemical reactions are present at the steel surface:

- Iron dissolution

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^{-}$$

- Proton reduction

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \frac{1}{2}\mathrm{H}_2$$

STUDY SETTINGS

The problem is solved with an auxiliary sweep on a stationary solver in order to investigate the impact of important parameters such as partial pressure of CO_2 and temperature on corrosion.

Results and Discussion

Figure 2 displays the concentration deviation from the bulk of the four species along the boundary layer at partial pressure of CO_2 of 1 bar and 20°C. The concentration of iron ions is significantly higher at the steel surface due to the dissolution of iron. The deviation of carbon dioxide and bicarbonate ions show considerable hydration of the carbon

dioxide. Carbonic acid shows little variation in concentration compared to the bulk throughout the boundary layer.

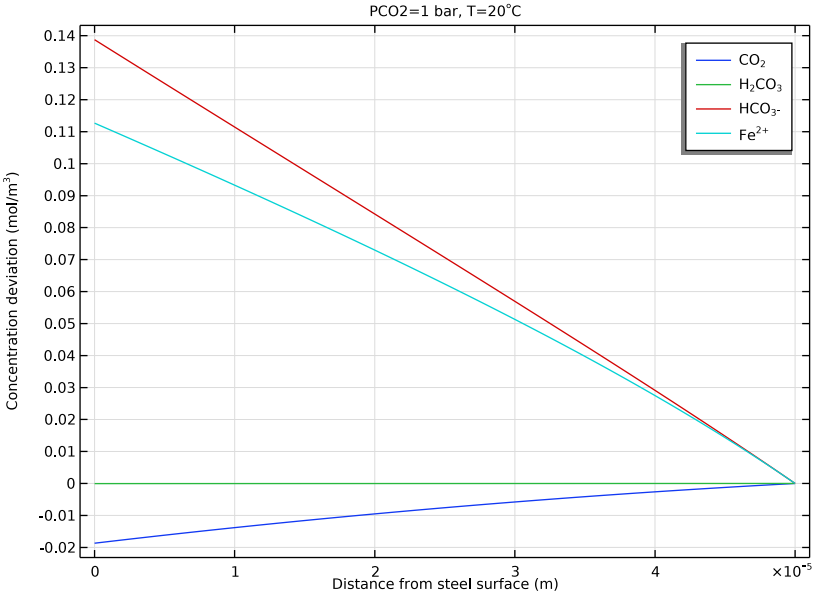

Figure 2: Deviation in concentration of the species compared to the bulk along the liquid boundary layer.

Figure 3 shows the corrosion rate of the steel surface at different partial pressures of CO_2 for operating temperatures ranging from 20°C to 80°C. The corrosion rate is directly proportional to the corrosion current (that is, the iron dissolution current, since no other anodic reaction is considered). Increased partial pressure of CO_2 and temperature increase the corrosion rate.

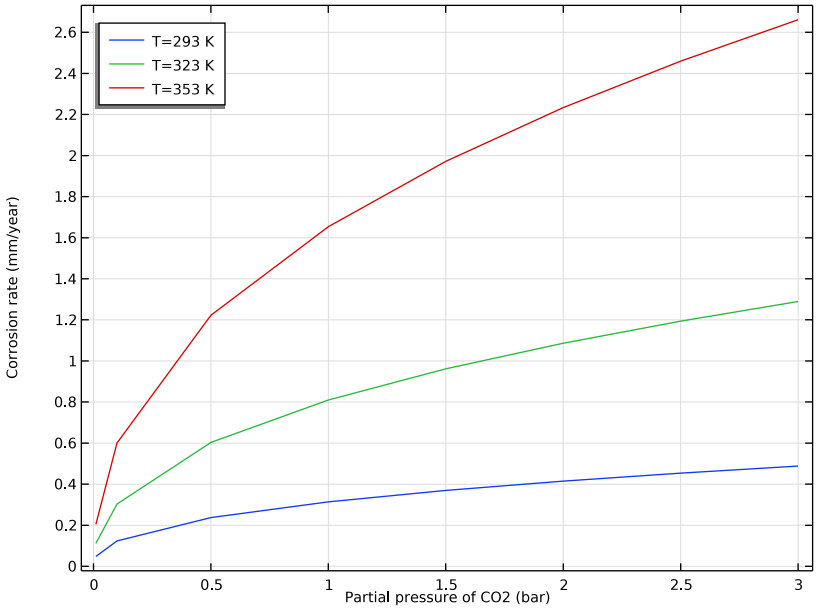

Figure 3: Corrosion rate in mm/year for different partial pressures of CO_2 and operating temperatures range of 20°C–80°C.

Figure 4 and Figure 5 show the change in pH at the steel surface and bulk electrolyte, respectively, for different partial pressures of CO_2 and for operating temperatures ranging from 20°C to 80°C. The higher pH is observed for lower partial pressure of CO_2 at both the electrode surface as well as the bulk electrolyte for all operating temperatures considered in the model. The increase in pH with an increase in temperature is observed to be more significant at the electrode surface when compared to the bulk electrolyte.

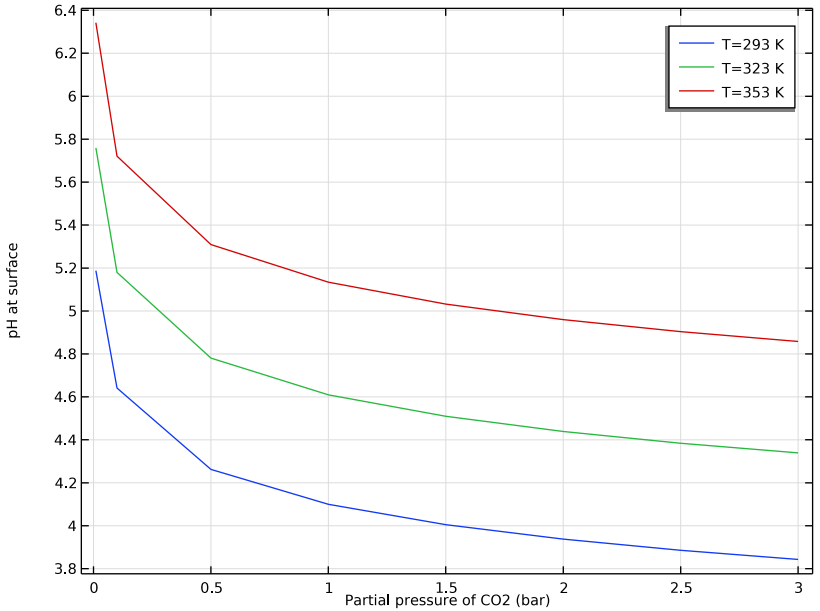

Figure 4: pH at the electrode surface for different partial pressures of CO_2 and operating temperatures range of 20°C–80°C.

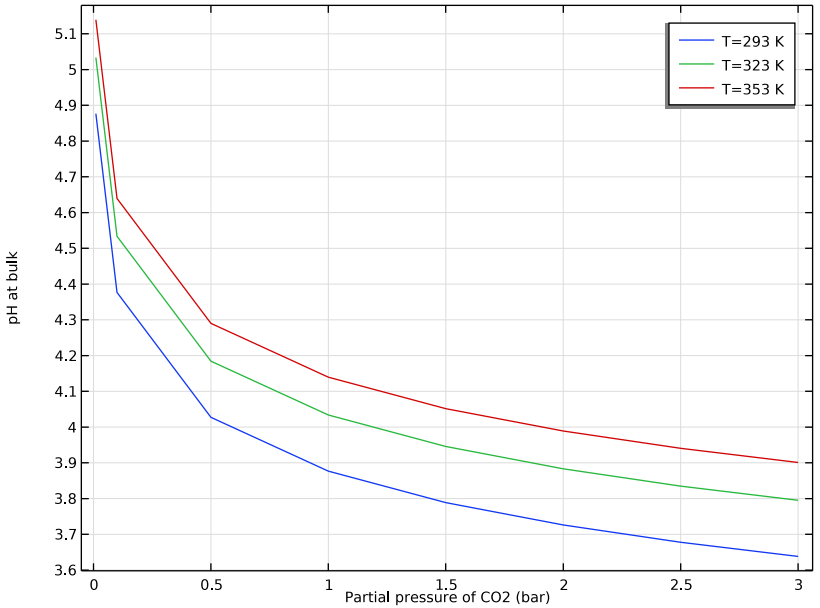

Figure 5: pH at the bulk electrolyte for different partial pressures of CO_2 and operating temperatures range of 20°C–80°C.

References

1. M. Nordsveen, S. Nesic, R. Nyborg, and A. Stangeland, "A Mechanistic Model for Carbon Dioxide Corrosion of Mild Steel in the Presence of Protective Iron Carbonate Films-Part 1: theory and Verification," *Corrosion*, vol. 59, no. 5, pp. 443–455, 2003.

2. S. Nesic, J. Postlethwaite, and S. Olsen, "An Electrochemical Model for Prediction of Corrosion of Mild Steel in Aqueous Carbon Dioxide Solutions," *Corrosion*, vol. 52, no. 4, pp. 280–294, 1996.

3. A. Kahyarian and S. Nesic, "On the mechanism of carbon dioxide corrosion of mild steel: Experimental investigation and mathematical modeling at elevated pressures and non-ideal solutions," *Corrosion Science*, vol. 173, no. 108719, pp. 1–27, 2020.

Application Library path: `Corrosion_Module/General_Corrosion/co2_corrosion`

From the **File** menu, choose **New**.

NEW

In the **New** window, click **Model Wizard**.

MODEL WIZARD

1 In the **Model Wizard** window, click **1D**.

2 In the **Select Physics** tree, select **Electrochemistry>Tertiary Current Distribution, Nernst-Planck>Tertiary, Water-Based with Electroneutrality (tcd)**.

3 Click **Add**.

4 In the **Number of species** text field, type 4.

5 In the **Concentrations (mol/m³)** table, enter the following settings:

cCO2
cH2CO3
cHCO3
cFe

6 Click **Study**.

7 In the **Select Study** tree, select **General Studies>Stationary**.

8 Click **Done**.

GLOBAL DEFINITIONS

Load the model parameters from a text file.

Parameters 1

1 In the **Model Builder** window, under **Global Definitions** click **Parameters 1**.

2 In the **Settings** window for **Parameters**, locate the **Parameters** section.

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `co2_corrosion_parameters.txt`.

GEOMETRY 1

The geometry consists of a single interval.

Interval 1 (i1)

1 In the **Model Builder** window, under **Component 1 (comp1)** right-click **Geometry 1** and choose **Interval**.

2 In the **Settings** window for **Interval**, locate the **Interval** section.

3 In the table, enter the following settings:

Coordinates (m)
0
delta

4 Click **Build Selected**.

TERTIARY CURRENT DISTRIBUTION, NERNST-PLANCK (TCD)

Start defining the physics.

Species Charges 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Tertiary Current Distribution, Nernst-Planck (tcd)** click **Species Charges 1**.

2 In the **Settings** window for **Species Charges**, locate the **Charge** section.

3 In the z_{cHCO3} text field, type `-1`.

4 In the z_{cFe} text field, type `2`.

Electrolyte 1

1 In the **Model Builder** window, click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Diffusion** section.

3 In the D_{cCO2} text field, type `DCO2`.

4 In the D_{cH2CO3} text field, type `DH2CO3`.

5 In the D_{cHCO3} text field, type `DHCO3`.

6 In the D_{cFe} text field, type `DFe`.

7 In the D_{cH} text field, type `DH`.

8 In the D_{cOH} text field, type `DOH`.

Initial Values 1

Set the initial values to the concentration of the species in the bulk.

1 In the **Model Builder** window, click **Initial Values 1**.

2 In the **Settings** window for **Initial Values**, locate the **Initial Values** section.

3 In the $cCO2$ text field, type `cCO2O`.

4 In the *cH2CO3* text field, type `cH2CO30`.

5 In the *cHCO3* text field, type `cHCO30`.

6 In the *cFe* text field, type `cFe0`.

7 In the *phil* text field, type `phi0`.

Electrode Surface 1

Use the Dissolving-Depositing species formulation to estimate the corrosion rate. Also, set fluxes according to the electrochemical reactions at the steel surface.

1 In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.

2 Select Boundary 1 only.

3 In the **Settings** window for **Electrode Surface**, click to expand the **Dissolving-Depositing Species** section.

4 Click **Add**.

5 In the table, enter the following settings:

Species	Density (kg/m^3)	Molar mass (kg/mol)
s1	rho_steel	Mw_steel

Electrode Reaction 1

1 In the **Model Builder** window, click **Electrode Reaction 1**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Stoichiometric Coefficients** section.

3 In the n text field, type `2`.

4 In the ν_{cFe} text field, type `-1`.

5 In the **Stoichiometric coefficients for dissolving-depositing species:** table, enter the following settings:

Species	Stoichiometric coefficient (1)
sl	-1

6 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Eeq_ref_Fe`.

7 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_Fe`.

8 In the α_a text field, type `alphaa_Fe`.

Electrode Surface 1

In the **Model Builder** window, click **Electrode Surface 1**.

Electrode Reaction 2

1 In the **Physics** toolbar, click **Attributes** and choose **Electrode Reaction**.

2 In the **Settings** window for **Electrode Reaction**, locate the **Equilibrium Potential** section.

3 In the $E_{\mathrm{eq,ref}}(T)$ text field, type `Eeq_ref_H2`.

4 Locate the **Electrode Kinetics** section. In the $i_{0,\mathrm{ref}}(T)$ text field, type `i0_ref_H2`.

5 In the α_a text field, type `alphaa_H2`.

Equilibrium Reaction 1

Set two equilibrium reactions.

1 In the **Physics** toolbar, click **Domains** and choose **Equilibrium Reaction**.

2 In the **Settings** window for **Equilibrium Reaction**, locate the **Domain Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Locate the **Equilibrium Condition** section. In the K_{eq} text field, type `KCO2H`.

5 Locate the **Stoichiometric Coefficients** section. In the ν_{cCO2} text field, type `-1`.

6 In the ν_{cH2CO3} text field, type `1`.

Equilibrium Reaction 2

1 In the **Physics** toolbar, click **Domains** and choose **Equilibrium Reaction**.

2 In the **Settings** window for **Equilibrium Reaction**, locate the **Domain Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Locate the **Equilibrium Condition** section. In the K_{eq} text field, type `KH2CO3`.

5 Locate the **Stoichiometric Coefficients** section. In the ν_{cH2CO3} text field, type `-1`.

6 In the ν_{cHCO3} text field, type `1`.

7 In the ν_{cH} text field, type `1`.

Concentration 1

Set bulk concentrations at the rightmost boundary.

1 In the **Physics** toolbar, click **Boundaries** and choose **Concentration**.

2 Select Boundary 2 only.

3 In the **Settings** window for **Concentration**, locate the **Concentration** section.

4 Select the **Species cCO2** check box.

5 Select the **Species cFe** check box.

6 In the $c_{0,\mathrm{cCO2}}$ text field, type `cCO20`.

7 In the $c_{0,\mathrm{cFe}}$ text field, type `cFe0`.

MESH 1

Build a user-defined mesh with a maximum element size in the domain of 1e-6 and at the leftmost boundary 1e-7.

1 In the **Model Builder** window, under **Component 1 (comp1)** click **Mesh 1**.

2 In the **Settings** window for **Mesh**, locate the **Sequence Type** section.

3 From the list, choose **User-controlled mesh**.

Size

1 In the **Model Builder** window, under **Component 1 (comp1)>Mesh 1** click **Size**.

2 In the **Settings** window for **Size**, locate the **Element Size** section.

3 Click the **Custom** button.

4 Locate the **Element Size Parameters** section. In the **Maximum element size** text field, type `1e-6`.

Size 1

1 In the **Model Builder** window, right-click **Edge 1** and choose **Size**.

2 In the **Settings** window for **Size**, locate the **Geometric Entity Selection** section.

3 From the **Geometric entity level** list, choose **Boundary**.

4 Select Boundary 1 only.

5 Locate the **Element Size** section. Click the **Custom** button.

6 Locate the **Element Size Parameters** section.

7 Select the **Maximum element size** check box. In the associated text field, type `1e-7`.

8 Click **Build Selected**.

STUDY 1

1 In the **Model Builder** window, click **Study 1**.

2 In the **Settings** window for **Study**, locate the **Study Settings** section.

3 Clear the **Generate default plots** check box.

Parametric Sweep

Use parametric sweep to investigate the impact of CO2 partial pressure and temperature.

1 In the **Study** toolbar, click **Parametric Sweep**.

2 In the **Settings** window for **Parametric Sweep**, locate the **Study Settings** section.

3 Click **Add** twice.

4 In the table, enter the following settings:

Parameter name	Parameter value list	Parameter unit
PCO2 (Partial pressure of CO2 in bar)	`0.01 0.1 range(0.5,0.5, 3)`	
T (Operating temperature)	`293.15[K] 323.15[K] 353.15[K]`	K

5 From the **Sweep type** list, choose **All combinations**.

Solution 1 (sol1)

1 In the **Study** toolbar, click **Show Default Solver**.

2 In the **Model Builder** window, expand the **Solution 1 (sol1)** node.

3 In the **Model Builder** window, under **Study 1>Solver Configurations>Solution 1 (sol1)** click **Stationary Solver 1**.

4 In the **Settings** window for **Stationary Solver**, locate the **General** section.

5 In the **Relative tolerance** text field, type `1e-6`.

6 In the **Study** toolbar, click **Compute**.

RESULTS

The following steps reproduces the plots from the Results and Discussion section.

Concentrations

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Concentrations` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/Solution 1 (sol1)**.

4 From the **Parameter selection (PCO2)** list, choose **Last**.

5 From the **Parameter selection (T)** list, choose **First**.

6 Click to expand the **Title** section. From the **Title type** list, choose **Manual**.

7 In the **Title** text area, type `PCO2=1 bar, T=20<sup>\circ</sup>C`.

8 Locate the **Plot Settings** section.

9 Select the **x-axis label** check box. In the associated text field, type `Distance from steel surface (m)`.

10 Select the **y-axis label** check box. In the associated text field, type `Concentration deviation (mol/m<sup>3</sup>)`.

Line Graph 1

1 Right-click **Concentrations** and choose **Line Graph**.

2 In the **Settings** window for **Line Graph**, locate the **Selection** section.

3 From the **Selection** list, choose **All domains**.

4 Locate the **y-Axis Data** section. In the **Expression** text field, type `cCO2-cCO20`.

5 Click to expand the **Title** section. From the **Title type** list, choose **None**.

6 Locate the **x-Axis Data** section. From the **Parameter** list, choose **Expression**.

7 In the **Expression** text field, type `x`.

8 Click to expand the **Legends** section. Select the **Show legends** check box.

9 From the **Legends** list, choose **Manual**.

10 In the table, enter the following settings:

Legends
`CO<sub>2</sub>`

11 Right-click **Line Graph 1** and choose **Duplicate**.

Line Graph 2

1 In the **Model Builder** window, click **Line Graph 2**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cH2CO3-cH2CO30`.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
`H<sub>2</sub>CO<sub>3</sub>`

5 Right-click **Line Graph 2** and choose **Duplicate**.

Line Graph 3

1 In the **Model Builder** window, click **Line Graph 3**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cHCO3-cHCO30`.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
`HCO<sub>3</sub><sup>-</sup>`

5 Right-click **Line Graph 3** and choose **Duplicate**.

Line Graph 4

1 In the **Model Builder** window, click **Line Graph 4**.

2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `cFe-cFe0`.

4 Locate the **Legends** section. In the table, enter the following settings:

Legends
`Fe<sup>2+</sup>`

5 In the **Concentrations** toolbar, click **Plot**.

Corrosion rate

1 In the **Home** toolbar, click **Add Plot Group** and choose **1D Plot Group**.

2 In the **Settings** window for **1D Plot Group**, type `Corrosion rate` in the **Label** text field.

3 Locate the **Data** section. From the **Dataset** list, choose **Study 1/Solution 1 (sol1)**.

4 Locate the **Title** section. From the **Title type** list, choose **None**.

5 Locate the **Plot Settings** section.

6 Select the **x-axis label** check box. In the associated text field, type `Partial pressure of CO2 (bar)`.

7 Select the **y-axis label** check box. In the associated text field, type `Corrosion rate (mm/year)`.

Point Graph 1

1 Right-click **Corrosion rate** and choose **Point Graph**.

2 Select Boundary 1 only.

3 In the **Settings** window for **Point Graph**, click **Replace Expression** in the upper-right corner of the **y-Axis Data** section. From the menu, choose **Component 1 (comp1)> Tertiary Current Distribution, Nernst-Planck>Dissolving-depositing species>tcd.vbtot - Total electrode growth velocity - m/s**.

4 Locate the **y-Axis Data** section. From the **Unit** list, choose **mm/yr**.

5 Locate the **x-Axis Data** section. From the **Axis source data** list, choose **PCO2**.

6 From the **Parameter** list, choose **Expression**.

7 In the **Expression** text field, type `PCO2`.

8 Click to expand the **Legends** section. Select the **Show legends** check box.

9 From the **Legends** list, choose **Evaluated**.

10 In the **Legend** text field, type `T=eval(T) K`.

Corrosion rate

1 In the **Model Builder** window, click **Corrosion rate**.

2 In the **Settings** window for **1D Plot Group**, locate the **Legend** section.

3 From the **Position** list, choose **Upper left**.

4 In the **Corrosion rate** toolbar, click **Plot**.

5 Right-click **Corrosion rate** and choose **Duplicate**.

pH at surface

1 In the **Model Builder** window, under **Results** click **Corrosion rate 1**.

2 In the **Settings** window for **1D Plot Group**, type `pH at surface` in the **Label** text field.

3 Locate the **Plot Settings** section. In the **y-axis label** text field, type `pH at surface`.

Point Graph 1

1 In the **Model Builder** window, expand the **pH at surface** node, then click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `tcd.pH`.

pH at surface

1 In the **Model Builder** window, click **pH at surface**.

2 In the **Settings** window for **1D Plot Group**, locate the **Legend** section.

3 From the **Position** list, choose **Upper right**.

4 In the **pH at surface** toolbar, click **Plot**.

5 Right-click **pH at surface** and choose **Duplicate**.

pH at bulk

1 In the **Model Builder** window, under **Results** click **pH at surface 1**.

2 In the **Settings** window for **1D Plot Group**, type `pH at bulk` in the **Label** text field.

3 Locate the **Plot Settings** section. In the **y-axis label** text field, type `pH at bulk`.

Point Graph 1

1 In the **Model Builder** window, expand the **pH at bulk** node, then click **Point Graph 1**.

2 In the **Settings** window for **Point Graph**, locate the **Selection** section.

3 Click to select the **Activate Selection** toggle button.

4 In the list, select **1**.

5 Select Boundary 2 only.

6 In the **pH at bulk** toolbar, click **Plot**.