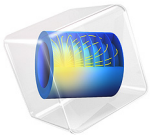

Carbon Dioxide Corrosion in Steel Pipes

Introduction

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

This model simulates the corrosion taking place on the steel surface of a pipe for turbulent flow of carbon dioxide and water. The model reproduces results by Nordsveen and others (Ref. 1) and Nesic and others (Ref. 2).

Model Definition

The corrosion is investigated at an arbitrary position within a steel pipe through which a turbulent flow of dissolved carbon dioxide 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 dependent upon the Reynolds number. The model geometry and physical considerations are shown in Figure 1. The diffusion and turbulent sublayers vary and are accounted for with the mass transport parameters.

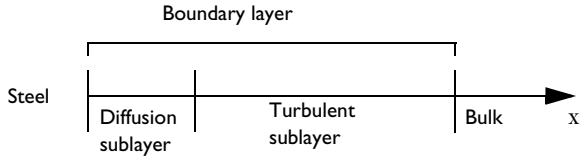

Figure 1: Description of the boundary layer adjacent to the steel surface.

All species are assumed to be diluted in water and the mass transport is modeled by diffusion. The Electroanalysis interface is used in the model. Carbon dioxide hydration, water dissociation, three reduction reactions, and iron dissolution are accounted for; resulting in seven species 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
CO_3^{2-}	0.92
H^+	9.31

TABLE 1: MODELED SPECIES WITH THEIR RESPECTIVE DIFFUSION COEFFICIENTS.

SPECIES	D (m^2/s)·10^{-9}
OH^-	5.26
Fe^{2+}	0.72

The turbulent sublayer is modeled by adding a turbulent diffusivity term to the diffusion coefficient. The term depends on the flow rate, viscosity, density of the liquid, and distance from the steel surface (Ref. 1).

The Electrode Surface boundary feature is used to calculate the corrosion potential at the steel surface using the mixed potential theory. The net total current of all electrochemical reactions is set to zero, the equation that is solved is described by

$$\sum_j i_j = 0 \tag{1}$$

where i (SI unit: A/m^2) is the current density of j number of electrochemical reactions. The initial value is set to –0.5 V around the free corrosion potential (Ref. 2).

For the Electroanalysis interface, uniform concentrations of species in chemical equilibrium are used as initial values for concentration for all species (Ref. 1). The outer point of the boundary layer is also set to these equilibrium concentrations for all species. Fluxes of species converted in the electrochemical reactions, i_j/F (Faraday's constant = 96, 485 C/mol), are applied on the steel surface.

EQUILIBRIUM REACTIONS

The following equilibrium reactions are present in the electrolyte:

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

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

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

$$HCO_3^-(aq) \Leftrightarrow H^+(aq) + CO_3^{2-}(aq) \qquad K_4 = 1.382 \cdot 10^{-10}$$

where K_1 through K_4 are the equilibrium constants at 293.15 K(Ref. 1).

These 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 (Equation 1):

Iron dissolution

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

Proton reduction

$$\mathrm{H^+ + e^- \rightarrow \frac{1}{2}H_2}$$

Water reduction

$$\mathrm{H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-}$$

Carbonic acid reduction

$$\mathrm{H_2CO_3 + e^- \rightarrow \frac{1}{2}H_2 + HCO_3^-}$$

The current densities depend on mass transport limitations and charge transfer resistances as given in Ref. 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 pH and temperature on corrosion.

Results and Discussion

Figure 2 displays the concentration deviation from the bulk of the seven species along the boundary layer at pH 6 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 sodium carbonate ions show considerable hydration of the carbon dioxide. All species show little variation in concentration compared to the bulk within a large part of the

boundary layer adjacent to the bulk and demonstrating the presence of a turbulent sublayer.

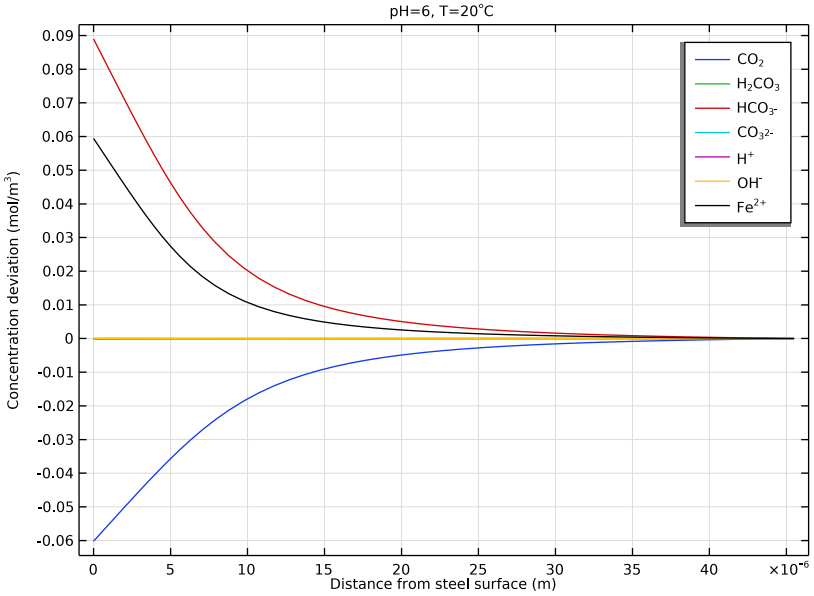

Figure 2: Deviation in concentration of the species compared to the bulk along the liquid boundary layer.

Figure 3 shows the corrosion rate of the steel surface at three different pH 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). Lowered pH and increased temperature increase the rate of corrosion.

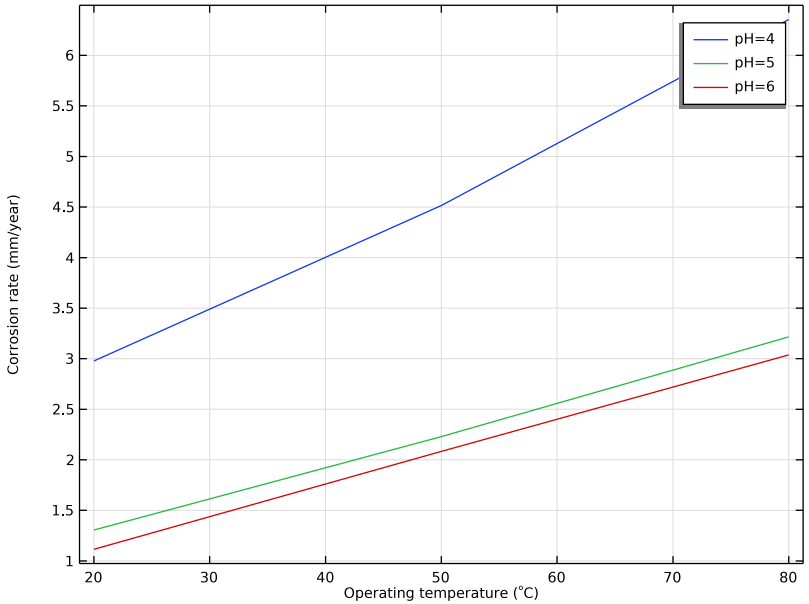

Figure 3: Corrosion rate in mm/year for pH 4, 5, and 6 and operating temperatures range of 20°C–80°C.

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.

Application Library path: `Corrosion_Module/General_Corrosion/co2_corrosion`

Modeling Instructions

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>Electroanalysis (tcd)**.

3 Click **Add**.

4 In the **Number of species** text field, type 7.

5 In the **Concentrations** table, enter the following settings:

cCO2
cH2CO3
cHCO3
cCO3
cH
cOH
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`.

DEFINITIONS

Load the variables from a text file.

Variables 1

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

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

3 Click **Load from File**.

4 Browse to the model's Application Libraries folder and double-click the file `co2_corrosion_variables.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**.

ELECTROANALYSIS (TCD)

Start defining the physics. The turbulent contribution is accounted for with a turbulent diffusivity, Dt.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)>Electroanalysis (tcd)** click **Electrolyte 1**.

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

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

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

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

6 In the D_{cCO3} text field, type `DCO3+Dt`.

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

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

9 In the D_{cFe} text field, type `DFe+Dt`.

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 `cCO2`.

4 In the $cH2CO3$ text field, type `cH2CO3`.

5 In the $cHCO3$ text field, type `cHCO3`.

6 In the $cCO3$ text field, type `cCO3`.

7 In the cH text field, type `cH`.

8 In the cOH text field, type `cOH`.

9 In the cFe text field, type `cFe`.

Electrode Surface 1

Use the Dissolving-Depositing species formulation to estimate the corrosion rate. Set the net total current of all the electrochemical reactions to zero. 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

6 Locate the **Electrode Phase Potential Condition** section. From the **Electrode phase potential condition** list, choose **Total current**.

7 In the $I_{\mathrm{l,total}}$ text field, type `0`.

8 In the $\phi_{\mathrm{s,ext,init}}$ text field, type `-0.5`.

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. From the E_{eq} list, choose **User defined**. In the associated text field, type `Erev_Fe`.

7 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Anodic Tafel equation**.

8 In the i_0 text field, type `i0_Fe`.

9 In the A_a text field, type `b_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 **Stoichiometric Coefficients** section.

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

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

5 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Erev_H2CO3`.

6 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.

7 In the i_0 text field, type `i0_H2CO3`.

8 In the A_c text field, type `-b_H2CO3`.

9 Select the **Limiting current density** check box.

10 In the i_{lim} text field, type `ilimH2CO3`.

Electrode Surface 1

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

Electrode Reaction 3

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

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

3 In the ν_{cH} text field, type `-1`.

4 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Erev_H2`.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.

6 In the i_0 text field, type `i0_H2`.

7 In the A_c text field, type `-b_H2`.

8 Select the **Limiting current density** check box.

9 In the i_{lim} text field, type `ilimH2`.

Electrode Surface 1

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

Electrode Reaction 4

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

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

3 In the ν_{cOH} text field, type `1`.

4 Locate the **Equilibrium Potential** section. From the E_{eq} list, choose **User defined**. In the associated text field, type `Erev_H2O`.

5 Locate the **Electrode Kinetics** section. From the **Kinetics expression type** list, choose **Cathodic Tafel equation**.

6 In the i_0 text field, type `i0_H2O`.

7 In the A_c text field, type `-b_H2O`.

Equilibrium Reaction 1

Set four 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 `KH2O`.

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

6 In the ν_{cOH} 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 `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 3

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`.

Equilibrium Reaction 4

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 `KHCO3`.

5 Locate the **Stoichiometric Coefficients** section. In the ν_{cHCO3} text field, type `-1`.

6 In the ν_{cCO3} 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 cH** check box.

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

7 In the $c_{0,cCO2}$ text field, type `cCO20`.

8 In the $c_{0,cH}$ text field, type `cH0`.

9 In the $c_{0,cFe}$ 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 pH 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
pH (Operating pH)	`4 5 6`	
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-4`.

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/ Parametric Solutions 1 (sol2)**.

4 From the **Parameter selection (pH)** 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 `pH=6, 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>`

Line Graph 2

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

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>`

Line Graph 3

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

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>`

Line Graph 4

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

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

3 In the **Expression** text field, type `cCO3-cCO3O`.

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

Legends
`CO<sub>3</sub><sup>2-</sup>`

Line Graph 5

1 Right-click **Line Graph 4** and choose **Duplicate**.

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

3 In the **Expression** text field, type `cH-cHO`.

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

Legends
`H<sup>+</sup>`

Line Graph 6

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

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

3 In the **Expression** text field, type `cOH-cOHO`.

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

Legends
`OH<sup>-</sup>`

Line Graph 7

1 Right-click **Line Graph 6** and choose **Duplicate**.

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

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

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/ Parametric Solutions 1 (sol2)**.

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 `Operating temperature (<sup>\circ</sup>C)`.

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)> Electroanalysis>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 **Parameter** list, choose **Expression**.

6 In the **Expression** text field, type `T`.

7 From the **Unit** list, choose **degC**.

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 `pH=eval(pH)`.

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