Model created in COMSOL Multiphysics 6.4

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. 4).

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.

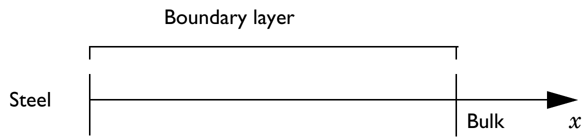


Figure 1: The model geometry comprising of the boundary layer adjacent to the steel surface.

All species are assumed to be diluted in water and the mass transport is modeled by diffusion and migration. The **Aqueous Electrolyte Transport** interface is used in the model. Water dissociation, carbonic acid dissociation, and ferrous ion hydrolysis are accounted for; resulting in eight 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 $(m^2/s)\cdot 10^{-9}$
$CO_2(aq)$	1.96
H_2CO_3	2.00
HCO_3^-	1.11
CO_3^{2-}	0.92
H^+	9.31
OH^-	5.26
Fe^{2+}, $FeOH^+$, $Fe(OH)_2(aq)$	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, close to the free corrosion potential (Ref. 3).

Fluxes of species, J_i (mol/m^2·s), converted in the electrochemical reactions are applied on the steel surface in accordance to Faraday's law

$$J_i = \frac{\nu_i \cdot i_{j,\mathrm{loc}}}{n \cdot F}$$

where ν_i is the stoichiometric coefficient for reactant i, $i_{j,\mathrm{loc}}$ (A/m^2) the current density for reaction j, n the number of transferred electrons, and F Faraday's constant (96,485 As/mol)

Uniform total concentrations of carbonic acid species and ferrous species are used as initial values for the concentration.

EQUILIBRIUM REACTIONS

These are the equilibrium reactions present in the electrolyte:

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3 \qquad K_1 = 2.58 \cdot 10^{-3}$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad K_2 = 1.91 \cdot 10^{-3}$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad K_3 = 4.84 \cdot 10^{-11}$$

$$Fe^{2+} + H_2O \Leftrightarrow FeOH^+ + H^+ \qquad K_4 = 3.09 \cdot 10^{-10}$$

$$FeOH^+ + H_2O \Leftrightarrow Fe(OH)_2(aq) + H^+ \qquad K_5 = 7.943 \cdot 10^{-12}$$

where K_1 through K_6 are the equilibrium constants at 298.15 K (Ref. 1 and Ref. 2).

The water dissociation equilibrium reaction is built in for the interface. The carbonic acid can be added with the Carbonic Acid node that is customized for these reactions. The ferrous ion hydrolysis reactions are defined using the Ampholyte node.

ELECTROCHEMICAL REACTIONS

The following electrochemical reactions are present at the steel surface:

- Iron dissolution

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

- Proton reduction

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

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 between carbon dioxide and bicarbonate ions show considerable dissociation of the carbon dioxide.

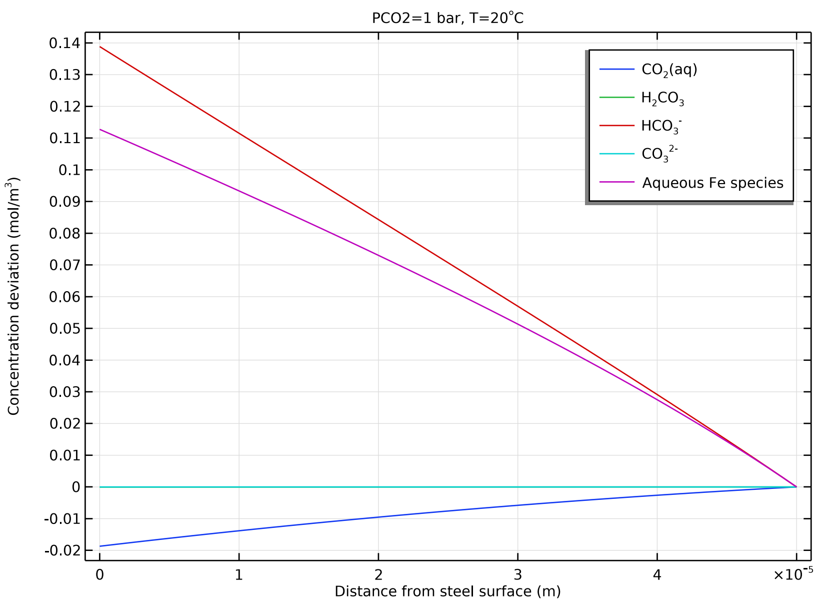


Figure 2: Deviation in concentration of the species compared to the bulk along the liquid boundary layer.

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.

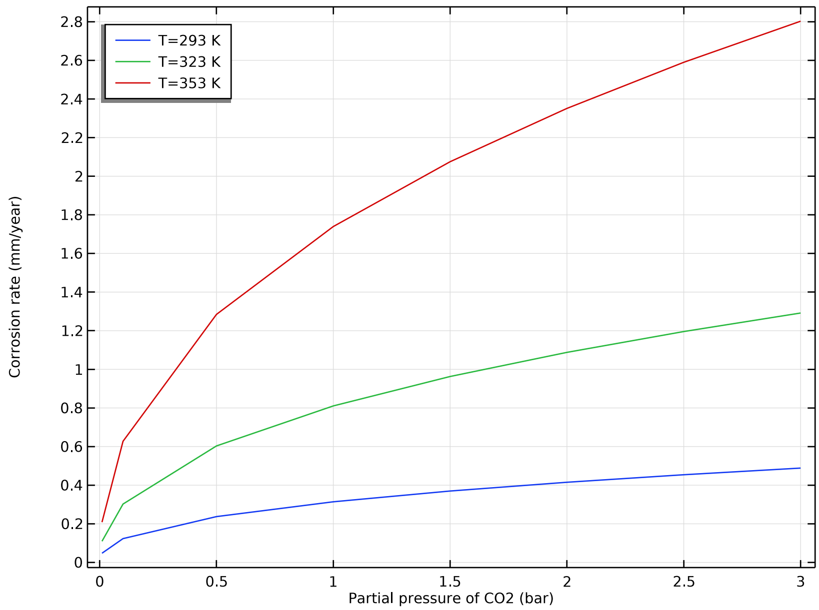


Figure 3: Corrosion rate in mm/year for different partial pressures of CO_2 and operating temperatures in the range 20°C–80°C.

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.

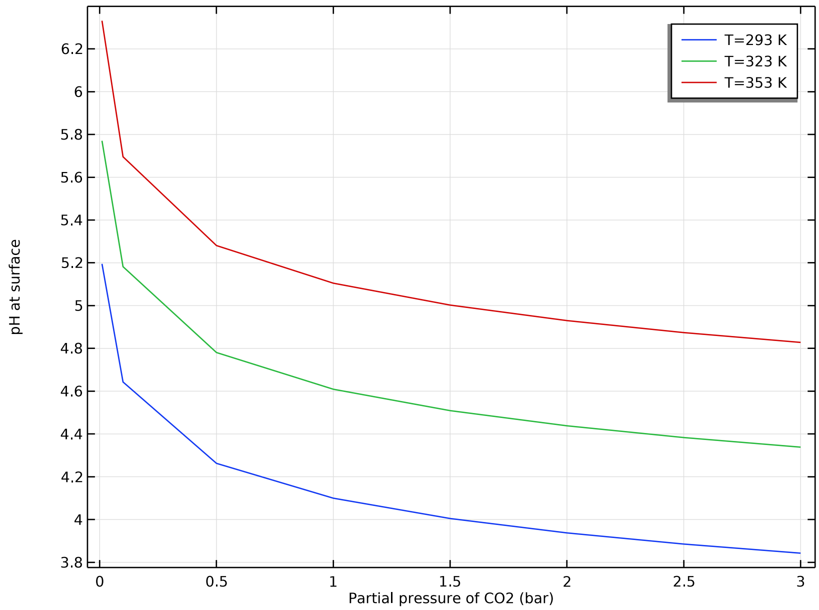


Figure 4: pH at the electrode surface for different partial pressures of CO_2 and operating temperatures in the range $20^o C$–$80^o C$.

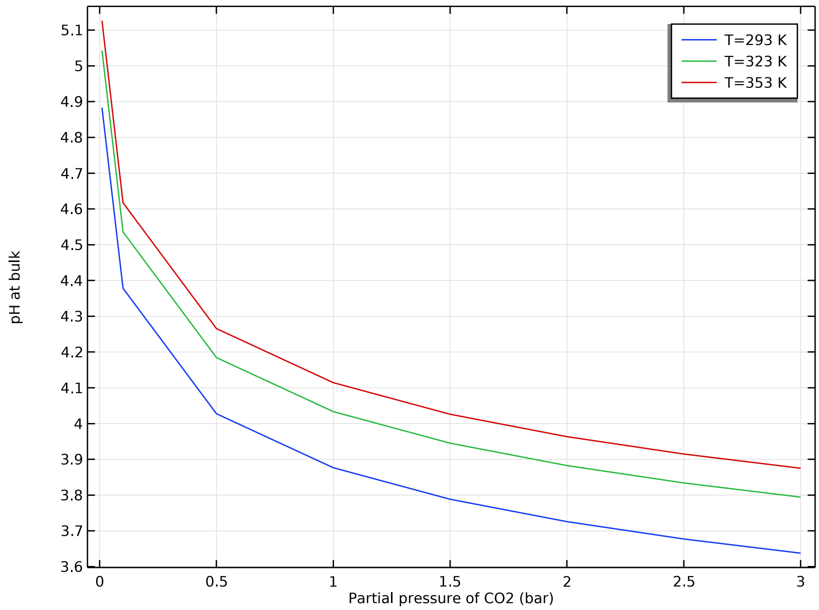


Figure 5: pH at the bulk electrolyte for different partial pressures of CO_2 and operating temperatures in the range 20^oC–80^oC.

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. F. J. Millero, W. Yao, and J. Aicher, “The speciation of Fe(II) and Fe(III) in natural waters,” *Marine Chemistry*, vol. 50, pp. 21–39, 1995.

3. 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.

4. 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`

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** > **Aqueous Electrolyte Transport (aqt)**.
3 Click **Add**.
4 Click **Study**.
5 In the **Select Study** tree, select **General Studies** > **Stationary**.
6 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**.

AQUEOUS ELECTROLYTE TRANSPORT (AQT)

Define the physics, start with the solvent (water) parameters.

Electrolyte 1

1 In the **Model Builder** window, under **Component 1 (comp1)** > **Aqueous Electrolyte Transport (aqt)** click **Electrolyte 1**.

2 In the **Settings** window for **Electrolyte**, locate the **Proton and Hydroxide Ion Transport Properties** section.

3 In the D_{H^+} text field, type `DH`.

4 In the D_{OH^-} text field, type `DOH`.

Add an **Ampholyte** node and define the ferrous ion hydrolysis reactions.

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

Ampholyte - Fe

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

2 In the **Settings** window for **Ampholyte**, type `Ampholyte - Fe` in the **Label** text field.

3 Locate the **Ampholyte** section. In the **Species name** text field, type `Fe`.

4 In the table, enter the following settings:

Dissociation step (1)	pKa (1)
1	`-log10(KFeOH)`
2	`-log10(KFeOH2)`

5 In the z_0 text field, type `0`.

6 Locate the **Diffusion and Migration** section. In the D text field, type `DFe`.

Add a **Carbonic Acid** node that is solely devoted to dissociated species of carbonic acid.

Electrolyte 1

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

Carbonic Acid 1

In the **Physics** toolbar, click **Attributes** and choose **Carbonic Acid**.

Set the initial values. The interface computes all hydrolyzed (Ampholyte - Fe) and dissociated (Carbonic Acid) species (that is, the species originating from the equilibrium reactions) automatically. Only the total species concentrations are required to be set. For the carbonic acid, the solution is assumed to be saturated with aqueous carbon dioxide.

Initial Values 1

1. In the **Model Builder** window, under **Component 1 (comp1)** > **Aqueous Electrolyte Transport (aqt)** click **Initial Values 1**.
2. In the **Settings** window for **Initial Values**, locate the **Electrolyte Potential** section.
3. In the $\phi_{l,0}$ text field, type `phil_init`.
4. Locate the **Concentration** section. In the $c_{H2CO3,0}$ text field, type `cH2CO3_init`.

Define the concentrations at the bulk boundary of the layer using the **Reservoir** node. Just as for the **Initial Values** settings, only total species concentrations are required.

Reservoir 1

1. In the **Physics** toolbar, click **Boundaries** and choose **Reservoir**.
2. Select Boundary 2 only.

   The reservoir is assumed to be completely saturated with aqueous carbon dioxide.
3. In the **Settings** window for **Reservoir**, locate the **Concentration** section.
4. In the $c_{0,H2CO3}$ text field, type `cH2CO30`.

Define the electrochemical reactions with an **Electrode Surface** node.

Electrode Surface 1

1. In the **Physics** toolbar, click **Boundaries** and choose **Electrode Surface**.
2. Select Boundary 1 only.

   Use the Dissolving-Depositing species formulation to estimate the corrosion rate. Also, set fluxes according to the electrochemical reactions at the steel surface.
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 name	Molar volume (m^3/mol)	Initial concentration (mol/m^2)
Fe	Vm_steel	0[mol/m^2]

Define each electrochemical reaction in an **Electrode Reaction** child node.

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 $\nu_{Fe^{2+}}$ text field, type `-1`.
4 Find the **Stoichiometric coefficients for dissolving-depositing species** subsection. In the table, enter the following settings:

Species name	Stoichiometric coefficient (1)
Fe	1

5 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Eeq_ref_Fe`.
6 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_Fe`.
7 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 **Stoichiometric Coefficients** section.
3 In the ν_{H^+} text field, type `-1`.
4 Locate the **Equilibrium Potential** section. In the $E_{eq,ref}(T)$ text field, type `Eeq_ref_H2`.
5 Locate the **Electrode Kinetics** section. In the $i_{0,ref}(T)$ text field, type `i0_ref_H2`.
6 In the α_a text field, type `alphaa_H2`.

Set up an integration operator for the bulk boundary for easier post processing.

DEFINITIONS

Bulk Boundary

1 In the **Definitions** toolbar, click **Nonlocal Couplings** and choose **Integration**.
2 In the **Settings** window for **Integration**, type `Bulk Boundary` in the **Label** text field.
3 In the **Operator name** text field, type `intop_bulk`.

4 Locate the **Source Selection** section. From the **Geometric entity level** list, choose **Boundary**.

5 Select Boundary 2 only.

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** checkbox. 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** checkbox.

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**.

By default, a special parametric solver setup is used to speed up computation. You will see a warning in the solver configurations when sweeping parameters that affect initial expressions. In this case, the warning can be ignored.

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

RESULTS

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

Concentrations

1 In the **Results** toolbar, click **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^{\circ}C.

8 Locate the **Plot Settings** section.

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

10 Select the **y-axis label** checkbox. In the associated text field, type Concentration deviation (mol/m³).

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 `aqt.c4_H2CO3-intop_bulk(aqt.c4_H2CO3)`.

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** checkbox.

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

10 In the table, enter the following settings:

Legends
CO₂(aq)

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 `aqt.c3_H2CO3-intop_bulk(aqt.c3_H2CO3)`.

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

Legends
H₂CO₃

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 `aqt.c2_H2CO3-intop_bulk(aqt.c2_H2CO3)`.

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

Legends
HCO₃⁻

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 `aqt.c1_H2CO3-intop_bulk(aqt.c1_H2CO3)`.

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

Legends
CO₃²⁻

Line Graph 5

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

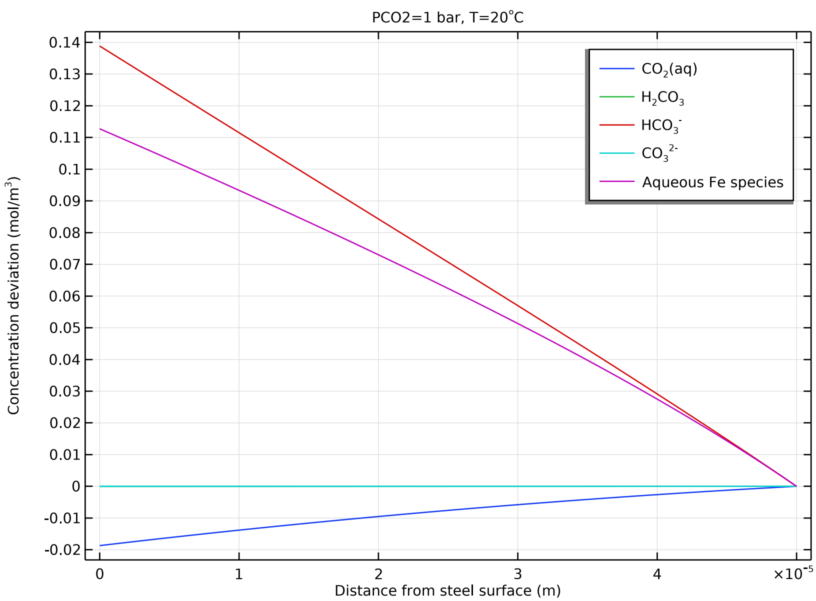
2 In the **Settings** window for **Line Graph**, locate the **y-Axis Data** section.

3 In the **Expression** text field, type `aqt.c_Fe-intop_bulk(aqt.c_Fe)`.

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

Legends
Aqueous Fe species

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



Corrosion rate

1 In the **Results** toolbar, click **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** checkbox. In the associated text field, type `Partial pressure of CO2 (bar)`.
7. Select the **y-axis label** checkbox. In the associated text field, type `Corrosion rate (mm/year)`.
8. Locate the **Legend** section. From the **Position** list, choose **Upper left**.

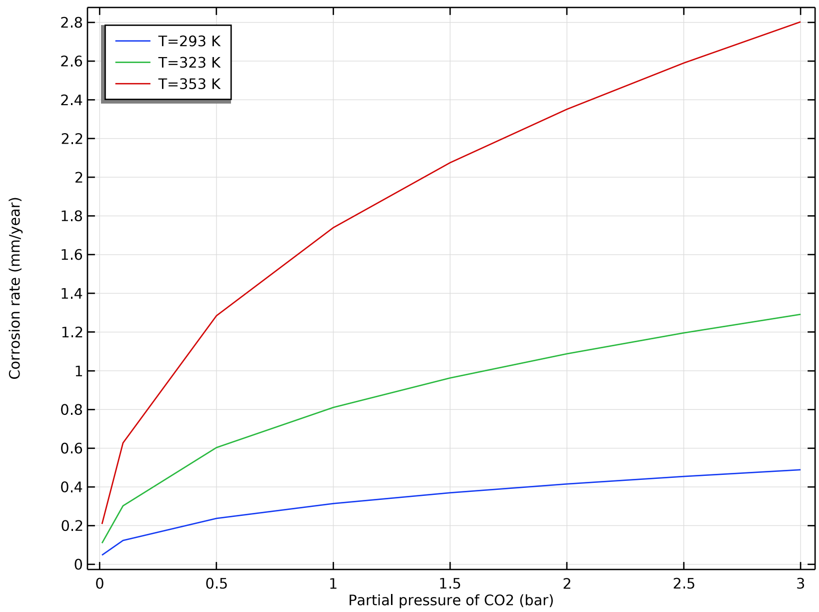
Point Graph 1

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)** > **Aqueous Electrolyte Transport** > **Dissolving–depositing species** > **aqt.vtot - Total growth velocity - m/s**.
4. Locate the **y-Axis Data** section. In the **Expression** text field, type `-aqt.vtot`.
5. From the **Unit** list, choose **mm/yr**.
6. Locate the **x-Axis Data** section. From the **Axis source data** list, choose **PCO2**.
7. From the **Parameter** list, choose **Expression**.
8. In the **Expression** text field, type `PCO2`.
9. Click to expand the **Legends** section. Select the **Show legends** checkbox.
10. From the **Legends** list, choose **Evaluated**.
11. In the **Legend** text field, type `T=eval(T) K`.

Corrosion rate

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

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



pH at surface

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

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`.

4 Locate the **Legend** section. From the **Position** list, choose **Upper right**.

Point Graph 1

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

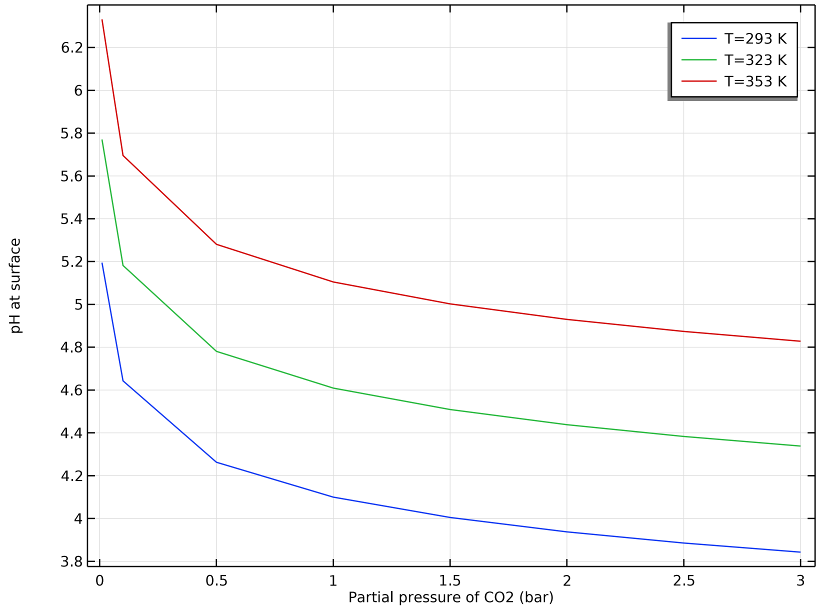
2 In the **Settings** window for **Point Graph**, locate the **y-Axis Data** section.

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

pH at surface

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

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



pH at bulk

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

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 box, select **1**.

5 Select Boundary 2 only.

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